XXIInd International Symposium on the Jahn-Teller Effect

Dynamics of Electron-Nuclear Coupling in Solids, Molecules, and Chemical Reactions

PROGRAM
BOOK OF ABSTRACTS

Topics covered:

- Basic Jahn-Teller theory
- Jahn-Teller and pseudo Jahn-Teller coupling in molecules and clusters
- Conical intersections, dynamics on intersecting potential energy surfaces
- Fullerenes and Fullerides
- Graphene, silicene, and related systems

18th - 22nd August 2014, Graz, Austria
Institute of Experimental Physics

TU Graz
Graz University of Technology

XXIInd International Symposium on the Jahn-Teller Effect

Dynamics of Electron-Nuclear Coupling in Solids, Molecules, and Chemical Reactions

PROGRAM

BOOK OF ABSTRACTS

JT 2014
Jahn-Teller Effect

18th – 22nd August 2014, Graz, Austria
Institute of Experimental Physics

Impressum

Editor:
W.E. ERNST
Institute of Experimental Physics
Graz University of Technology

Coverfoto & Layout:
W.E. ERNST

JT2014 Logo:
Courtesy of F. Schacher, Fribourg

www.ub.tugraz.at/Verlag

ISBN (print) 978-3-85125-315-3

ISBN (E-Book) 978-3-85125-316-0
DOI: 10.3217/978-3-85125-315-3

Conference History and Scope

The series of the International Jahn-Teller Symposia was started 44 years ago. Since then, the meeting took place every second year. The past three conferences were organized in Heidelberg, Germany, in 2008, in Fribourg, Switzerland, in 2010 and in Tsukuba, Japan, in 2012.The unique feature of this meeting is that it brings together researchers working in molecular physics and chemistry with researchers working in solid-state physics. While the Jahn-Teller effect is the unifying concept, the research topics are as varied as the spectroscopy of molecules and clusters in supersonic jets, molecular reaction dynamics, organic and inorganic photochemistry, spectroscopy of crystals, phase transitions in solids, or electronic transport phenomena, such as superconductivity or spintronics.

Practical Hints

Conference site:

All lectures are held in the physics building of TU Graz in Petersgasse 16, lecture room P2. The poster sessions as well as the sponsors' exhibition will take place in the foyer area. Posters may be mounted on Tuesday morning and remain in place until Thursday night. Lunch and coffee breaks will be organized in the entrance hall to the large physics lecture theatre P1 adjacent to the foyer to P2.
The conference office is located on the same floor as the lecture room and is to be accessed through the entrance to the Institute of Experimental Physics. The conference office is open on Sunday, August 17, 16 to 19 h, Monday and Tuesday (Aug. 18 and 19), 8 to 11 h, and Wednesday to Friday from 8 to 9 h. Outside these hours, help by the conference team is available at the secretarial office of the institute opposite the conference office.

Internet access:

Wlan-based internet access is available in all areas of the physics building. User IDs and passwords will be printed on the inside of the name badges.

Conference excursion and dinner on Wednesday:

The conference excursion will start at 13:00 h with a bus transfer to Stift Vorau about 60 km east of Graz, a monastery founded in the year 1163 (http://www.stift-vorau.at/?LNG=en). After a guided tour including the church and the impressive library, we will continue by bus to the small town of Pöllau with its castle, which was originally also founded as monastery and now houses a history of physics museum with an exhibition of old instruments (http://www.echophysics.org/exhibition/radiation/img_0880-modified.jpg/view?set_language=en).
At 19:00 h, the conference dinner in "Berg-Gasthof König" on Pöllau Hill will begin. Buses will take us back to the conference site.

Committees

International Steering Committee

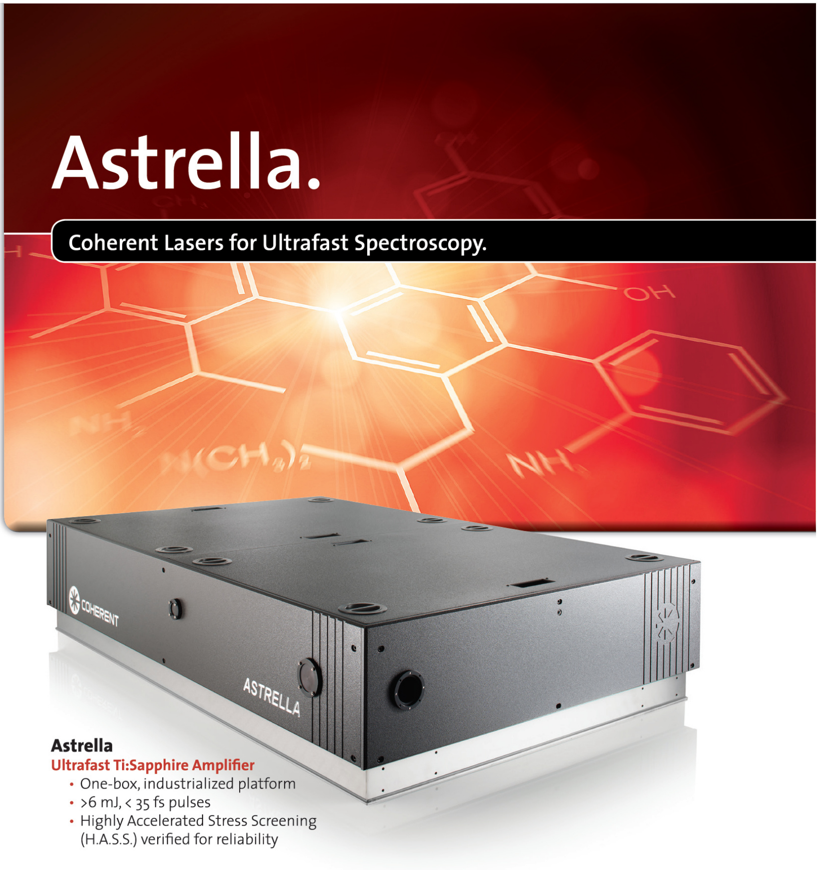
Isaac Bersuker (UT Austin, USA), Chair
Arnout Ceulemans (U. Leuven, Belgium)
Janette Dunn (U. Nottingham, UK)
Wolfgang E. Ernst (TU Graz, Austria)
Vladimir Hiznyakov (U. Tartu, Estonia)
Michael Kaplan (Boston U., USA)
Daniel Khomskii (U. Koeln, Germany)
Horst Köppel (U. Heidelberg, Germany)
Hiroyasu Koizumi (U. Tsukuba, Japan)
Susanta Mahapatra (U. Hyderabad, India)
Nicola Manini (U. Milano, Italy)
Spiridoula Matsika (Temple U., Philadelphia, USA)
Frederic Merkt (ETH Zurich, Switzerland)
Terry Miller (Ohio State U., USA)
Tohru Sato (U. Kyoto, Japan)
Boris Tsukerblat (Beer-Sheva, Israel)

Program Committee

Lilia Boeri (TU Graz, Austria)
Wolfgang Domcke (TU München, Germany)
Wolfgang E. Ernst (TU Graz, Austria)
Horst Köppel (U. Heidelberg, Germany)

Local Conference Team (TU Graz)

Sandra Brunner
Wolfgang E. Ernst
Bettina Gsoels-Bedenik
Andreas Kautsch
Josef Pichler
Gernot Pottlacher
Elisabeth Weiß


OH
NH
N(CH3)2
NH
COHERENT
ASTRELLA

Sunday, 17 August 2014

16:00 – 18:00	Registration Desk opens **REGISTRATION**
18:00 – 19:00	Welcome Reception

Monday, 18 August 2014

8:00 – 9:00	**REGISTRATION**
8:50 – 9:00	**Welcome and Opening**
Chair:	**Wolfgang ERNST**
9:00 – 9:45	**Isaac B. BERSUKER** (The University of Texas at Austin) **The Pseudo Jahn-Teller Effect: Special Features, Novel Findings, and Applications** (REV1)
9:45 – 10:30	**Vladimir HIZHNYAKOV** (University of Tartu) **Time-dependent Jahn-Teller Problem in Solids: Phonon-Induced Relaxation** (REV2)
10:30 – 11:00	Coffee Break
Chair:	**Hiroyasu KOIZUMI**
11:00 – 11:25	**Markus AICHHORN** (Graz University of Technology) **Cooperative effects of Jahn-Teller distortion, magnetism and Hund's coupling in BaCrO$_3$** (O01)
11:25 – 11:55	**Mihail ATANASOV** (Max-Planck Institute for Chemical Energy Conversion) **Ab initio Studies on the Role of the Jahn-Teller and Renner-Teller Effects in Single Molecule Magnets** (INV1)
11:55 – 12:20	**Max SORANTIN** (Graz University of Technology) **Vibronic effects on the steady state current through a molecular ring structure** (O02)
12:30 – 14:00	Lunch Break
Chair:	**Horst KÖPPEL**
14:00 – 14:45	**Nimrod MOISEYEV** (Technion-Israel Institute of Technology) **Light induced conical intersections** (REV3)
14:45 – 15:15	**Gerald AUBÖCK** (École Polytechniqe Fédérale de Lausanne) **The Photochemistry of Iron Hexacyanide in Water** (INV2)

15:15 – 15:40	**Regina DE VIVIE-RIEDLE** (LMU München) **Deceleration of dissociating molecular wave packets by solvent cage: the dynamic continuum ansatz** (O03)
15:40 – 16:05	**Spiridoula MATSIKA** (Temple University of Philadelphia) **Dynamics on radical cations governed by conical intersections** (O04)
16:05 – 16:45	Coffee Break

Chair: Wolfgang ERNST

17:00 – 18:00	**Karl Alexander MÜLLER** (University of Zürich) **Over half a century of research in oxides** (PL)
19:00	**Reception at City Hall**

Tuesday, 19 August 2014

8:00 – 9:00	**REGISTRATION**

Chair: Miguel MORENO

9:00 – 9:45	**Jörg WRACHTRUP** (Stuttgart University) **Defects in Diamond: New Hardware for the Quantum World** (REV4)
9:45 – 10:10	**Bin ZHANG** (Chinese Academy of Sciences, Beijing) **Organic-Inorganic Hybrid Dual-functional Molecular Crystal from Copper-Oxalate-Framework with Jahn-Teller Distortion** (O05)
10:10 – 10:35	**Dennis P. CLOUGHERTY** (University of Vermont) **Dissipation and Decoherence of a Jahn-Teller Impurity in a Solid** (O06)
10:35 – 11:15	Coffee Break

Chair: Mihail ATANASOV

11:15 – 11:40	**Vladimir V.GUDKOV** (Ural Federal University, Ekaterinburg) **Evidence of magnetic field dependent relaxation in ZnSe:Cr crystal in ultrasonic experiment** (O07)
11:40 – 12:05	**Kliment KUGEL** (Russian Academy of Sciences, Moscow) **Orbital and spin structures in transition metal compounds with face-sharing octahedral** (O08)

12:05 – 12:30
Simon NEVILLE (University of Birmingham)
Multi-mode, Multi-State Quantum Dynamics Studies of Heteroaromatic Molecules (O09)

12:30 – 14:00
Lunch Break

Chair: Terry MILLER

14:00 – 14:45
John F. STANTON (The University of Texas at Austin)
Ground State of NO_3: From Lewis Structures to Spin-Orbit Coupling Effects (REV5)

14:45 – 15:15
Mitchio OKUMURA (California Institute of Technology, Pasadena)
Spectroscopy and Dissociation Dynamics of the Excited States of the Nitrate Cation NO_3^+ (INV3)

15:15 – 15:40
Matija ZLATAR (University of Belgrade)
Computational Analysis of Intrinsic Distortions of Jahn-Teller and Pseudo Jahn-Teller Active Molecules (O10)

15:40 – 16:05
Claude DAUL (University of Fribourg)
Explicit Control Over Spin-states using combined Density Functional and Ligand Field Theory (O11)

16:05 – 16:30
Coffee Break

Chair: Spiridoula MATSIKA

16:30 – 16:55
Daniel OPALKA (University of Cambridge)
Construction of analytic multi-sheeted potential-energy surfaces from ab initio data (O12)

16:55 – 17:20
David S. PERRY (The University of Akron)
A System of e×E Conical Intersections Between Vibrationally Adiabatic Surfaces In Methanol (O13)

17:20 – 17:45
Satrajit ADHIKARI (Indian Association for the Cultivation of Science, Kolkata)
Conical Intersections in D_{3h} molecules: Diabatic PESs for Spectroscopic & Scattering Processes (O14)

18:00
Poster Session

Wednesday, 20 August 2014

8:00 – 9:00	**REGISTRATION**
Chair:	**Mitchio OKUMURA**
9:00 – 9:45	**Terry A. MILLER** (The Ohio State University, Columbus) **Reconciliation of Spectroscopic Results and Electronic Structure Calculations for Jahn-Teller-Active Molecules** (REV6)
9:45 – 10:30	**Yuxiang MO** (Tsinghua University, Beijing) **Jahn-Teller effect in CH3X: spin-vibronic coupling, mode coupling and tunneling splitting** (REV7)
10:30 – 11:00	Coffee Break
Chair:	**Wolfgang DOMCKE**
11:00 – 11:30	**Iain WILKINSON** (National Research Council of Canada, Ottawa) **Sensitivities of Strong Laser Field Spectroscopies to Evolving Molecular Structure in Polyatomic Systems** (INV4)
11:30 – 11:55	**Camille LEVEQUE** (UPMC Université Paris) **Ab initio quantum study of the photodynamics for the coupled 1^1A_2 and 1^1B_1 states of SO_2** (O15)
11:55 – 12:20	**Sebastian MAI** (University of Vienna) **Internal Conversion and Intersystem Crossing in SO_2 Studied by Surface-Hopping Molecular Dynamics** (O16)
13:00	**Departure for Conference Excursion:** **Stift Vorau, Science Museum Pöllau**
19:00	**Conference Dinner**

Thursday, 21 August 2014

8:00 – 9:00	**REGISTRATION**
Chair:	**Vladimir HIZHNYAKOV**
9:00 – 9:45	**Frank BRIDGES** (University of California, Santa Cruz) **Dynamic Jahn-Teller distortions in crystalline materials** (REV8)

9:45 – 10:30	**Pablo GARCÍA-FERNÁNDEZ** (Universidad de Cantabria, Santander) **Influence of Jahn-Teller and Pseudo Jahn-Teller over magnetism in 3d systems: A first-principles view** (REV9)
10:30 – 11:15	Coffee Break
Chair:	**Claude DAUL**
11:15 – 11:40	**Miguel MORENO** (Universidad de Cantabria, Santander) **Why the properties of K_2CuF_4, K_2ZnF_4:Cu^{2+} and $KZnF_3$:Cu^{2+} model systems are so different?** (O17)
11:40 – 12:05	**Annette BUSSMANN-HOLDER** (Max-Planck-Institut für Festkörperforschung, Stuttgart) **Probing spin fluctuations in the paramagnetic phase of $EuTiO_3$ by muon spin rotation techniques** (O18)
12:05 – 12:30	**Grace MORGAN** (University College Dublin) **Broken Symmetry and Ordering Phenomena in Mn^{III} Spin Crossover Solids** (O19)
12:30 – 14:00	Lunch Break
Chair:	**Frederic MERKT**
14:00 – 14:45	**Martin JANSEN** (Max Planck Institute for Solid State Research, Stuttgart) **Fullerides: Radical Anions, Jahn-Teller Effect and Orbital Ordering** (REV10)
14:45 – 15:10	**Erio TOSATTI** (International Centre for Theoretical Physics, Trieste) **Orbital excitation of a Mott-Jahn-Teller insulator revealed by infrared spectra** (O20)
15:10 – 15:40	**Janette L. DUNN** (University of Nottingham) **Experimental signatures of Jahn-Teller effects in fullerene anions** (INV5)
15:40 – 16:05	**Tohru SATO** (Kyoto University) **Regioselectivity in Chemical Reactions: Vibronic Coupling Density as a Reactivity Index** (O21)
16:05 – 16:30	Coffee Break
Chair:	**Lilia BOERI**
16:30 – 17:00	**Liviu F. CHIBOTARU** (Katholieke Universiteit Leuven) **Dynamical Jahn-Teller instability in alkali-doped fullerides** (INV6)

17:00 – 17:25	**Denis ARČON** (Jožef Stefan Institute, Ljubljana) **Jahn-Teller orbital glass in the Mott insulating parent state of the molecular superconductor Cs_3C_{60}** (O22)
17:25 – 17:50	**Katalin KAMARÁS** (Wigner Research Centre for Physics, Budapest) **Dynamic Jahn-Teller effect in IR spectra of expanded Cs_3C_{60} fullerides at low temperature** (O23)
18:00	**Poster Session**

Friday, 22 August 2014

Chair: Janette DUNN

9:00 – 9:45	**Jamie WARNER** (University of Oxford) **Defects in graphene and the role of Jahn Teller reconstructions** (REV11)
9:45 – 10:15	**Ayan DATTA** (Indian Association for the Cultivation of Science, Kolkata) **Silicene: Its different from Graphene** (INV7)
10:15 – 10:40	**Victor POLINGER** (University of Washington, Seattle) **Jahn-Teller-promoted superconductivity in cuprates and iron pnictides** (O24)
10:40 – 11:15	Coffee Break

Chair: Markus AICHHORN

11:15 – 11:45	**Hiroyasu KOIZUMI** (University of Tsukuba) **Supercurrent generation in Cuprate: Spin-vortex model** (INV8)
11:45 – 12:10	**Lilia BOERI** (University of Technology, Graz) **Electron-phonon superconductivity in AP_3P compounds: From weak to strong coupling** (O25)
12:10 – 12:35	**Takashi KATO** (Graduate School of Engineering, Nagasaki) **New interpretation of the role of vibronic interactions in superconductivity** (O26)

Public Lecture

Over half a century of research in oxides

K. A. MÜLLER
Physik Institut, University of Zürich, Switzerland

An attempt will be made to recall some of the highlights of the research in oxides achieved by the author and various collaborators over a period of 58 years. These were the observation of the paramagnetic resonance of transition metal ions of high valency like Fe^{3+}, Fe^{4+}, Fe^{5+}, Co^{4+}, and their photochromic behaviour. Then the detection of Mn^{4+} in $BaTiO_3$ and the proof for the presence of order-disorder character in these ferroelectric transitions. Then the temperature dependence of the rotational order parameter of the structural phase transitions in $LaAlO_3$ and $SrTiO_3$. Near the transition the observation of critical behaviour compatible with renormalisation group theory, and the presence of a Potts transition line, a critical end point, a Lifshitz point under uniaxial stress in $SrTiO_3$ and $CaGdF_3$. This will be followed by the determination of the stabilisation energy of the Jahn – Teller effect with octahedral oxygen neighbours to various ions; leading over to the concept of Jahn –Teller polarons as quasi particles for the generation of superconductivity, and the experimental observation of Jahn – Teller bipolarons and their stabilisation energy determined in one of the HTS copper oxides.

Lecture Abstracts

The Pseudo Jahn-Teller Effect: Special Features, Novel Findings, and Applications

Isaac B BERSUKER

Institute for Theoretical Chemistry, The University of Texas at Austin, Austin TX 78712, USA

This review talk includes original work. The pseudo Jahn-Teller effect (PJTE) is well known to be the only source of instability and spontaneous symmetry breaking (SSB) in molecular systems and solids in nondegenerate electronic states, and together with the JTE lays in the background of all the SSB in the material world [1, 2]. In spite of widespread applications, there are still some misunderstandings of the real meaning of this effect by layman chemists. We demonstrates several examples of published literature data in which the PJTE is mistreated. In a more serious aspect, some authors (even experts in this field) confuse the real (physical) effect with the mathematical scheme of calculations, sometimes confusing the PJTE with configuration interaction; the observable properties induced by the PJTE do not depend on the method of calculation if correctly applied. In this respect a novel problem emerges when one tries to reveal the PJTE by ab initio calculations. As the SSB in the PJTE depends on the symmetries of the specific mixing electronic states, the ab initio methods that include an indiscriminate mixing of many states (e. g., in the SA-CASSCF method) may hide the SSB if it is not sufficiently large.

With regard to the general aspects of the PJTE, proportionally not enough attention is paid to its role in the origin of global SSB problems in the formation of matter at different levels, including the parallel with the formation of elementary particles [2].

Among the novel findings, it was shown that in linear molecules the Renner-Teller effect (RTE) just splits the degenerate electronic term and softens the ground state, but it does not produce instability; all SSB in linear molecules are of PJTE origin [3]. This result interferes significantly with the existing interpretation of electronic and rovibronic spectra of linear molecules. In the same respect, a novel effect of broken cylindrical symmetry in linear molecules was revealed [4]. Further achievements were reached in application of the PJTE to solid state problems, in particular, in revealing the origin of ferroelectric and multiferroic properties [5, 6]. Methods of experimental evaluation of JTE and PJTE parameters in impurity centers and vacancies in crystals by means of ultrasound measurements were worked out [7]. A novel kind of tunnelling splitting in small molecules with the PJTE, including tunnelling induced by puckering, is predicted [8, 9].

A series of recent publications devoted to other application of the PJTE will be reviewed following the materials received from other authors.

1. I. B. Bersuker, The Pseudo Jahn-Teller Effect – a Two-State Paradigm in Formation, Deformation, and Transformation of Molecular Systems and Solids, *Chem. Rev.* **113** (2013) 1351-1390.
2. I. B. Bersuker, Spontaneous Symmetry Breaking in Matter Induced by Degeneracy and Pseudodegeneracy, in *Adv. Chem. Phys.*, to be published.
3. P. Garcia-Fernandez and I.B. Bersuker, Pseudo Jahn-Teller Origin of Bending Distortions in Renner-Teller Molecules and its Spectroscopic Implications, *Internat. J. Quant. Chem.* **112** (2012) 3025-3032.
4. W. Hermoso and I. B. Bersuker, A Novel Effect of Broken Cylindrical Symmetry in Linear Molecules, *to be published*.
5. I. B. Bersuker, Pseudo Jahn-Teller Origin of Perovskite Multiferroics, Magnetic-Ferroelectric Crossover, and Magnetoelectric Effects. The d^0-d^{10} problem, *Phys. Rev. Lett.*, **108** (2012) 137202.
6. V. Z. Polinger, P. Garcia-Fernandez, and I. B. Bersuker, Pseudo Jahn-Teller Origin of Ferroelectric Instability in $BaTiO_3$ Type Perovskites. The Green's Function Approach and Beyond, *to be published*
7. V. V. Gudkov and I. B. Bersuker, Experimental Evaluation of Jahn-Teller Effect Parameters by Means of Ultrasonic Measurements. Applications to Impurity Centers in Crystals, in *Vibronic Interactions and the*

Jahn-Teller Effect: Theory and Applications, M. Atanasov, C. Daule, and P. Tregenna-Pigot, Eds., Progress in Theoretical Chemistry and Physics, v. 23 (Springer, Heidelberg, 2012), Ch. 7, 143-161.
8. H. Kayi, P. Garcia-Fernandez, I. B. Bersuker, and J. E. Boggs, Deviations From Born−Oppenheimer Theory in Structural Chemistry: Jahn−Teller, Pseudo Jahn−Teller, and Hidden Pseudo Jahn−Teller Effects in C_3H_3 and $C_3H_3^-$, *J. Phys. Chem. A*, 117 (2013) 8671−8679.
9. I. B. Bersuker, Tunneling splitting in molecular systems with PJTE induced puckering, to be published.

REV2

Time-dependent Jahn-Teller Problem in Solids: Phonon-Induced Relaxation

Vladimir HIZHNYAKOV
Institute of Physics University of Tartu, Tartu, Estonia
e-mail: hizh@fi.tartu.ee

A theoretical description of the time-dependent dynamical Jahn-Teller (JT) and pseudo-Jahn-Teller (PJT) effect in an impurity center in solids is presented. A strict quantum mechanical treatment of the problem, taking into account a vibronic interaction with few local (pseudolocal) modes and with phonon continuum, is given, supposing that the latter interaction is sufficiently weak. The presented theory allows one to describe the time evolution of JT centers, taking into account the energy loss due to the emission of phonons to the bulk. The idea of our consideration is based on the observation of O'Brien [1] that in principle, the multimode vibronic interaction may be replaced by a vibronic interaction with a single mode if one uses a proper quadratic potential energy of vibrations. However, no explicit equation for the required potential energy in Ref. [1] has been given. In [2,3] we derived the equation for the quadratic interaction of a local/pseudolocal mode with phonons, allowing one to replace the linear vibronic interaction with phonon continuum. When using this equation, the calculations of the dynamical JT effect can be performed in two steps. First, seed vibronic states, taking into account only the vibronic interaction with the main mode(s), are calculated numerically. Then, by using the calculated eigenstates as a basis, the derived quadratic interaction of the local (pseudolocal) vibration(s) with phonons is taken into account by applying the cumulant expansion of the evolution operator.

The applied method enables us to calculate the evolution of the populations of vibronic levels and of the distribution function of the basic configurational coordinates of JT and PJT systems in time. Actually, we have performed a series of numerical calculations of the relaxation of a dimer due to the interaction with phonons [4]. We have elucidated in details how the distribution function of the main coordinate of the dimer changes in time for different initial excitations and for different parameters of electronic, vibronic and electron-phonon interactions. Analogous calculations have also been made for the E-e-type JT system. An essential feature of this case is the Berry phase, which leads to the existence of the momentum quantum number of vibronic levels. In the energy relaxation the Berry phase manifests itself as the nonzero momentum of emitted phonons (the latter belong to the e-representation, as the main mode). A special attention was paid to elucidating the details of the phonon-induced relaxation of this system through the conical intersection of the potential energy. In particular, we have clarified how the Slonczewsky quantization of the states in a conical intersection affects the relaxation.

[1] O'Brien M. (1972). The dynamic jahn-teller effect with many frequencies: a simple approach to a complicated problem (1972). Journal of Physics C: Solid State Physics. 5, 2054.
[2] Hizhnyakov, V.; Pae, K.; Vaikjärv, T. (2012). Optical Jahn-Teller effect in the case of local modes and phonons. Chemical Physics Letters, 525–526, 64 - 68.
[3] Pae, K.; Hizhnyakov, V. (2013). Nonadiabaticity in a Jahn-Teller system probed by absorption and resonance Raman scattering. Journal of Chemical Physics, 138(10), 104103.
[4] Vaikjarv T.; Hizhnyakov V. (2014). Time-dependent pseudo Jahn-Teller effect: phonon-mediated long-time nonadiabatic relaxation. Journal of Chemical Physics, 140, 064105.

Cooperative effects of Jahn-Teller distortion, magnetism and Hund's coupling in $BaCrO_3$.

Gianluca GIOVANNETTI[1], Markus AICHHORN[2], and Massimo CAPONE[1]

[1]CNR-IOM-Democritos National Simulation Centre and International School
for Advanced Studies (SISSA), Via Bonomea 265, I-34136, Trieste, Italy
[2]Institute of Theoretical and Computational Physics, TU Graz,
Petersgasse 16, Graz, Austria

We employ a combination of first-principle density functional theory and many-body techniques to investigate the correlated electronic structure of the recently synthesized insulator $BaCrO_3$. The band structure of the system is calculated within the local density approximation, and the resulting lattice Hamiltonian is solved through the dynamical mean-field theory, a method that captures local dynamic electronic correlation effects exactly. Our calculations show that Hund's coupling, which is one of the interaction parameters in a multiorbital system, is responsible for strong correlation effects. However, these effects are not strong enough to turn the system insulating.

As a result of electronic correlations, the electronic ground state is very fragile agains perturbations. We show in our calculations, that a natural perturbation is orbital ordering. The ordering pattern is anti-ferro-orbital, which couples to lattice degrees of freedom and induces a Jahn-Teller distortion. Following the rules of Goodenough-Kanamori, magnetism in a G-type antiferromagnetic pattern occurs, further lowering the energy.

All those ingredients together, electronic correlations, Jahn-Teller distortions, and magnetism now can explain the insulating state, and even reproduce nicely the value of the excitation gap that is found experimentally.

INV1

Ab initio Studies on the Role of the Jahn-Teller and Renner-Teller Effects in Single Molecule Magnets

Mihail ATANASOV[1,2] and Frank NEESE[2]
[1]Max-Planck Intitute for Chemical Energy Conversion, Mülheim a.d. Ruhr, Germany
[2]Institute for General and Inorganic Chemistry, Bulgarian Academy of Sciences,Sofia,Bulgaria

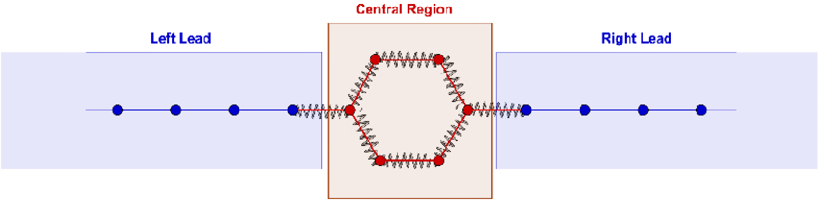
Single molecule magnets are paramagnetic molecules which are magnetized by an external magnetic field and remain magnetic upon removal of the field. They can eventually find use in high-density information storages and quantum computers. The key quantity for such a property is the magnetic anisotropy quantified by the axial zero-field splitting (D) of the ground state spin S sublevels. It leads to magnetic bi-stability and creates an energy barrier to inversion of the total molecular moment. The origin of this anisotropy is spin-orbit coupling which in combination with axial, three fold and fourfold symmetries leads to a preferred spin–direction. This preferred intrinsic direction of the magnetization is due to contributions of orbital moments to the net molecular spin. Such a phenomenon typically arises in transition metal complexes with orbitally degenerate ground states where Jahn-Teller (for non-linear complexes) or Renner-Teller (for linear complexes) vibronic coupling however also operate. These vibronic interactions tend to lower the symmetry statically or dynamically and thus destroy the magnetic anisotropy on a time scale comparable with the characteristic time of the magnetic experiment. It therefore governs not only the value of D but the magnetic relaxation time as well. A computational protocol was developed in our group to compute magnetic sublevels while accounting for both spin-orbit and vibronic coupling [1]. The infrastructure for such computations is given by the ORCA program package [2] allowing one to carry out efficient multireference *ab initio* calculations of systems with an unprecedented size. In this lecture an overview of our activities will be given focusing on four coordinate trigonal $Fe^{II}(tpa^{R})$ complexes (tpa=tris-pyrrolyl-α-methyl amine, R=tert-butyl, mesityl, phenyl, 2,6-difluorophenyl) with $FeN_{ax}(N_{eq})_3$ cores [1] and pseudo linear Fe^{II} complexes with $F^{II}X_2$ linear cores (X=N, C and N donors) [3-5], all being in a ^5E electronic ground state and all showing slow relaxation of the magnetization under an applied static magnetic field. A theoretical framework for the computation of the static multimode Jahn-Teller effect in the first class of compounds and the single mode dynamical Renner-Teller effects in the second class of complexes will be demonstrated. Factors toward a suppression of the vibronic coupling will be discussed. These include first of all choice of bulky ligands enforcing rigid ligand strain and choice of soft covalent ligands to decrease the ligand field, suppress vibronic coupling and, due to ligand intrinsic spin-orbit coupling to eventually increase the value of D. Within a fruitful collaboration with synthetic and magneto chemic experimental groups [3-4], these studies culminated in the first transition metal complex with a $Fe^{I}C_2$ core and magnetic hysteresis due to blocking of the magnetization below T=4.5 K [5].

[1] M.Atanasov, D.Ganyushin, D.A.Pantazis, K.Sivalingam, F.Neese, Detailed *Ab Initio* First-Principles Study of the Magnetic Anisotropy in a Family of Trigonal Pyramidal Iron(II) Pyrrolide Complexes, Inorg.Chem. **50** (2011) 7460-7477.
[2] F.Neese, The ORCA program system, WIREs Comput Mol Sci **2**(2012) 73-78.
[3] J.M.Zadrozny, M.Atanasov, A.M.Bryan, C.-Y. Lin, B.D.Rekken, P.P.Power, F.Neese, J.Long, Slow Magnetization Dynamics in a Series of Two-coordinate Iron(II) complexes, Chemical Science, **4**(2013) 125-138.
[4] M.Atanasov, J.M.Zadrozny, J.R.Long, F.Neese, A Theoretical Analysis of Chemical Bonding, Vibronic Coupling, and Magnetic Anisotropy in Linear Iron(II) Complexes with Single-Molecule Magnet Behavior, Chemical Science, **4**(2013) 139-156.
[5] J.M.Zadrozny, D.J.Xiao, M.Atanasov, G.J.Long, F.Grandjean, F.Neese, J.R.Long, Magnetic Blocking in a Linear Iron(I) Complex, Nature Chemistry, **5**(2013) 577-581.

Vibronic effects on the steady state current through a molecular ring structure

Max SORANTIN, Enrico ARRIGONI, and Wolfgang VON DER LINDEN
Institute of Theoretical and Computational Physics, Graz University of Technology, 8010 Graz, Petersgasse 16/II

We study *theoretically* vibrational effects on the steady state current through a molecular ring structure (benzene) by application of Cluster Perturbation Theory (CPT) in conjunction with Exact Diagonalization Techniques. The coupling between the electronic and vibronic degrees of freedom (e-ph coupling) is modeled by the Su-Schriefer-Heeger (SSH) hamiltonian which also captures the Jahn-Teller effect. This allows us, in contrast to the widely studied Anderson-Holstein model [1], to study vibrational effects on a molecular junction with an extended molecule as central region. We extend the work of Ref. [2] by taking into account the vibrations of the *contacted* molecule and extend the linear SSH model to its exponential generalisation to investigate the system at strong e-ph coupling. From weak to strong e-ph interactions the current voltage characteristics can be qualitatively predicted from the equilibrium Density Of States of the central region. For intermediate e-ph coupling, where the *linear* SSH model is applicable, the steady state current obtained from CPT matches well with a calculation within the Born-Oppenheimer approximation (frozen phonons). Deviations start to arise for values of the parameters where the linear SSH model breaks down. In this strong coupling regime the I/V curves can not be interpreted by the frozen phonons anymore and many-body correlation effects like the Franck-Condon blockade become crucial.



[1] T. Koch, J. Loos, A. Alvermann, and H. Fehske: Nonequilibrium transport through molecular junctions in the quantum regime, Phys. Rev. B **84**, 125131 (2011).
[2] M. Knap, E. Arrigoni, and W. von der Linden: Vibration-mediated correlation effects in the transport properties of a benzene molecule, Phys. Rev. B **88**, 054301 (2013).

Light induced conical intersections

Nimrod MOISEYEV
Schulich Faculty of Chemistry and Faculty of Physics,
Technion-Israel Institute of Technology

The role of conical intersections (CIs) in different types of chemical reactions including molecular photochemistry has been amply studied in the literature. A CI can only exist for molecules that have more than three atoms. Therefore, in diatomic molecules two electronic states that belong to the same point group symmetry exhibit an avoided-crossing and there is no CI for diatomic molecules.

In 2008 we have shown how light can induce CIs in diatomic molecules. These light-induced CIs (LICIs) emerge from the fact that light couples electronic states and this coupling involves the vibrational and rotational degrees of freedom. When standing lasers are used, the LICIs involve in addition couplings of the above degrees of freedom with that of the center of mass. Consequently, LICIs are expected to play a key role in photo-induced reactions and in trapping of cold molecules in optical traps and have an impact on the formation of molecular optical lattices. In polyatomics the interplay of the various nuclear degrees of freedom can be exploited to manipulate and may be control processes via LICIs. In this talk we will review the LICI phenomenon and its effect on photo-induced dynamics. We also sketch future planned studies that might open new fields of research on large variety of topics.

[1] Nimrod Moiseyev, Milan Sindelka and Lorenz S Cederbaum, "Laser-induced conical intersections in molecular optical lattices", J. Phys. B: At. Mol. Opt. Phys. **41** (2008) 221001.
[2] Milan Sindelka, Nimrod Moiseyev and Lorenz S Cederbaum, "Strong impact of light-induced conical intersections on the spectrum of diatomic molecules", J. Phys. B: At. Mol. Opt. Phys. **44** (2011) 045603.
[3] Nimrod Moiseyev and Milan Sindelka, "The effect of polarization on the light-induced conical intersection phenomenon", J. Phys. B: At. Mol. Opt. Phys. **44** (2011) 111002.
[4] Gabor J. Halasz, Milan Sindelka, Nimrod Moiseyev, Lorenz S. Cederbaum, and Agnes Vibok, "Light-Induced Conical Intersections: Topological Phase, Wave Packet Dynamics, and Molecular Alignment", J. Phys. Chem. A **116** (2012), 2636–2643.
[5] Gabor J. Halasz, Agnes Vibok, Milan Sindelka, Lorenz S. Cederbaum, Nimrod Moiseyev, "The effect of light-induced conical intersections on the alignment of diatomic molecules", Chem. Phys. **399** (2012) 146-150.
[6] Gabor J Halasz, Agnes Vibok, Nimrod Moiseyev and Lorenz S Cederbaum, "Light-induced conical intersections for short and long laser pulses: Floquet and rotating wave approximations versus numerical exact results", J. Phys. B: At. Mol. Opt. Phys. **45** (2012) 135101.
[7] Lorenz S. Cederbaum, Ying-Chih Chiang, Philipp V. Demekhin, and Nimrod Moiseyev, "Resonant Auger Decay of Molecules in Intense X-Ray Laser Fields: Light-Induced Strong Nonadiabatic Effects", Phys.Rev.Lett. **106** (2011), 123001.
[8] Ph. V. Demekhin and L. S. Cederbaum, "Light−induced conical intersections in polyatomic molecules: General theory, strategies of exploitation, and application", J. Chem. Phys. **139** (2013), 154314.

The Photochemistry of Iron Hexacyanide in Water

Marco REINHARD, Gerald AUBÖCK, and Majed CHERGUI
Laboratory of Ultrafast Spectroscopy,
École Polytechniqe Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Transition metal complexes are usually of high geometric symmetry (often O_h) and thus exhibit electronically degenerate states, which naturally are subject to Jahn Teller [JT] coupling with degenerate vibrational modes. In solution, however, these complexes are perturbed by solvent molecules, which break the symmetry, thus lift degeneracies and compete with JT coupling. To what extent a JT effect is still relevant and how it influences their photochemistry is largely unexplored.

Iron hexacyanide [$Fe(CN)_6^{4-}$] is a prototype metal center complex of O_h symmetry and exhibits a rich photochemistry upon UV excitation when dissolved in water. Photo-oxidation competes with photo-aquation (a CN^- ligand is replaced by a water molecule) and relaxation via intersystem crossing. We investigated these processes using ultrafast UV 2D -, and UV/visible transient absorption spectroscopy. These measurements are complemented with results from time resolved X-ray absorption spectroscopy [1].

Our results allowed us to partially disentangle the various decay pathways and to determine excitation energy dependent quantum yields for the aforementioned photochemical processes. We further found that photo-aquation is complet in ~15 ps and proceeds via a transition state which has a symmetry lower than C_{4v} and is formed within ~4 ps. Here I will discuss the photochemistry of transition metal complexes and in particular iron hexacyanide and its relation to JT coupling.

[1] M. Reinhard et al., Photooxidation and photoaquation of iron hexacyanide in aqueous solution: A picosecond X-ray absorption study. Structural dynamics 1 (2014) 024901

Deceleration of dissociating molecular wave packets by solvent cage: the dynamic continuum ansatz

S. THALLMAIR[1,2], M. KOWALEWSKI[1,3], and R. DE VIVIE-RIEDLE[1]
[1]LMU München, Department Chemie, 81377 München, Germany
[2]LMU München, Lehrstuhl für BioMolekulare Optik, 80538 München, Germany
[3]University of California, Department of Chemistry, Irvine, California 92697-2025, USA

Carbocations are intensely studied reactive species in organic chemistry and biochemistry. A well-established approach to generate them in solution is photolytic bond cleavage (BC). Electrostatic solvent effects are known to influence the reactivity of the solute significantly. In photochemical reactions where dissociative processes are included not only the electrostatic but also the dynamic impact of the solvent becomes important. For bulky leaving groups, like in phosphonium salts [1], the solvent cage substantially decelerates the photogenerated fragments depending on the viscosity of the solvent. We present theoretical insight into the BC process after photo excitation of diphenylmethylphosphonium ions. After a local π-π* excitation a charge transfer state initiates the BC [2]. It is homolytic in the first excited state leading to carbon radical formation missing the conical intersection (CoIn) with the ground state (Fig. 1). On the contrary ultrafast broadband transient absorption measurements almost exclusively show the formation of diphenylmethyl cations implying a heterolytic BC [1].

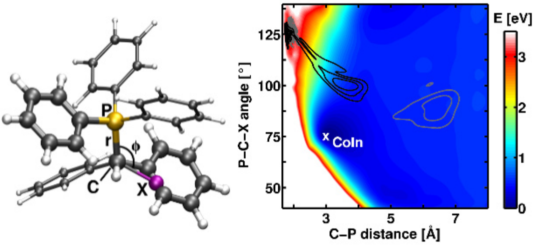


Fig. 1: Reactive coordinates for the photochemical BC of diphenylmethyltriphenylphosphonium ions (left) and dissociating wave packets on the first excited state (right). The snapshots are taken for 100 fs (black) and 220 fs (grey).

Both homolytic and heterolytic channel lead to the formation of one neutral and one positively charged fragment. Therefore the electrostatic solvent effect does not change the reaction dynamics. Only the dynamic effect of the solvent cage comes into play [3]. During the BC both fragments are accelerated. This leads to a deformation of the first solvation shell which in response slows down the dissociation process. Its frictional deceleration is treated by our dynamic continuum ansatz in a quantum mechanical formalism including Stokes law and the dynamic viscosity. About 200 fs after the dissociation has started, the wave packet has lost almost all its kinetic energy. It now can evolve along an angular coordinate with smaller gradient, which directly points towards the CoIn that enables the fast and efficient formation of the carbocations. The photolytic BC of diphenylmethylphosphonium ions particularly illustrates the importance of the dynamic solvent effect treated with our dynamic continuum ansatz. It affects the bond cleavage on a 200 fs timescale and explains the reaction outcome.

[1] J. Ammer, C. F. Sailer, E. Riedle, H. Mayr, J. Am. Chem. Soc. 134 (2012) 11481-11494.
[2] S. Thallmair, B. P. Fingerhut, R. de Vivie-Riedle, J. Phys. Chem. A **117** (2013) 10626-10633.
[3] S. Thallmair, M. Kowalewski, B. P. Fingerhut, C. F. Sailer, R. de Vivie-Riedle, *Proceedings of the XVIIIth International Conference on Ultrafast Phenomena,* Edited by M. Chergui, A. Taylor, S. Cundiff, R. de Vivie-Riedle, K. Yamanouchi (EDP Sciences, Les Ulis, 2013) 05043-p.1-05043-p.3.

Dynamics on radical cations governed by conical intersections

Spiridoula MATSIKA, and Mariana ASSMANN
Temple University, Department of Chemistry, Philadelphia, PA, USA

In time resolved photoelectron spectroscopy and strong field dissociative ionization techniques ionization of neutral molecules to create radical cations is used as a probe of molecular dynamics. Several excited ionic states can be created during the ionization leading to fragmentation, and it is not clear whether the fragments are produced directly in the excited ionic states or if fast relaxation to the ground ionic state occurs first and fragmentation follows. In a collaborative work we have examined the dynamics of several molecules using strong field dissociative ionization [1,2]. In order to understand better the processes occurring after ionization and interpret the experimental observables we have investigated dynamics of radical cations. Polyatomic radical cations often have closely spaced electronic states with several two and three-state conical intersection seams making the dynamics even more interesting [3]. We have applied trajectory surface hopping molecular dynamics and the MultiConfigurational Time-Dependent Hartree (MCTDH) approach to study the dynamics of several cations, such as uracil and cyclohexadiene radical cations. Findings of this work will be reported.

[1] S.Matsika, M. Spanner, M. Kotur and T. C.Weinacht: Ultrafast Relaxation Dynamics of Uracil Probed via Strong Field Dissociative Ionization, J. Phys. Chem. A **117** (2013) 12796-12801.
[2] M. Kotur, C. Zhou, S. Matsika, S. Patchkovskii, M. Spanner and T. C.Weinacht: Final State Distributions in Strong Field Molecular Ionization, Phys. Rev. Lett. **109**, (2012) 203007.
[3] S. Matsika: Two- and Three-State Conical Intersections in Uracil Cation Radical, Chem. Phys. **349**, (2008), 356-362.

Defects in Diamond: New Hardware for the Quantum World

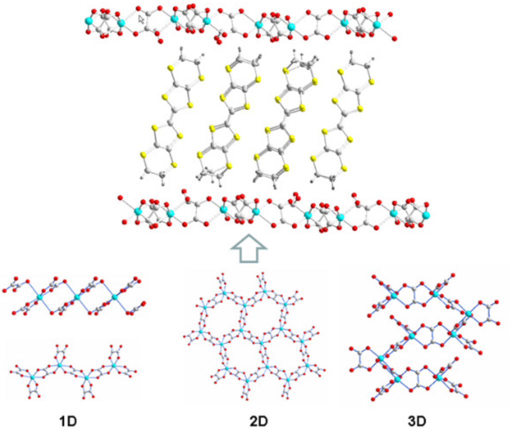
J. WRACHTRUP
3rd Institute of Physics, Stuttgart University, Germany

In the recent years diamond detects have become a playground for solid-state quantum optics. Mostly this is due to two characteristic properties. On the one hand paramagnetic defects show a complex level structure which allow to correlate defect degrees of freedom like electron spin with photon properties like polarization. On the other hand, photons emitted from defect do show favorable coherence properties, i.e. photon emission in their zero phonon line is transfer limited. Together with the outstanding spin coherence properties of defects quantum coherence can be generated efficiently, manipulated easily and hence exploited in quantum technology. Examples comprise efficient transfer of information by single defect center photons and generation of entangled defect states by using interacting defect center spins. A remaining challenge is structuring of photonic elements from diamond and efficient coupling of defect to phonon modes in such structures. A recent promising road towards application is the use of defects for precision sensing of e.g. temperature, pressure and electric as well as magnetic fields. The sensor properties rely on the outstanding spin control of defects. Long defect center coherence times, for example are a prerequisite for sensitive magnetic field measurements. The talk will outline the basics of diamond defect center quantum physics and highlight some of the recent sensor applications.

Organic-Inorganic Hybrid Dual-functional Molecular Crystal from Copper-Oxalate-Framework with Jahn-Teller Distortion

Bin ZHANG, Daoben ZHU
Organic Solid Laboratory, BNLMS, CMS & Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

The Jahn-Teller distortion of CuO_6 octahedon plays a key role in inorganic superconductor, such as the Jahn-Teller distortion of MnO_6 octahedron in magneto-resistance materials. Oxalate ($C_2O_4^{2-}$) anion, one of the most commonly used short connectors as O^{2-}, plays an important role in molecular-based magnet and conductor. The resonating valence bond state constructed from the Jahn-Teller distorted Cu^{2+} and resonance organic ligand with π-electron – $C_2O_4^{2-}$ should be a good candidate for functional molecular crystal with unexpected electronic and magnetism. The one-dimensional, two-dimensional and three-dimensional ammonium salts of Cu-oxalato-framework were obtained, and no long-range magnetic ordering was observed above 2 K. Single chain magnetism was observed in a ferromagnetic one-dimensional zigzag chain. Two-dimensional, three-dimensional antiferromagnetic compounds suggested candidates to quantum spin liquid. The proton conductivity was observed in ammonium salts containing H_2O with hydrogen bond between oxalate ligand and H_2O. The charge-transfer salts of organic donors and two-dimensional Cu-oxalato anions were obtained by electrocrystallization. When BEDT-TTF was replaced by BETS while crystal structure remained same in Donor$_3[Cu_2(C_2O_4)_3](CH_3OH)_2$, the conductivity increased from room-temperature semiconductor to metal, and the antiferromagnetic interaction between Cu^{2+} enhanced. An antiferromagnetic molecular conductor with metallic to 2 K was obtained when (4,4) grid Cu-O/C_2O_4 was used as counteranion. The XPS shows the coexistence of Cu^{2+} and Cu^{+} in charge-transfer salts.



This work was supported by NSFC. 21173230, 973 Project: 2011CB932302, 2013CB933403, P. R. China.

[1] B. Zhang, Y. Zhang, D. Zhu, Chem. Commun., 2012, 48, 197-199.
[2] B. Zhang, Y. Zhang, D. Zhu, Dalton Trans. 2012, 14, 8509-8511.
[3] B. Zhang, Y. Zhang, Z. Wang, S. Gao, F. Liu, Y. Guo, D. Zhu, CrystEngComm., 2013, 15, 3529-3535.

Dissipation and Decoherence of a Jahn-Teller Impurity in a Solid

Dennis P. CLOUGHERTY
Department of Physics, University of Vermont, Burlington, VT 05405-0125 USA

A continuum model for distortions of a charged nanoparticle embedded in an elastically isotropic, electrically insulating solid is proposed. The nanoparticle is regarded as a Jahn-Teller impurity whose shape distortions couple mechanically to the phonons of the elastic solid. This problem can be mapped to a generalization of the dissipative impurity model interacting with multiple phonon baths. Such dissipative models are typically classified by the behavior of a spectral density function J(ω) at low frequency. Here, matters are complicated by the existence of multiple baths. Multiple baths are a source of "quantum frustration" for the impurity [1], and the decoherence rate of the system can be suppressed even at strong coupling as a result. The ground state and dissipative dynamics are explored analytically with the use of a small polaron variational ansatz that has been successfully used recently to treat low-energy dynamics in atom-surface scattering [2].

[1] A.H. Castro Neto, E. Novais, L. Borda, G. Zarand, I. Affleck: Quantum Magnetic Impurities in Magnetically Ordered Systems, Phys. Rev. Lett. **91** (2003) 096401.

[2] D.P. Clougherty and Y. Zhang: Orthogonality Catastrophe in Quantum Sticking, Phys. Rev. Lett. **109** (2012) 120401.

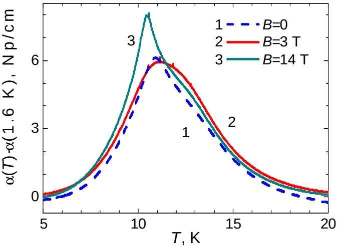
Evidence of magnetic field dependent relaxation in ZnSe:Cr crystal in ultrasonic experiment

N.S.AVERKIEV[1], K.A.BARYSHNIKIV[1], I.B.BERSUKER[2], V.V.GUDKOV[3,4], A.V.KOROSTELIN[5], A.I.LANDMAN[5], A.M.MONAKHOV[1], A.N.SARYCHEV[3], S.YASIN[6], S.ZHERLITSYN[7], and I.V.ZHEVSTOVSKIKH[3,7]

[1]A.F.Ioffe Physical Technical Institute of the RAS, 194021, St.-Petersburg, Russia
[2]Institute for Theoretical Chemistry, University of Texas at Austin, TX 78712, Austin, USA
[3]Ural Federal University, 620002, Ekaterinburg, Russia
[4]Russian Vocational Pedagogical University, 620012, Ekaterinburg, Russia
[5]P.N.Lebedev Physical Institute of the RAS, 119991, Moscow, Russia
[6]Hochfeld-Magnetlabor Dresden, Helmholtz-Zentrum Dresden-Rossendorf, D-01314 Drezden, Germany
[7]Institute for Metal Physics, Ural Department of the RAS 620990, Ekaterinburg, Russia

Resonant anomalies in the magnetic field dependences of ultrasonic (US) attenuation α and phase velocity have been found in the investigation of the ZnSe:Cr crystal at low temperatures [1]. The anomalies are observed with US frequency $\omega/2\pi=23.7$ MHz at $B\approx0.2$ T. Earlier, we have reported about observation of the relaxational anomalies in the temperature dependences of attenuation and elastic moduli. They have been found for to the longitudinal and slow shear wave propagating along the crystallographic axis <110> that produce tetragonal distortions of the tetrahedral Jahn-Teller (JT) complex $CrZn_4Se$. The $Cr^{2+}(d^4)$ ion in the $^5T_2(e^2t^2)$ high spin ground state is subject to the $T\times(e+t_2)$ JT problem with the global minima of the adiabatic potential energy surface of tetragonal symmetry. Relaxation occurs due to the transitions between the equivalent configurations of the JT complex through the orthorhombic saddle points (see [2] and references therein).

Here we report novel data that reveal the dependence of this type of relaxation on the magnetic field **B**. The experiments consist of the measurements of (i) the temperature dependences of attenuation and velocity at fixed B=0, 3, 5, 10, 12, 14 T, and (ii) their magnetic field dependences at fixed T=1.4, 2, 4, 6, 8, 9, 10, 12.5, 15, 17.5, 20 K. The figure shows the data obtained at $\omega/2\pi=39.6$ MHz. The curves derived at fixed T show monotonic magnetic field dependences at B>2 T which is well described by the spin-orbit Hamiltonian for the impurity complex: six-fold degenerate ground state at B=0 splits in the strong magnetic field, while the variation of population distribution increases the attenuation. Besides, the curves shown in the figure confirm the magnetic field dependence of the relaxation time.



Support by RFBR grant №12-02-00476-a is acknowledged. K.A.Baryshnikov is grateful for the financial support of the Dynasty Foundation.

[1] V.V. Gudkov, I.B. Bersuker, S. Yasin, *et al.*: Magnetoacoustic investigation of the Jahn-Teller effect in chromium doped ZnSe crystal, Solid State Phenomena **190** (2012) 707-710.

[2] V.V.Gudkov, I.B.Bersuker: Experimental evaluation of the Jahn-Teller effect parameters by means of ultrasonic measurements. Application to impurity centers in crystals; in Vibronic Interaction and the Jahn-Teller Effect, M.Atanasov, C.Daul, Ph.L.W.Tregenna-Piggot (eds) (Springer, Heidelberg, 2012) 143-161.

Orbital and spin structures in transition metal compounds with face-sharing octahedra

Kliment KUGEL[1], Daniel KHOMSKII[2], Artem SBOYCHAKOV[1],
and Sergey STRELTSOV[3]
[1]Institute for Theoretical and Applied Electrodynamics, Russian Academy of Sciences,
Izhorskaya str. 13, 125412 Moscow, Russia
[2]II. Physikalisches Institut, Universität zu Köln,
Zülpicher Str. 77, 50937 Köln, Germany
[3]Institute of Metal Physics, Ural Branch, Russian Academy of Sciences,
S. Kovalevskaya str. 18, Ekaterinburg, 620990 Russia

The study of correlated systems with orbital ordering (OO) is currently a very active field of research in solid state physics. Orbital ordering is not only accompanied (or caused) by structural transitions, but it also largely determines magnetic properties of many materials, e.g. transition metal (TM) oxides. Besides more traditional electron-lattice (Jahn-Teller) mechanism of OO, also a purely electronic (exchange) mechanism can lead to both orbital and magnetic orderings, which then turn out to be coupled.

For the doubly degenerate case in simple lattices as that of perovskites AMO_3 with MO_6 octahedra having common corner, the typical situation is such that ferro-orbital ordering gives rise to the antiferromagnetic spin exchange, whereas antiferro-OO is rather favorable for spin ferromagnetism. This statement became a kind of "folklore" and is often used to explain or to predict the type of magnetic ordering for particular systems. However, this conclusion is applicable for systems with particular geometry, with 180° M-O-M superexchange. There exist, however, many different situations in solids, with different geometries of the lattice, and this general paradigm (ferro-orbital–antiferro-spin and *vice versa*) may not, and does not work in other cases. One is that with neighboring TM ions having two common oxygens; for systems with MO_6 octahedral this is the case of common edge, with ~90° M-O-M bonds. This is, for example, typical for B-sites of spinels, where for e_g electrons the exchange interaction is ferromagnetic both for ferro- as for the antiferro-orbital ordering. Both these situations, with MO_6 octahedra with common corners and with common edge, are rather well studied theoretically. There exists, however, the third, much less studied situation – that with neighboring MO_6 octahedra having common face. Here, the superexchange occurs via three oxygens. The situation with the orbital ordering in this case and the form of the resulting (spin and orbital) exchange is practically not studied. Nevertheless, experimentally there are many TM compounds with such geometry. Such are for example hexagonal crystals $BaCoO_3$ or $CsCuCl_3$, containing infinite columns of face-sharing octahedra; many other similar systems have finite face-sharing blocks, e.g. $BaIrO_3$ or $BaRuO_3$. The first problem to consider for such systems is the question of a possible orbital and magnetic exchange in this geometry. This question will be addressed in the present talk. We consider in it the form of the spin-orbital superexchange for TM with double or triple orbital degeneracy for neighboring TM ions with face-sharing octahedra. One surprising result of our study is that, whereas for doubly degenerate system of perovskite type with 180° M-O-M bonds, the form of orbital term in the Hamiltonian is rather complicated, for common face the symmetric model is realized, with the orbital interaction of Heisenberg type. Often in this geometry the MO_6 octahedra have trigonal distortions. Such local distortions lead to splitting of t_{2g} orbitals into an a_{1g} singlet and e_g^{π} doublet. We show that for the partially filled e_g^{π} doublet, the resulting superexchange is very similar to the case of "real" e_g electrons, but here the orbital moment is not quenched and the real relativistic spin-orbit leads to rather non-trivial effects, which we also discuss in detail.

Multi-mode, Multi-State Quantum Dynamics Studies of Heteroaromatic Molecules

Simon NEVILLE[1], and Graham WORTH[1]
[1]University of Birmingham, United Kingdom

Small heteroaromatic molecules such as phenols, pyrroles and indoles represent computationally tractable models for the chromophores of many important biomolecules, including the DNA bases and aromatic amino acids. The photochemistry of these systems has generally been interpreted in terms of the roles played by low-lying, bound ππ* states and states of 3s/πσ* character that are quasi-bound with respect to a heteroatom-hydrogen or heteroatom-alkyl bond [1,2]. Common to many of these systems, however, is the existence of a number of low-lying 3p-type Rydberg states, the photochemical activity of which has previously been neglected.

We present here the results of multidimensional, multistate quantum dynamics studies of pyrrole and N-methylpyrrole following electronic excitation using the powerful multi-configurational time-dependent Hartree (MCTDH) and recently developed multi-layer MCTDH methods. For both systems, a re-evaluation of the roles played by previously neglected Rydberg states is made. In the case of pyrrole, it is found that excitation to low-lying 3s and 3p Rydberg states dominates the first band in the molecule's absorption spectrum, in stark contrast to previous assignments. In the case of N-methylpyrrole, the strong non-adiabatic coupling of 3s and 3p Rydberg states is found to result in a massive enhancement of the rate of tunneling of the methyl group of the N-CH_3 bond through the barrier to dissociation in the first excited state. The theoretical results discussed are compared to recently performed time-resolved photoelectron spectroscopy studies, to which good agreement is found.

[1] M. N. R. Ashfold, B. Cronin, A. L. Devine, R. N. Dixon, M. G. D. Nix, Science, **312** (2006) 1637.
[2] A. L. Sobolewski, W. Domcke, Chem. Phys., **259** (2000) 181.

Ground State of NO_3: From Lewis Structures to Spin-Orbit Coupling Effects

John F. STANTON
Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry
The University of Texas at Austin, Austin, TX 78712

The vibronic level structure associated with the ground electronic state of NO_3 has been studied for almost forty years, and these investigations have not been without controversy. Based on high-level vibronic calculations combining the framework of Köppel, Domcke and Cederbaum (KDC) with very accurate quantum chemistry calculations, results have been generated over the last several years that will form the core of this talk. The results of these calculations reveal a number of surprising things: 1) the fundamental of the ν_3 vibrational level is located more than 400 cm^{-1} below its formerly unchallenged assignment; 2) the infrared intensity of this band is very small, owing to a fortuitous cancellation of what are best termed (in a diabatic picture) "electronic" and "vibrational" transition moments; 3) the level is almost coincident (within 10 cm^{-1}) with the ν_1 level; 4) the strength of coupling between the ground $\tilde{X}^2A_2'$ and excited $\tilde{B}^2E'$ state is almost exactly the amount required for the lower adiabatic surface to be "flat" (having a zero second derivative in the direction of coupling modes), which complicates the question of "is it C_{2v} or is it D_{3h}" (from the point of view of a quantum chemist, i.e. r_e); 5) a number of very strong bands are seen below 2500 cm^{-1} (both computationally and observationally), which can be understood only by considering that the infrared spectra of NO_3 has considerable "electronic" character. All of these issues will be reviewed from the point of view of theory. In addition, newly developed quantum-chemical methods are used to calculate the spin-orbit coupling in the degenerate $\tilde{A}^2E''$ and $\tilde{B}^2E'$ excited Jahn-Teller active states of NO_3, and their influence on various types of spectra are discussed.

Spectroscopy and Dissociation Dynamics of the Excited States of the Nitrate Cation NO_3^+

Kana TAKEMATSU[1], Gustavo GARCIA[2], Laurent NAHON[2],
John STANTON[3], and Mitchio OKUMURA[1]
[1]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125 USA
[2]Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin, BP 48, 91192 Gif sur Yvette Cedex, France
[3]Department of Chemistry and Biochemistry, University of Texas, Austin, TX 78712 USA

The nitrate radical NO_3 has been an important benchmark system for theoretical treatments of non-adiabatic interactions. The first two excited states are both Jahn-Teller active, with significant non-adiabatic coupling among all three of the lowest states.

Much less is known about the NO_3^+ cation. The ground state (IP = 12.55 eV) possesses D_{3h} symmetry and is nondegenerate with $^1A_1'$ symmetry, while three of the lowest excited states, which all lie within 1.5 eV of the ground state, Jahn-Teller-active. However, the existence and nature of the excited states remains controversial.

There have been two low resolution experiments on the spectroscopy of the NO_3^+ cation, first by photoionization mass spectroscopy (PIMS) [1] and then by He I photoelectron spectroscopy (PES) of NO_3 [2]. While both experiments confirmed the D_{3h} symmetry of the ground state, the PIMS experiment found no evidence for excited states. In contrast, the PES spectrum revealed peaks that were assigned to excited states of NO_3^+. However, large background contributions in the PES experiment – arising from high concentrations of precursors (N_2O_5 and NO_2), raised concerns about the assignments. Ab initio calculations have attempted to address the discrepancy [3,4] and predict that the excited states may undergo dissociative ionization [5].

We report an experimental/theoeretical study on the Threshold PhotoElectron-PhotoIon Coincidence (T-PEPICO) spectroscopy of the cation NO_3^+. Experiments were performed on the DELICIOUS3 coincidence spectrometer on the DESIRS beamline at the Soleil Synchrotron. , Nitrate radicals NO_3 were formed by pyrolysis of N2O5 The experiment provide a definitive threshold photoelectron spectrum of NO_3^+ from the IP up to 18 eV. Photoelectron spectra and angular distributions derived from Velocity Map Imaging provide insights into the nature of the complex electronic structure, while photofragment kinetic and energy distributions provide information on the dissociation dynamics. We have also performed high level calculations using Equation of Motion methods to assign the observed spectra and explain the observed dynamics. In the region of the predicted Jahn-Teller states, we find dissociative ionization spectra with partially resolved vibronic structure that correlate with NO_2^+ and NO+ fragment ions. The current results resolve the controversy concerning the excited states of NO_3^+.

[1] P. S. Monks, L. J. Stief, M. Krauss, S. C. Kuo, Z. Zhang, R. B. Klemm, *J. Phys. Chem.* **98** (1994) 10017-10022.
[2] D. Wang , P. Jiang , X. Qian , G. Y. Hong, *J. Chem. Phys.* **106** (1997) 3003.
[3] D. Heryadi and D. L. Yeager *J. Chem. Phys.* **108** (1999) 1292.
[4] M. Wladyslawski and M. Nooijen, in *Low-Lying Potential Energy Surfaces*, (eds. Hoffmann, MR; Dyall, KG), ACS Symposium Series, **828** (2002) 65.
[5] H. Ndome and M. Hochlaf, J. Chem. Phys. **130** (2009) 204301.

Computational Analysis of Intrinsic Distortions of Jahn-Teller and Pseudo Jahn-Teller Active Molecules

Matija ZLATAR[1], Claude DAUL[2], Pablo GARCÍA-FERNÁNDEZ[3],
and Maja GRUDEN-PAVLOVIĆ[4]
[1]Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Belgrade, Republic of Serbia
[2]Department of Chemistry, University of Fribourg, Fribourg, Switzerland
[3]Ciencias de la Tierra y Física de la Materia Condensada, Universidad de Cantabria, Santander, Spain
[4]Faculty of Chemistry, University of Belgrade, Belgrade, Republic of Serbia

Any structural distortion of a polyatomic system is a consequence, of the Jahn-Teller, Pseudo Jahn-Teller, or Renner-Teller origin [1]. Analysis of the Adiabatic Potential Energy Surfaces (APES) of the molecules that are subject to the JT type effect will be presented, based on the model that utilizes the information from DFT calculations on a distorted stationary point on the APES. The essence of the model is to express the distortion along a model minimal energy path called Intrinsic Distortion Path (IDP) [2, 3], projecting the geometry of the system on the normal modes of the either high-symmetry or low symmetry nuclear configuration. This allows direct calculation of the vibronic coupling constants, and determination of the significance of all of the involved normal modes along a relevant particular path of distortion. The structural analysis is complemented by analysing the role played by the different electronic interactions (electron-nuclei, electron-electron, etc.) present in the Hamiltonian leading to a more complete and balanced view of the changes undergone by the system along the distortion [2].

The analysis of the Intrinsic Distortions will be briefly illustrated by the discussion of the single-mode JT distortions in VCl_4, As_4^- and Sb_4^- [4], multi-mode distortions in C_5H_5, $C_6H_6^{+/-}$, C_7H_7 [2], and $C_{60}^{+/-}$ [3]. It has been found that JT relaxation in multi-mode problems occurs in two well-differentiated phases. The first phase is governed by the electron-nuclear interactions, as it is typical for the JT problems, while in a second phase changes in the electron density, driven by the PJT effect, significantly modify the kinetic and electron-electron contributions to the total energy.

As an example of the PJT effect, pyramidal distortion in ammonia will be analysed, revealing the strong importance of the kinetic energy of the electrons in the lowest a_2'' orbital to trigger the instability [5].

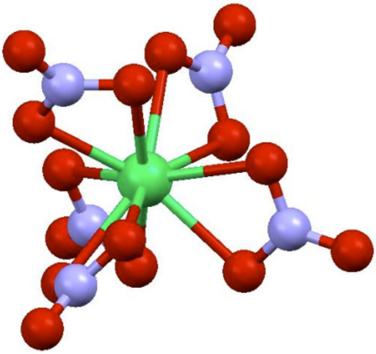
[1] I. B. Bersuker: The Jahn-Teller Effect, (Cambridge University Press, Cambridge, 2006).
[2] M. Gruden-Pavlović, P. García-Fernández, Lj. Andjeković, C. Daul, M. Zlatar: Treatment of the Multimode Jahn-Teller Problem in Small Aromatic Radicals, JPCA **115** (2011) 10801-108013.
[3] H. Ramanantoanina, M. Zlatar, P. García-Fernández, C. Daul, M. Gruden-Pavlović: General treatment of the multimode Jahn–Teller effect: study of fullerene cations, PCCP **15** (2013) 1252-1259.
[4] M. Perić, Lj. Andjelković, M. Zlatar, C. Daul, M. Gruden-Pavlović: DFT investigation of the influence of Jahn-Teller distortion on the aromaticity in square-planar arsenic and antimony clusters, Polyhedron (2014) 10.1016/j.poly.2014.02.005
[5] P. García-Fernández, J. A. Aramburu, M. Moreno, M. Zlatar, M. Gruden-Pavlović: A Practical Computational Approach to Study Molecular Instability Using the Pseudo-Jahn–Teller Effect, JCTC, **10** (2014) 1824-1833.

Explicit Control Over Spin-states using combined Density Functional and Ligand Field Theory.

Maja GRUDEN-PAVLOVIC[1], Claude DAUL[2], Werner URLAND[2] and Matija ZLATAR[1]
[1]University of Belgrade, Serbia
[2]University of Fribourg, Switzerland

It has long been recognized that metal spin states play a central role the new technologies, in the reactivity of important biomolecules, in industrial catalysis and in spin crossover compounds. While several classes of these bistable systems exist, Single Ion Magnets (SIM), where each state represents a different magnetization that relaxes very slowly are, perhaps, the ones that have attracted highest expectations for practical application. Elucidating the role and effect of different spin states on the properties of a system is presently one of the most challenging endeavours both from an experimental and theoretical point-of-view. It is of utmost importance to understand the interplay between various factors responsible for magnetic properties, in particular vibronic and spin-orbit coupling.

Considering Tetraphenylarsonium Pentakis(nitrato)ytterbate(III) as prototype for SIMs, we present methodological advances and state-of-the art computations analysing the electronic structure and its relationship with the magnetic properties due to the Yb(III) ion.



The results of the quantum chemical calculations are quantitatively decrypted in the framework of Ligand Field (LF) theory, extracting the full parametric sets and interpreting in heuristic key the outcome. An important result is the characterization of the UV-Vis spectra and of the magnetic properties in the ground and excited states.
The methodology is based on the exploitation of the data from the black box of the *non-empirical:* Multiplet and Spin-Orbit (SO) calculations. The ground state is characterized by the anisotropy of the g-tensor and the excited states by the optical spectra. The predicted and observed findings are in excellent mutual agreement.

[1] W. Urland and R. Kremer: Electron Spin Resonance Spectra of Low-Symmetry Rare-Earth Complexes Tetraphenylarsonium Pentakis(nitrato)ytterbate(III), Inorg. Chem. **23** (1984), 1550-1553

Construction of analytic multi-sheeted potential-energy surfaces from ab initio data

Daniel OPALKA[1], Wolfgang DOMCKE[2]
[1]Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom
[2]Department of Chemistry, Technische Universität München, D-85747 Garching, Germany

Quantum dynamical simulations of non-adiabatic processes are limited by the lack of multi-dimensional multi-sheeted potential-energy (PE) surfaces. Jahn-Teller systems are prototypical examples for strongly coupled PE surfaces and various molecular PE surfaces have been developed exploiting their inherent molecular point-group symmetry. More generally, qualitatively correct adiabatic PE surfaces must be symmetric with respect to molecular translation, rotation, inversion and permutation of identical nuclei. In contrast to an increasing number of such analytic PE surfaces for closed-shell molecules in their electronic ground state [1], very few full-dimensional multi-sheeted PE surfaces for more than four nuclei have been reported so far.

In this contribution we present a recently developed method for the construction of permutationally invariant multi-sheeted PE surfaces [2]. While particularly useful for Jahn-Teller systems, the technique is also suitable for clusters and molecules without molecular point group symmetry. Although based on adiabatic ab initio data, difficulties in the analytic representation arising from cusps and conical intersections are avoided by applying a non-linear transformation to the electronic energies. Hence no diabatic model is required at this stage and the nonlinear fitting problem is effectively converted into a linear least-squares minimization procedure for a set of smooth polynomials of the adiabatic energies.

The methodology is illustrated for the example of the methane cation in its strongly coupled T_2 electronic ground state. A full 9D PE surface for the three sheets of the T_2 electronic state is presented with high accuracy over a wide range of geometries. Moreover, a numerical scheme for the construction of diabatic PE surfaces from a topological model is presented as required for wavepacket propagations in quantum dynamics. As will be shown, the topology of the PE surfaces is closely related to the well-known linear Jahn-Teller models and, more generally, can be derived from an Euclidean distance matrix.

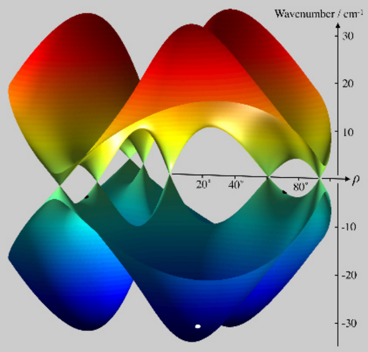
[1] B. J. Braams, J. M. Bowman: Permutationally invariant potential energy surfaces in high dimensionality, Int. Rev. Phys. Chem., **28** (2009) 577-606

[2] D. Opalka, W. Domcke: Interpolation of multi-sheeted multi-dimensional potential-energy surfaces via a linear optimization procedure, J. Chem. Phys. **138** (2013) 224103.

A System of $e \times E$ Conical Intersections Between Vibrationally Adiabatic Surfaces In Methanol.

Mahesh B. DAWADI and David S. PERRY
Department of Chemistry, The University of Akron, Akron OH 44325, USA

The discovery of a set of seven conical intersections (CI's) between vibrationally adiabatic surfaces in methanol is reported. The intersecting surfaces represent the energies of the two asymmetric CH stretch vibrations, ν_2 and ν_9, regarded as adiabatic functions of the torsional angle, γ, and COH bend angle, ρ. One conical intersection, required by symmetry, is located at the C_{3v} geometry where the COH group is linear ($\rho = 0°$); the other six are in eclipsed conformations with $\rho = 62°$ and 94°. The three CI's at $\rho = 62°$ are close to the equilibrium geometry ($\rho = 71.4°$), within the zero-point amplitude of the COH bending vibration. CI's between electronic surfaces have long been recognized as crucial conduits for ultrafast relaxation, and recently Hamm and Stock [1,2] have shown that vibrational CI's may also provide a mechanism for ultrafast vibrational relaxation.



The ab initio data reported here are well fit by an extended Zwanziger and Grant model [3] for $E \otimes e$ Jahn-Teller systems in which Renner-Teller coupling is also active. However, in the present case, the distortion ρ from C_{3v} symmetry is much larger than is typical in the Jahn-Teller coupling of electronic surfaces and accordingly higher-order terms in ρ are required.

When the dimensionality of the low-frequency space is extended to include the CO bond length as well as γ and ρ, the individual CI's become seams of CI's. It is shown that the CI's at ρ = 62° and 94° lie along the same seam of CI's is this higher dimensional space.

Since four CI's are enclosed by the torsional minimum energy path (MEP), the Zwanziger and Grant theorem [3] predicts a geometric phase of +1 in agreement with the findings of Xu at al. [4]. However, from a semiclassical point of view, one might consider additional classical paths for a 2π torsional rotation that could enclose an odd number of CI's, say 1 or 3. Thus, in a fully coupled treatment, the ν_2 and ν_9 wavefunctions may be linear combinations of basis states of differing geometric phase, with the +1 contribution being dominant.

The presence of CI's explains the sharp, almost discontinuous, change the vibrational characters of ν_2 and ν_9 found [4] for a small change in γ along the MEP near the eclipsed conformation. The CI's provide a connection between the vibrationally adiabatic surfaces pointing to the expectation of accelerated energy transfer processes in localized regions around the CI's.

[1] P. Hamm and G. Stock, *Phys. Rev. Lett.* 109, 173201 (2012)
[2] P. Hamm and G. stock, *Mol. Phys.* 111, 2046 (2013).
[2] J.W. Zwanziger and E.R. Grant, *J. Chem. Phys.* **87**, 2954 (1987).
[4] L.-H. Xu, J.T. Hougen, R.M. Lees, *J. Mol. Spectrosc.* 293-294, 38 (2013).

Conical Intersections in D_{3h} molecules: Diabatic PESs for Spectroscopic & Scattering Processes

Satrajit ADHIKARI
Department of Physical Chemistry, Indian Association for the Cultivation of Science,
Kolkata - 700 032, INDIA
E-mail: pcsa@iacs.res.in

We calculate adiabatic Potential Energy Surfaces (PESs) and Non-Adiabatic Coupling Terms (NACTs) for the excited electronic states ($2^2E'$ and $1^2A_1'$) of alkali trimers (Na_3 and K_3) [1-3] and the three lowest electronic singlet states ($1^1A'$, $2^1A'$ and $3^1A'$) of H_3^+ system [4], where symmetry enforced and accidental degeneracies are identified. In case of alkali trimers, the collapse of Conical Intersections (CIs) at D_{3h} symmetry point is an interesting observation. While performing Adiabatic to Diabatic Transformation (ADT), the NACTs are adapted with Molecular Symmetry (MS) to assign their Irreducible Representations (IREPs) in order to construct totally symmetric nuclear Hamiltonian. Finally, we carry out reactive scattering dynamics [5,6] on the adiabatic and diabatic surfaces of H_3^+ system in hyperspherical coordinates for total angular momentum zero and non-zero situation to reproduce experimental cross sections and rate coefficients for reactive non-charge and charge transfer processes [7,8].

[1] S. Mukherjee, S.Bandyopadhyay, A. K. Paul and S. Adhikari, J. Phys. Chem. A **117** (2013) 3475.
[2] S. Mukherjee, S.Bandyopadhyay, A. K. Paul and S. Adhikari, J. Phys.: Conf. Ser. **428** (2013) 012008.
[3] S. Mukherjee and S. Adhikari, Chem. Phys. (in revision, 2014).
[4] S. Mukherjee and S. Adhikari, J. Chem. Phys. (submitted, 2014).
[5] S. Adhikari and A. J. C. Varandas, Comp. Phys. Comm. **184** (2013) 270.
[6] T. Sahoo, S. Ghosh, S. Adhikari, R. Sharma, A. J. C. Varandas, J. Phys. Chem. A (submitted, 2014).
[7] G. Ochs and E. Teloy, J. Chem. Phys. **61** (1974) 4930.
[8] D Gerlich, Adv. Chem. Phys. Part 1. **82** (2007) 1.

Reconciliation of Spectroscopic Results and Electronic Structure Calculations for Jahn-Teller-Active Molecules

Terry A. MILLER
Department of Chemistry and Biochemistry, The Ohio State University,
Columbus Ohio 43210, USA

Molecules that are Jahn-Teller active (JTA) are often difficult with which to deal from either an experimental or a theoretical point of view. Most electronic structure calculations assume the Born-Oppenheimer approximation and produce adiabatic potential energy surfaces (PES). Treating JTA molecules usually requires consideration of vibronic coupling between diabatic PESs. The spectra of such molecules are often much more complex than corresponding molecules that are well described by the Born-Oppenheimer approximation. Their vibrational structure can be quite irregular and their rotational structure often departs markedly from that expected for simple rigid rotors. Due to their open-shell nature JTA molecules are typically chemically reactive and experimentally elusive, so that obtaining good spectra can be challenging.

Fortunately much progress has been made in recent years both in the theoretical treatment of these molecules and the ability to obtain high quality vibrational and rotational spectra of these species. This talk will focus on comparing theoretical and experimental results for several JTA and pseudo-JTA molecules, for which we have obtained and analyzed vibronically and rotationally resolved spectra. These molecules include methoxy, CH_3O and CD_3O, and its asymmetrically substituted derivatives, $CH_nD_{3-n}O$ and $CH_n(CH_3)_{3-n}O$. Other examples include the nitrate radical, NO_3, cyclopentadienyl, C_5H_5, and its asymmetrically deuterated derivatives $C_5H_nD_{5-n}$. Experimental results will be compared to the results of state-of-the-art electronic structure calculations for these molecules.

Jahn-Teller effect in CH_3X: spin-vibronic couping, mode coupling and tunneling splitting

Yuxiang MO
Department of Physics, Tsinghua University, Beijing 100084, China

The Jahn-Teller effects in molecules provide benchmark examples to study spin-vibronic coupling that is vital important in photochemistry and molecular reaction dynamics. The molecules $CH_3F^+(X^2E)$, $CH_3Cl^+(X^2E)$ and $CH_3CN^+(X^2E)$ that have degenerate electronic states in C_{3v} symmetry are prototypical molecules to study the Jahn-Teller effect. Recently, we have measured the spectra of these molecules up to 3000 cm^{-1} above the ground states using high resolution zero kinetic energy photoelectron spectroscopic method (ZEKE)[1-4]. Theoretical calculations using diabatic models including high order vibronic coupling and vibrational mode coupling terms and also using high level *ab initio* calculation of adiabatic potential energy surfaces have been performed.

For $CH_3Cl^+(X^2E)$, it is found that the JT effect mainly arises from the linear vibronic couplings, the mode couplings between the degenerate CH_3 deform and CH_3 rock vibrations, and also the mode couplings between the symmetric C-Cl streching vibration and the degenerate vibrational modes. In contrast with CH_3Cl^+, the degenerate vibrations in $CH_3F^+(X^2E)$ split greatly the adiabatic potential energy surfaces (PESs), the lower PES forms three deep potential energy wells for each vibraional modes resulting in the tunneling splitting of vibrational energy levels. For example, the energy splitting for the first excited vibrational energy level is calculated as 111 cm^{-1} that is confirmed by the experimental value. For both molecules, the theoretical calculations can reproduce the experimental energy levels within 8 cm^{-1}.

We also performed theoretical calculations on spin-vibronic energy levels of isotopologues $CH_2DO/CHD_2O(X^2E)$ that have Jahn-Teller effect. For $CH_3O/CD_3O(X^2E)$, only the degenerate vibrational modes break the C_{3v} geometric symmetry. For CH_2DO/CHD_2O, all their normal vibrational motions break the C_{3v} geometric symmetry, which results in a splitting of the adiabatic potential energy surfaces, that is, all vibrational modes are Jahn-Teller active. Therefore, each fundamental vibrational energy level of CH_2DO/CHD_2O splits into two levels due to a combination of Jahn-Teller and spin-orbit interactions. The calculated spin-vibronic energy splittings for the vibrational ground states of CH_2DO/CHD_2O are in good agreement with the reported experimental results.

[1] Y. Yang *et al.***,** The Jahn-Teller effects in $CH_3CN^+(X^2E)$ and $CD_3CN^+(X^2E)$ studied by zero kinetic energy photoelectron spectroscopy, J. Phys. Chem. A, **109** (2005)9964.
[2] Z. Shao *et al*., The Jahn-Teller effect in $CH_3Cl^+(X^2E)$: A combined high-resolution experimental measurement and *ab initio* theoretical study, J. Chem. Phys. **136** (2012) 064308.
[3] Z. Shao and Y. Mo, Jahn-Teller effect in $CH_2DO/CHD_2O(X^2E)$, vibronic coupling of all vibrational modes, J. Chem. Phys. **138** (2013) 244309.
[4] S.Gao *et al*., Tunneling splittings in vibronic energy levels of $CH_3F^+(X^2E)$ studied by high resolution photoelectron spectroscopy and ab initio calculation, J. Chem. Phys. **139**(2013), 064302 .

Sensitivities of Strong Laser Field Spectroscopies to Evolving Molecular Structure in Polyatomic Systems

Iain WILKINSON[1], Andrey E. BOGUSLAVSKIY[1,2], Jochen MIKOSCH[1,3], Julien B. BERTRAND[1,2], Hans Jakob WÖRNER[1,4], David VILLENEUVE[1], Michael SPANNER[1], Serguei PATCHKOVSKII[1], and Albert STOLOW[1,2,3]
[1]National Research Council of Canada, 100 Sussex Drive, Ottawa, K1A 0R6, Canada
[2]Department of Physics, University of Ottawa, MacDonald Hall, 150 Louis Pasteur, Ottawa, Ontario, K1N 6N5, Canada
[3]Department of Physics, Queen's University, 99 University Avenue, Kingston, Ontario, K7L 3N6, Canada
[4]Laboratorium fur Physikalische Chemie, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

Time-resolved (TR) high harmonic spectroscopy (HHS) has emerged as an intriguing probe of evolving excited state electronic structure [1, 2]. The technique is intrinsically sensitive to variations in vertical ionisation potential as well as the electronic character of the probed valence states. As such, the method appears well suited to probing excited state dynamics in molecules. However, difficulties may arise in the interpretation of TR high harmonic spectra of polyatomic systems due to the inherent complexity of the probe. Therefore, careful cross-calibration with established techniques such as TR photoelectron spectroscopy (PES) will be beneficial.

Using the non-adiabatic and spin-orbit coupling induced dynamics following Clements band excitation in SO_2 [3, 4, 5] as an explorative example, the same excited state wave packet has been probed using the TR HHS, TR above threshold ionisation (ATI) and TR PES techniques. High-level electronic structure theory and the results obtained with the different probe techniques allowed the relative sensitivities of these methods to be examined. In contrast to the TR PES method, the strong laser field probes were found to be surprisingly insensitive to the periodic vibronic motion known to occur on the $(B)^{1}B_{1}/(A)^{1}A_{2}$ lower adiabatic potential energy surface. Moreover, they offered little insight into the intersystem crossing found to occur from the same surface. This can be explained using a simple 1D bending mode model based on calculated angle-resolved strong-field ionisation yields and recombination dipole matrix elements. Implications for future TR HHS and TR ATI experiments with polyatomic molecules will be discussed.

[1] H. J. Wörner *et al.*, Following a Chemical Reaction Using High-Harmonic Interferometry, Nature **466** (2010) 604
[2] H. J. Wörner *et al.*, Conical Intersection Dynamics in NO_2 Probe by Homodyne High-Harmonic Spectroscopy, Science **29** (2011) 121
[3] J. H. Clements, On the Absorption Spectrum of Sulphur Dioxide, Phys. Rev. **47** (1935) 224
[4] C. Lévêque *et al.*, Ab Initio Quantum Study of the Photodynamics and Absorption Spectrum for the coupled 1 $^{1}A_{2}$ and 1 $^{1}B_{1}$ states of SO_2, J. Chem. Phys. **138** (2013) 044320
[5] I. Wilkinson *et al.*, Excited States Dynamics in SO_2 I: Bound State Relaxation Studied by Time-Resolved Photoelectron-Photoion Coincidence Spectroscopy, J. Chem. Phys., in press (2014)

Ab initio quantum study of the photodynamics for the coupled 1^1A_2 and 1^1B_1 states of SO_2.

Camille LEVEQUE[1,2,3], Richard TAIEB[1,2], and Horst KOPPEL[3]
[1]UPMC Univ. Paris 6, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, (Paris, France)
[2]CNRS, UMR 7614, LCPMR, (Paris, France)
[3]Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Germany

The presence of conical intersections in molecules is known to play a key role in ultrafast nonradiative de-excitation processes after photoexcitation. In the SO_2 molecule the conical intersection between the two lowest excited states gives rise to such a non-radiative transfer from one state to the other. However, little is known in the literature about the details of this process and its implication on the UV absorption spectrum.

In this work we perform a comprehensive study of the nuclear dynamics occurring on the two lowest singlet-excited states of SO_2 (1^1A_2 and 1^1B_1). To deal with the conical intersection we diabatize the potential energy surfaces (PES) using the concept of regularized diabatic states [1]. Solving the time-dependent Schrödinger equation on coupled surfaces [2], we get insight into the dynamics and compute the photo-absorption spectrum. The latter is in very good agreement with the experimental one in the range of 29000-42000 cm^{-1} [3].

As mentioned above, nuclear dynamics in the vicinity of conical intersection is fast. Iain Wilkinson *et al*. [4] proposed the use of a multi-photon ionization pump-probe scheme to follow the dynamics on the lowest excited states of SO_2. Theoretically we investigated [5], the same process and obtain results in excellent agreement with the observations. It turns out that the collection of the photoelectrons for various time delays between the pump and the probe pulses relates directly to the coupling between the 1^1A_2 and 1^1B_1 states, giving for the first time an experimental access to this dynamics in the time-domain.

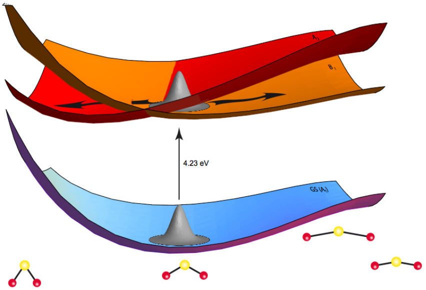


Fig. 1. Schematic illustration of the nuclear dynamic occuring after UV absorption in SO_2. The nuclear wavepacket, start its evolution from the 1^1B_1 state (dipole allowed transition) resented by the orange surface, and reaches the 1^1A_2 state (red surface) through non-adiabatic coupling.

[1] H. Köppel *et al.*: Construction scheme for regularized diabatic states. J. Chem. Phys. **115** (2001) 2377.
[2] H.-D. Meyer *et al.*, Physics Reports **324** (2000) 1.
[3] C. Lévêque *et al.*: Ab initio quantum study of the photodynamics and absorption spectrum for the coupled 1^1A_2 and 1^1B_1 states of SO_2 J. Chem. Phys. **138** (2013) 044320.
[4] I. Wilkinson *et al.*, J. Chem. Phys. (submitted).
[5] C. Lévêque *et al.*, J. Chem. Phys. (accepted).

Internal Conversion and Intersystem Crossing in SO_2 Studied by Surface-Hopping Molecular Dynamics

Sebastian MAI[1], Philipp MARQUETAND[1], and Leticia GONZÁLEZ[1]
[1]Institute of Theoretical Chemistry, University of Vienna, Währinger Straße 17, 1090 Vienna, Austria

The two lowest singlet excited states of SO_2 exhibit a pseudo-Jahn-Teller instability [1]. This is the reason why the excited-state wavepacket remains on the lower excited-state PES of mixed $^1B_1/^1A_2$ character. This behavior explains the main features of the complicated vibrational structure of the first allowed band of the absorption spectrum of SO_2. Another very weak absorption band exists, which was proposed to originate from ISC [2] to close-lying triplet states. A large body of excited-state ab initio calculations revealed that three triplet states of $^3A_2$, $^3B_1$ and $^3B_2$ symmetry could be involved in ISC. However, the relative importance of these triplet states could so far not be elucidated experimentally, with quantum chemistry calculations or with a recent dynamics study [3].

Hence, in this work [4] the role of the triplet states in the photorelaxation dynamics of SO_2 has been studied using mixed quantum-classical dynamics simulations. The simulations were performed with our Surface Hopping including ARbitrary Couplings (SHARC) method [5]. Intersystem crossing processes caused by spin-orbit coupling were found to occur on an ultrafast, few-100-fs time scale, competing with the oscillatory population transfer between the $^1B_1$ and $^1A_2$ states already reported in earlier studies [1]. The $^3B_2$ state was found to be primarily populated by ISC, while the population of the $^3B_1/^3A_2$ coupled states remained low (see Figure 1), in agreement with recent wavepacket simulations also including triplet states [6].

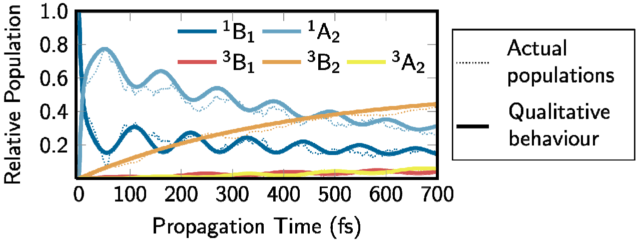


Figure 1: Excited-state populations in SO_2 during the surface hopping dynamics simulations.

[1] H. Müller, H. Köppel: Adiabatic wave-packet motion on conically intersecting potential energy surfaces. The case of SO_2 ($^1B_1$-$^1A_2$), Chem. Phys. **183**, (1994) 107-116.
[2] A. E. Douglas: The Zeeman effect in the spectra of polyatomic molecules, Can. J. Phys. **36** (1958) 147-149.
[3] C. Xie, X. Hu, L. Zhou, D. Xie and H. Guo: Ab initio determination of potential energy surfaces for the first two UV absorption bands of SO_2, J. Chem. Phys. **139** (2013) 014305.
[4] a) S. Mai, P. Marquetand, L. González: Non-adiabatic and Intersystem Crossing Dynamics in SO_2: II. The Role of Triplet States in the Bound State Dynamics Studied by Surface-Hopping Simulations, J. Chem. Phys., accepted (2014). b) S. Mai, P. Marquetand, L. González: arXiv:**1302.1438** (2014).
[5] M. Richter, P.Marquetand, J. González-Vázquez, I. Sola, L. González: SHARC: Ab initio Molecular Dynamics with Surface Hopping in the Adiabatic Representation Including Arbitrary Couplings, J. Chem. Theory Comput. **7** (2011) 1253-1258.
[6] C. Lévêque, R. Taïeb, H. Köppel: Theoretical prediction of the importance of the $^3B_2$ state in the dynamics of sulfur dioxide, J. Chem. Phys. Comm. **140** (2014) 091101.

REV8

Dynamic Jahn-Teller distortions in crystalline materials

Frank BRIDGES
Physics Dept. University of California, Santa Cruz, 96064, USA.

The typical Jahn-Teller (JT) distortion occurs for an isolated metal ion (M) with a 2-fold degenerate energy state in a high symmetry environment; the electronic energy can be lowered (the degenerate states split) if the local environment distorts. For octahedral symmetry such a distortion could result in two long and four short M-O bond lengths. JT distortions are also observed or expected in some crystalline materials; I'll discuss a few cases here. An important class of such materials has some (local) conductivity; the electrons (holes) can hop and then the distortion may follow each charge carrier. However, the extent of the observed distortions depends on various time scales; the charge hopping time, the lattice response times, and the probe response time. $LaMnO_3$ has large static distortions around each Mn ion, which is JT active because a single electron occupies a 2-fold degenerate e_g state. When doped with divalent atoms (Ca^{+2}, Sr^{+2}) on the La site, holes are introduced into the electron bands and remain localized on particular Mn atoms - at least for phonon time scales (10^{-12} to 10^{-13} sec). An open question is the extent of the hole wave function - is it localized primarily on one Mn atom or does it extend over two or more Mn atoms? The presence of a hole on a single Mn atom would eliminate the JT distortion on that atom, while if the hole extends over two (or more) Mn sites, the JT distortion on each site is expected to be reduced. For Ca doped $LaMnO_3$ we argue that at high T, above the ferromagnetic transition, the hole is delocalized over two sites forming a 2-site polaron, while at low T the hopping becomes fast enough that the lattice can no longer respond and the distortions disappear [1]. For the similar Sr doped cobaltites, $LaCoO_3$:Sr, the hole states are delocalized in band states, with a significant fraction of the hole located on the O atoms [2], and no JT distortion is observed. Another unusual system is $Ba_3CuSb_2O_9$ in which the Cu^{+2} (d^9 configuration) should be JT-active but for which there are conflicting results as to the presence of JT distortions [3]. Diffraction sees a hexagonal long-range structure with no direct indication of any JT distortion, while ESR experiments also show an isotropic g-factor. However JT distortions are observed in EXAFS. Either the JT distortions are dynamical and varying rapidly or there is a random static JT distortion of the Cu sites that has no long range order and can lead to an isotropic g-factor for an unusual coupling of the Cu spins on a triangular lattice.

[1] Detailed relationship between local structure, polarons, and magnetization for $La_{1-x}Ca_xMnO_3$ ($0.21 \leq x \leq 0.45$), F. Bridges, L. Downward, J. J. Neumeier, and T. A. Tyson. *Phys. Rev. B*, **81**, 184401 (2010).

[2] Evolution of Magnetic Oxygen States in Sr-Doped $LaCoO_3$. S. Medling, Y. Lee, H. Zheng, J.F. Mitchell, J.W. Freeland, B.N. Harmon and F. Bridges *Phys. Review Lett.*, **109**, 157204 (2012).

[3] Spin-orbital Short-range Order on a Honeycomb-based Lattice., S. Nakatsuji, K. Kuga, K. Kimura, R. Satake, N. Katayama, E. Nishibori, H. Sawa, et al., *Science* , **336**, 1212154 (2012).

REV9

Influence of Jahn-Teller and Pseudo Jahn-Teller over magnetism in 3d systems: A first-principles view

Pablo GARCÍA-FERNÁNDEZ[1]
[1]Universidad de Cantabria, Avenida de los Castros s/n, 39005 Santander, Spain.

Systems containing transition-metals present physical and chemical properties that are very different to those consisting only of main-elements or that incorporate rare-earth ions. The reason behind this behavior is an intermediate localization that is strong enough for the appearance of correlated phenomena, like magnetism, but that does not exclude the ions from participating in covalent bonding with ligands. Thus, in many of these systems a delicate balance is reached where the electronic properties are very sensitive to the geometric structure and are the subject of Jahn-Teller or pseudo Jahn-Teller interactions. While examples of this kind of behavior are almost innumerable, including multiferroics, colossal magnetoresistance manganites, spin-crossover systems, etc. in this talk we will discuss some interesting cases involving magnetism where we stress the necessity of using first-principles calculations to assess the magnitude of the interactions involved in these phenomena and validate the correct model to describe them.

An interesting, conflicting case is the nature of orbital-ordered systems where results have usually been interpreted in the light of either the Kugel-Khomskii model or the cooperative Jahn-Teller effect (see, e.g. [1]). While recent ab initio results for cubic systems indicate that both interactions have similar magnitude [2], we have studied [3] what happens in systems with lower symmetry where degeneracy is not possible. Our main finding is that while orbital-ordering persists its nature is largely determined by the usually ignored electrostatic potential created by the lattice over the magnetic transition-metal complex instead of superexchange as in the Kugel-Khomskii model. Moreover, we find that the staggered distortion pattern usually associated to the cooperative Jahn-Teller effect in the perovskites is only present when the electrostatic field favors localization of the electrons in the plane perpendicular to the main axis of the crystal. We show that unraveling the mechanism behind this pseudo Jahn-Teller effect is the key to understand the striking differences between the crystals K_2CuF_4 and La_2CuO_4 which, otherwise, would present very similar magnetic properties.

Another important class of systems that has attracted much attention recently is molecular magnets. Here, the scientific community is looking for molecules presenting a very large magnetic anisotropy that delays the inversion of the magnetic moment of the molecule in macroscopic times. Less studied, but equally important, is the magnetic tunneling between the spin-states on both sides of the barrier. We have developed a model where we explain the sensitivity of both barrier and tunneling in trigonal bipyramidal Ni(II) complexes to coordination and deformation of the complex using vibronic coupling theory. As a highlight, we find [4] that the complex $[NiCl_3(Hdabco)_2]^+$ (dabco is 1,4-diazabicyclo[2.2.2]-octane) displays both a very large magnetic anisotropy energy, 524 cm^{-1}, and a small tunneling splitting, 0.2 cm^{-1}, when compared to other systems containing the same metal due to the full suppression of the Jahn-Teller distortion by the spin-orbit coupling.

[1] V. Polinger in The Jahn-Teller Effect: Fundamentals and Implications for Physics and Chemistry, (Springer-Verlag, Berlin, 2009) 685-725
[2] E. Pavarini, E. Koch, A.I. Lichtenstein: Phys. Rev. Lett. **101** (2008) 266405.
[3] P. Garcia-Fernandez et al. J. Phys. Chem. C, (2014) DOI: 10.1021/jp412329x
[4] M. Gruden-Pavlović et al. Chem. Sci. **5** (2014) 1453-1462

Why the properties of K_2CuF_4, $K_2ZnF_4:Cu^{2+}$ and $KZnF_3:Cu^{2+}$ model systems are so different?

J.A. ARAMBURU[1], J. M. GARCÍA-LASTRA[2], P. GARCÍA-FERNÁNDEZ[1], M.T. BARRIUSO[1], and M. MORENO[1]
[1]Universidad de Cantabria, Avenida de los Castros s/n, 39005 Santander, Spain
[2]Department of Energy Conversion and Storage, Technical University of Denmark, DK-4000 Roskilde, Denmark

This work is aimed at clearing up the *actual origin* of the surprisingly different structural and spectroscopic properties displayed by three *model* systems, involving CuF_6^{4-} complexes [1,2], using *ab initio* calculations [3,4]. So while in $K_2ZnF_4:Cu^{2+}$, where Zn^{2+} is surrounded by a nearly perfect F^- octahedron, experimental data prove that the hole is placed in the $3z^2$-r^2 orbital along the crystal **c** axis, in a cubic perovskite like $KZnF_3$ the hole of a CuF_6^{4-} complex appears in the x^2-y^2 orbital. Moreover in K_2CuF_4 the CuF_6^{4-} units display an orthorhombic symmetry with the longest axis placed inside the CuF_2 layer. Remarkable differences also appear when looking at the experimental energy difference, Δ, between x^2-y^2 and $3z^2$-r^2 orbitals which is equal to 1.03 eV and ~0.7 eV for K_2CuF_4 and $K_2ZnF_4:Cu^{2+}$ respectively while $|\Delta| <0.5$ eV for $KZnF_3$: Cu^{2+} [2-4]. As a salient feature it is proved that for a perfect octahedral CuF_6^{4-} complex ($R_{ax} = R_{eq} = 2.03$ Å) in the layered K_2ZnF_4 compound the ground state is an *orbital singlet* with the hole *already* placed in a $3z^2$-r^2 orbital and $\Delta = 0.34$ eV [3]. This surprising fact is shown to be due to the action of the tetragonal electrostatic potential, $V_R(\mathbf{r})$, created by the rest of lattice ions on the electrons *localized* in the CuF_6^{4-} complex, a key point *usually ignored* in the realm of Transition Metal chemistry. The present calculations also prove that the hole *forced* to be in the $3z^2$-r^2 orbital induces a ligand relaxation ($R_{ax} = 1.93$ Å ; $R_{eq} = 2.04$ Å) [3], smaller than that derived from previous estimations [1], which increases Δ up to 0.61 eV in agreement with experimental data. This ligand relaxation in the $^2A_{1g}$ ground state involves the vibronic coupling with two a_{1g} modes [3] and thus *it is not* related to the Jahn-Teller (JT) effect such as it happens for $KZnF_3$: Cu^{2+} [2,4]. Moreover *another puzzling* fact is also explained in this work namely in $K_2MF_4:Ni^+$ (M:Mg,Zn) the hole is found in the x^2-y^2 and not in the $3z^2$-r^2 orbital [3].
Calculations carried out for K_2CuF_4 in the K_2NiF_4 *parent structure* prove again that the ground state is an orbital singlet with a hole in the $3z^2$-r^2 orbital and $\Delta = 0.36$ eV [4]. Moreover they show that this situation is not stable driven by $V_R(\mathbf{r})$ and a pseudo JT mechanism leading to orthorhombic CuF_6^{4-} complexes with the longest bond lying in the CuF_2 layer. Aside from reproducing the structural and optical properties [4] of K_2CuF_4 the present calculations demonstrate that, as a result of the influence of $V_R(\mathbf{r})$, the hole has however an ~80% $3z^2$-r^2 character, a fact consistent with magnetic resonance data.
The present results stress the key role played by $V_R(\mathbf{r})$ for understanding the *actual ground state* of fluorides *and oxides* containing d^9 ions and displaying a layered structure [4].

[1] D.Reinen. “The Modulation of Jahn−Teller Coupling by Elastic and Binding Strain Perturbations. A Novel View on an Old Phenomenon and Examples from Solid-State Chemistry”. *Inorg.Chem* **51**, 4458 (2012)

[2] L.Dubicki et al. “Electronic Structure of the Copper(II) Ion Doped in Cubic $KZnF_3$ “. *J. Chem. Phys.* **101**, 1930 (1994)

[3] J.Aramburu et al. **“**Cu^{2+} in Layered Compounds: origin of the Compressed Geometry in the Model System $K_2ZnF_4:Cu^{2+}$ *Inorg.Chem* **52**, 6923 (2013)”

[4] P.García-Fernandez et al. “Compounds Containing Tetragonal Cu^{2+} Complexes: Is the dx^2-y^2-$d3z^2$-r^2 Gap a Direct Reflection of the Distortion? *J.Phys.Chem.Letters* **4**, 2385 (2013)

Probing spin fluctuations in the paramagnetic phase of $EuTiO_3$ by muon spin rotation techniques

Hugo KELLER[1], Zurab GUGUCHIA[1], Jürgen KÖHLER[2],
Annette BUSSMANN-HOLDER[2]
[1]Physik-Institut der Universität Zürich, Winterthurerstr. 190, Ch-8057 Zürich, Switzerland
[3]Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

Muon spin rotation (μSR) technique is a powerful tool to detect correlated spin dynamics in various solid state systems. The method has the advantage of being bulk sensitive and extremely delicate in detecting even smallest amounts of spin correlated regions.

In view of this sensitivity, we have used this method to search for theoretically predicted spin fluctuations in $EuTiO_3$ (ETO) deep in the paramagnetic phase. ETO is a perovskite with cubic structure above T_S=282K, followed by a tetragonal phase below T_S and exhibits antiferromagnetic ordering at T_N=5.7K. Analogous to the isostructural $SrTiO_3$ (STO) ETO exhibits pronounced long wave length optic mode softening which is, however, not completed due to competing quantum fluctuations. A strong spin-lattice coupling exists at low temperatures since the optic mode related dielectric constant shows a kink upon the onset of the antiferromagnetic order. This anomaly can be reverted through the application of a magnetic field. Even though it is not apparent that this spin-lattice coupling continues to high temperatures, model calculations predict a strong paramagnon-phonon coupling at elevated temperatures.

In order to test these predictions and quantify the coupling, μSR is applied to ETO at temperatures above and below the structural phase transition. While the antiferromagnetic phase can clearly be seen by the muons, a finite signal remains also in the paramagnetic phase and follows closely the zone boundary soft mode temperature dependence. This unusual finding demonstrates that spin fluctuations are present deep in the paramagnetic phase and are closely tied to the soft zone boundary mode.

Broken Symmetry and Ordering Phenomena in Mn^{III} Spin Crossover Solids

Grace MORGAN[1], Helge MÜLLER-BUNZ[1], Michelle HARRIS,
and Michael GRIFFIN[1]
[1]School of Chemistry and Chemical Biology, University College Dublin, Ireland.

Spontaneous symmetry breaking[1] governs many transitions in nature, in condensed matter and in particle physics. In the last decade it has also emerged as a structural feature in many examples of two-step spin crossover (SCO) Figure (a), in Fe^{II},[2], Fe^{III}[3] and Co^{II}.[4] In correlated magnetic materials the underlying driving force for such structural phase transitions is often magnetic frustration, such as the ferrimagnetic ordering observed in $CsCoCl_3$,[5] Figure (b), but despite the increasing number of symmetry breaking events in SCO complexes the origin of the phenomenon in these systems is not well understood. Here we present some new examples of symmetry breaking two-step SCO transitions in Fe^{III} and in the less well-studied Mn^{III} ion,[5]-[7] and examine the nature of the ordering in the intermediate phase, Figure 1. In particular we examine the nature and direction of the Jahn-Teller distortion in the S=2 state of the Mn^{III} examples and how this affects the crystal packing.

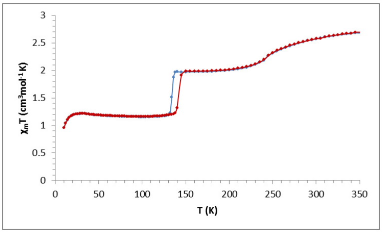


Figure 1. Plot of Plot of $\chi_M T$ *v* temperature for Mn^{III} spin crossover complex showing two step hysteretic spin switching between 10-350 K and spin state ordering on intermediate phase.

[1] P. W. Anderson, More is Different, *Science* 1972, **177**, 393-396.

[2] N. Brefuel, H. Watanabe, L. Toupet, J. Come, N. Matsumoto, E. Collet, K. Tanaka, J. –P. Tuchagues, Concerted Spin Crossover and Symmetry Breaking Yield Three Thermally and One Light-Induced Crystallographic Phases of a Molecular Material, *Angew. Chem. Int. Ed. Eng.*, **2009**, *48*, 9304-9307

[3] M. Griffin, S. Shakespeare, H. J. Shepherd, C. J. Harding, J. –F. Létard, C. Desplanches, A. E. Goeta, J. A. K. Howard, A. K. Powell, V. Mereacre, Y. Garcia, A. D. Naik, H. Müller-Bunz, G. G. Morgan, Symmetry Breaking Spin State Transition in Iron(III), *Angew. Chem. Int. Ed. Eng.*, 2011, 50, 896-900.

[4] a) M. G. Cowan, J. Olguín, S. Narayanaswamy, J. L. Tallon, S. Brooker, Reversible Switching of a Cobalt Complex by Thermal, Pressure and Electrochemical Stimuli: Abrupt, Complete, Hysteretic Spin Crossover, *J. Am. Chem. Soc.*, 2012, **134**, 2892-2894.

[5] A Manganese(III) Complex that Exhibits Spin Crossover Triggered by Geometric Tuning, G. G. Morgan, K. D. Murnaghan, H. Müller-Bunz, V. McKee and C. J. Harding, *Angew. Chem. Int. Ed.*, **2006**, *45*, 7172-7175.

[6] Cooperative Spin Transition in a Mononuclear Manganese(III) Complex, P. N. Martinho, B. Gildea, M. M. Harris, T. Lemma, A. D. Naik, H. Muller-Bunz, T. E. Keyes, Y. Garcia and G. G. Morgan, *Angew. Chem. Int. Ed.*, **2012**, *51*, 12597-12601.

[7] Lattice Effects on the Spin Crossover Profile of a Manganese(III) Cation, K. Pandurangan, B. Gildea, C. Murray, C. J. Harding, H. Müller-Bunz and G. G. Morgan, *Chem. Eur. J.*, **2012**, *18*, 2021-2029.

REV10

Fullerides: Radical Anions, Jahn-Teller Effect and Orbital Ordering

Martin JANSEN
Max Planck Institute for Solid State Research, Stuttgart

Carbon based nanostructures such as fullerenes, nanotubes and graphenes attract considerable attention because of their unique properties and potential applications. Despite great success in the total synthesis of many complex organic molecules, the rational construction of fullerenes, and nanotubes still remains challenging. The main task of direct synthesis is the controlled generation of the desired nanostructures by rational chemical methods. This approach is of practical interest for the production of individual higher fullerenes and nanotubes with defined chiralities, and thus specific physical properties. Our methodology is based on the synthesis of polycyclic aromatic hydrocarbons which already contain all necessary carbon atoms in appropriate positions. Subsequent intramolecular condensation leads to the desired nanostructures, the carbon connectivity of which is fully predefined by the precursor molecule. We demonstrate on the examples of C_{60} and the 6/6 SWCNT that fully selective synthesis of such carbon nanostructures has become feasible.

The ability of fullerenes to accept excess electrons, up to twelve in the case of C_{60}, is among the most conspicuous aspects of their chemistry and physics. The series of compounds as formed with alkali metals, A_xC_{60} (A= Na, K, Rb, Cs; x = 1-6), is particularly interesting. Since except for $A_6C_{60,}$ the conduction bands are partly filled for all of them, they are expected to show metallic conductivity. Surprisingly, A_2C_{60} and A_4C_{60} are reported to be insulating, while A_3C_{60} becomes superconducting at quite elevated transition temperatures. In the case of $C_{60}{}^{2-}$ one faces the so-called open-shell problem. The two added electrons partially occupy the lowest unoccupied molecular orbital (LUMO) of the neutral C_{60} which has t_{iu} symmetry and is three-fold degenerate. Yet, no evidence for a magnetic state has been found for $C_{60}{}^{2-}$ compounds. A singulet ground state can only be achieved by a Jahn-Teller (J-T) distortion. However, structural evidence for such a J-T effect has so far escaped detection. By analysing bond length alternation patterns in a series of high precision crystal structure data sets of ionic fullerides $C_{60}{}^{2-}$, we became aware of a systematic anisotropy of the bond alternation lowering the point symmetry to D_{3d}. By theoretical calculations it has been shown that these patterns unequivocally determine a particular singulet state as the electronic ground state of the $C_{60}{}^{2-}$ ions. Thus experimental data and calculations clearly confirm the first manifestation of a static J-T deformation in bulk fullerides. Interestingly, at the example of a $(C_{60})^-$ radical anion, we have been able to also trace the transition from static to dynamic J-T effect, by EPR spectroscopy and temperature dependent x-ray crystallography. Recently, also for $C_{60}{}^{4-}$, which is electronically inverse to $C_{60}{}^{2-}$, evidence for a singulet ground state has been obtained from STM investigations on K_4C_{60} mono-layers.

These findings on $C_{60}{}^{2-}$ and $C_{60}{}^{4-}$ are also relevant for superconductivity in the A_3C_{60} compounds. Here the C_{60}-ions are three-fold negatively charged in the average, however, electron transport implies intermediary charges of –2 and –4. Superconductivity may arise from structural relaxations related to charge fluctuations away from –3, accompanied by distortional modes. In the $C_{60}{}^{2-}$ fullerides treated here, these structural relaxations were seen in a quasi-frozen form.

Finally, we have spotted orbital ordering in a C_{60} radical monoanion anion salt, resulting in a counterintuitive anisotropy of the electronic conductivity.

Orbital excitation of a Mott-Jahn-Teller insulator revealed by infrared spectra

Shahab NAGHAVI[1], Michele FABRIZIO [1], Tao QIN[1], Erio TOSATTI[1,2]
[1]International School for Advanced Studies (SISSA), and CNR-IOM Democritos National Simulation Center, Via Bonomea 265, I-34136 Trieste, Italy
[2]International Centre for Theoretical Physics (ICTP), Strada Costiera 11, I-34151 Trieste, Italy

Orbital excitations have been so far elusive in strongly correlated molecular conductors and insulators. Recent IR absorption spectra of Cs_3C_{60}, a Mott insulator which turns under pressure into a strongly correlated superconductor, showed clear splittings and extra features due to the orbitally driven Jahn-Teller distortion of the C_{60} (3-) ions[1]. Puzzlingly, these splitting and features disappeared upon heating at a much lower temperature than the known and much large spin-excitation gap. Based on ab-initio electronic, vibrational, total energy and IR spectral calculations including all-important quantum nuclear motion, rotational symmetry, and nonlinear distortion effects, we account for the main low temperature spectral features. We also identify the purely orbital excitation whose energy is just above above the ground state yet with an unsplit IR spectrum. Even if silent, that orbital excitation is responsible for the early thermal demise of distortion-related features in the IR spectra, revealing for the first time its direct important role.

[1] G. Klupp, et al., Nature Communications 3, 912 (2012).

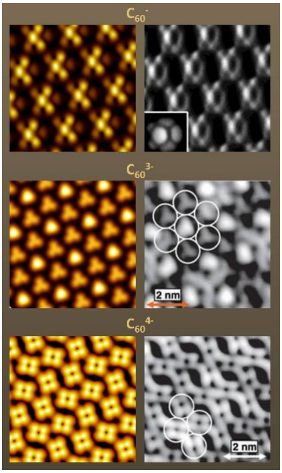
Experimental signatures of Jahn-Teller effects in fullerene anions

Andrew J LAKIN, Haifa S ALQANNAS, Joseph A FARROW,
Jeremy LEAF, Philip MORIARTY and Janette L DUNN
School of Physics & Astronomy, University of Nottingham, University Park, Nottingham,
NG7 2RD, UK

Modern imaging techniques, such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), can probe molecules such as the fullerene molecule C_{60} with subatomic resolution. STM images of the neutral molecule are generally well-understood (e.g. [1,2]). As C_{60} ions are subject to Jahn-Teller (JT) effects, these imaging techniques provide a potential means of observing the presence of the JT effect. However, the movement of atoms due to the JT effect is still orders of magnitude too small to be observed experimentally, and strong interactions with the surface substrate are also likely to reduce the number of equivalent JT distortions between which the system can dynamically pseudorotate. Therefore the presence of JT effects can only be inferred indirectly. In order to do this, it is necessary to have a good theoretical understanding of JT effects in fullerene ions. While the first work on this system was undertaken nearly 2 decades ago [3], there has not been a thorough investigation of the interplay between JT and Coulomb (electron-electron) interactions for anions with more than one electron.

In the first part of this talk, we will present results of investigations of possible changes in the symmetry of JT distortions in fullerene anions as the number of electrons changes [4]. We will show how published experimental STM images (from [5] and [6], reproduced on the right in the figure) can be explained using a JT model (as on the left). We will use these matches and other experimental evidence to estimate possible values for the linear and quadratic JT coupling constants in these ions.

In the second part of the talk, we will discuss very recent experiments aimed at imaging single C_{60} molecules on a buffer layer. The aim is to build a system which can charge single C_{60} molecules (as opposed to previous experiments in which charged ions are only obtained as part of a monolayer [5]) and also reduce interactions with the surface substrate so that JT distortions are not quenched.



[1] C. Chiutu, A.M. Sweetman, A.J. Lakin, A. Stannard, S. Jarvis, L. Kantorovich, J.L. Dunn and P. Moriarty: Precise Orientation of a Single C_{60} Molecule on the Tip of a Scanning Probe Microscope, Physical Review Letters **108** (2012) 268302.
[2] A.J. Lakin, C. Chiutu, A.M. Sweetman, P. Moriarty and J.L. Dunn: Recovering molecular orientation from convoluted orbitals, Physical Review B **88** (2012) 035447.
[3] C.C. Chancey and M.C.M. O'Brien: The Jahn-Teller effect in C_{60} and other icosahedral complexes, (Princeton University Press, Princeton, 1997).
[4] H.S. Alqannas, A.J. Lakin, J.A. Farrow and J.L. Dunn: Interplay between Coulomb and Jahn-Teller effects in icosahedral systems with triplet electronic states coupled to h-type vibration, Physical Review B **88** (2013) 165430.
[5] A. Wachowiak, R. Yamachika, K.H. Khoo,Y. Wang, M. Grobis, D.H. Lee, S.G. Louie and M.F. Crommie: Visualization of the molecular Jahn-Teller effect in an insulating K_4C_{60} monolayer, Science **310** (2005) 468-470.
[6] L.F. Yuan, J. Yang, H.Q. Wang, C.G. Zeng, Q.X. Li, B. Wang, J.G. Hou, Q.S. Zhu and D.M. Chen: Low-temperature orientationally ordered structures of two-dimensional C_{60}, Journal of the American Chemical Society **125** (2003) 169-172.

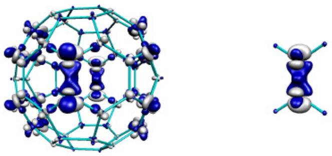
Regioselectivity in Chemical Reactions: Vibronic Coupling Density as a Reactivity Index

Tohru SATO[1,2], Naoki HARUTA[1], Naoya IWAHARA[1],
Kazuyoshi TANAKA [1], and Michel BARON[3]
[1] Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
[2] Unit of Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
[3] Université de Toulouse, Mines-Albi, CNRS UMR 5302, Centre Rapsodee, Campus Jarlard, 81013 Albi Cedex 09, France

Recent progresses of vibronic coupling density analysis for chemical reactions are reviewed. Vibronic coupling density[1] for a reaction mode is proposed as a reactivity index, and applied for cycloadditions in fullerenes[2,3]. The reactivity site of the nucleophilic cycloadditions to C_{60} is abond between adjacent hexagons[4]. The frontier orbital theory fails to explain the reactivity in C_{60}, since the LUMO of C_{60} is three-fold degenerate and delocalized. The reaction mode s is defined as the effective mode which is calculated from all the vibronic coupling constants for normal modes. Vibronic coupling density $\eta_s(\mathbf{r})$ is defined by

$$V_s = \int \eta_s(\mathbf{r}) d^3\mathbf{r}, \text{ where } \eta_s(\mathbf{r}) = \upsilon_s(\mathbf{r}) \times \Delta\rho(\mathbf{r}),$$

where V_s denotes the vibronic coupling of the reaction mode s, and $\Delta\rho$ is the electron density difference between the neutral state and the charge transfer state (anionic state in the present reaction). Potential derivative υ_s is the derivative of the attractive potential acting on a single electron with respect to the coordinate of the reaction mode s. Figure 1(a) shows the vibronic coupling density $\eta_s(\mathbf{r})$ in the $T_{1u}(z)$ electronic state of C_{60}. That of ethylene anion is also shown for comparison, since C_{60} acts as a dienophile like ethylene. The vibronic coupling density is localized on the two bonds between adjacent hexagons, and is almost the same form as that of ethylene. There are other T_{1u} states, $T_{1u}(x)$ and $T_{1u}(y)$. They also yield the same distributions with other orientations. In other words, C_{60} bears six ethylene moieties. The positions of the six ethylene moieties are consistent with experimental result that the hexakis adduct is a T_h structure[5]. We also applied the present analysis for Diels-Alder reactions of C_{70}[3], $La_2@C_{80}$, and other reactions[6]. Vibronic coupling density analysis can provide a picture of a functional group which is difficult to extract from delocalized frontier orbitals of large molecules.



(a) (b)

Figure 1: Vibronic coupling density of (a) C_{60} anion and (b) ethylene anion.

[1] T. Sato, K. Tokunaga, and K. Tanaka: J. Phys. Chem. A **112** (2008) 758–767. [2] T. Sato, N. Iwahara, N. Haruta, and K. Tanaka: Chem. Phys. Lett. **531** (2012) 257–260. [3] N. Haruta, T. Sato, and K. Tanaka: J. Org. Chem. **77** (2012) 9702–9706. [4] Y. Rubin, S. Khan, D. I. Freedberg, and C. Yeretzian: J. Am. Chem. Soc. **115** (1993) 344–345. [5] B. Kautler and J. Maynollo: Angew. Chem. Int. Ed. **34** (1995) 87–88. [6] N. Haruta, T. Sato, K. Tanaka, M. Baron: Tetrahedron Lett. **54** (2013) 5920–5923.

INV6

Dynamical Jahn-Teller instability in alkali-doped fullerides

Liviu F. CHIBOTARU and Naoya IWAHARA
Theory of Nanomaterials Group, Katholieke Universiteit Leuven,
Celestijnenlaan 200F, B-3001 Leuven, Belgium

The superconductivity of alkali-doped fullerides (A_3C_{60}, A = K, Rb, Cs) has received much attention because of its high critical temperature T_c of 38 K [1] which is the highest among organic superconductors and comparable to the T_c of cuprate and iron pnictide superconductors. Through the investigations on Cs_3C_{60} the existence of the Mott-Hubbard insulating phase close to the superconducting phase was revealed [1-3], which indicates the importance of the electron correlation in A_3C_{60}. On the other hand, electron-phonon coupling is considered to play a crucial role in the pairing mechanism. In fullerides electron-phonon coupling mainly comes from the local vibronic coupling on each fullerene site, which gives rise to the Jahn-Teller effect (JTE) of C_{60}^{3-}. However, the nature of the JTE has not been clarified. In this work, we address the nature of the JTE in insulating and metallic A_3C_{60} fully *ab initio* [4,5].

The low-lying vibronic states of C_{60}^{3-} are obtained by exact diagonalization of the linear $t_{1u}^3 \times 8h_g$ JT Hamiltonian. The low-lying vibronic excitations of rotational type are at ≥ 65 cm^{-1}, while the net kinetic contribution to the Jahn–Teller stabilization energy constitutes ca 90 meV. This means that no localization of distortions by intermolecular interactions is possible in insulating Cs_3C_{60}, therefore, free rotations of deformations take place independently on each C_{60}. The latter destroy the orbital ordering and establish a conventional exchange interaction between S = 1/2 on fullerene sites. The corresponding exchange model is derived and predicts the Néel temperature for A15 Cs_3C_{60} close to experiment.

The ground state of metallic fulleride K_3C_{60} is investigated with a concomitant self-consistent treatment of the electron correlation and the JTE. The potential energy surface has two minima with and without JT distortion. It is found that static JT instability on C_{60} sites is favored when the intrafullerene electron repulsion $U > 670$ meV. At the same time the amplitude of variations of the band energy as function of the direction of JT distortions are found to be much smaller than the energy gain from dynamical delocalization of JT deformations implying dynamical JT instability on C_{60} sites. The JT deformation enhanced by the JT dynamics approaches the value for isolated C_{60}^{3-} for $U > 550$ meV, leading to strong enlargement and complete removal of degeneracy of the LUMO band.

[1] A. Y. Ganin, *et al.*: “Bulk superconductivity at 38 K in a molecular system", Nat. Mater. **7** (2008) 367 – 371.

[2] Y. Takabayashi, *et al.*: “The disorder-free non-BCS superconductor Cs_3C_{60} emerges from an antiferromagnetic insulator parent state", Science **323** (2009) 1585 – 1590.

[3] A. Y. Ganin, *et al.*: “*Polymorphism control of superconductivity and magnetism in Cs_3C_{60} close to the Mott transition*", Nature **466** (2010) 221 – 225.

[4] N. Iwahara and L. F. Chibotaru: “Dynamical Jahn-Teller Effect and Antiferromagnetism in Cs_3C_{60}", Phys. Rev. Lett. **111** (2013) 056401 1-5.

[5] N. Iwahara and L. F. Chibotaru: “Dynamical Jahn-Teller instability in metallic fullerides", submitted.

Jahn-Teller orbital glass in the Mott insulating parent state of the molecular superconductor Cs_3C_{60}

Denis ARČON[1,2]
[1] Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia.
[2] Faculty of mathematics and physics, University of Ljubljana, Jadranska cesta 19, 1000 Ljubljana, Slovenia.

The most expanded fcc-structured alkali fulleride, Cs_3C_{60} is a Mott insulator at ambient pressure because of the weak overlap between the frontier t_{1u} molecular orbitals of the C_{60}^{3-} anions. It has a severely disordered antiferromagnetic ground state that becomes a superconductor with a high critical temperature, T_c of 35 K upon compression [1,2]. The effect of the localised t_{1u}^3 electronic configuration on the properties of the material is not well-understood. Here we report on a study of the relationship between the intrinsic crystallographic C_{60}^{3-} orientational disorder and the molecular Jahn-Teller (JT) effect dynamics in the Mott insulating state [3]. The high-resolution ^{13}C magic-angle-spinning (MAS) NMR spectrum at room temperature comprises three peaks in the intensity ratio 1:2:2 consistent with the presence of three crystallographically-inequivalent carbon sites in the fcc unit cell and revealing that the JT-effect dynamics are fast on the NMR time-scale of 10^{-5} s despite the presence of the frozen-in C_{60}^{3-} merohedral disorder disclosed by the ^{133}Cs MAS NMR fine splitting of the tetrahedral and octahedral ^{133}Cs resonances. Cooling to sub-liquid-nitrogen temperatures leads to severe broadening of both the ^{13}C and ^{133}Cs MAS NMR multiplets, which provides the signature of an increased number of inequivalent ^{13}C and ^{133}Cs sites. This is attributed to the freezing out of the C_{60}^{3-} JT dynamics and the development of a t_{1u} electronic orbital glass state guided by the merohedral disorder of the fcc structure. The observation of the dynamic and static JT effect in the Mott insulating state of the metrically cubic but merohedrally disordered Cs_3C_{60} fulleride in different temperature ranges reveals the intimate relation between charge localization, magnetic ground state, lifting of electronic degeneracy, and orientational disorder in these strongly-correlated systems.

[1] A. Y. Ganin, Y. Takabayashi, P. Jeglič, D. Arčon, A. Potočnik, P. J. Baker, Y. Ohishi, M. T. McDonald, M. D. Tzirakis, A. McLennan, G. R. Darling, M. Takata, M. J. Rosseinsky, and K. Prassides: Polymorphism control of superconductivity and magnetism in Cs_3C_{60} close to the Mott transition, Nature **466** (2010) 221–225.
[2] A. Potočnik, A. Krajnc, P. Jeglič, Y. Takabayashi, A. Y. Ganin, K. Prassides, M. J. Rosseinsky, and D. Arčon: Size and symmetry of the superconducting gap in the f.c.c. Cs_3C_{60} polymorph close to the metal-Mott insulator boundary, Sci. Rep. **4** (2014) 4265.
[3] A. Potočnik, A. Y. Ganin, Y. Takabayashi, M. T. McDonald, I. Heinmaa, P. Jeglič, R. Stern, M. J. Rosseinsky, K. Prassidesc, and D. Arčon: Jahn-Teller orbital glass state in the expanded fcc Cs_3C_{60} fulleride, accepted in Chem. Sci. (2014).

Dynamic Jahn-Teller effect in IR spectra of expanded Cs_3C_{60} fullerides at low temperature

Katalin KAMARÁS[1], Judit HORVÁTH[1], Gyöngyi KLUPP[1,3],
Vilmos KOCSIS[2], István KÉZSMÁRKI[2,4], Alexey Y. GANIN[5,6],
Matthew J. ROSSEINSKY[5], Ross COLMAN[3], Ruth H. ZADIK[3],
Manolis D. TZIRAKIS[3], Yasuhiro TAKABAYASHI[3],
and Kosmas PRASSIDES[3,7]

[1]Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, P.O. Box 49, 1525 Budapest, Hungary
[2]Department of Physics, Budapest University of Technology and Economics, Budafoki út 8, 1111 Budapest, Hungary
[3]Department of Chemistry, Durham University, Durham DH1 3LE, UK
[4]Experimentalphysik V, Universität Augsburg, Universitätsstr. 1, 86135 Augsburg, Germany
[5]Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK
[6] School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK
[7]WPI Research Center, Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Cs_3C_{60} fullerides are prototypical examples of the molecular Jahn-Teller effect combined with Mott localization of electrons and are therefore ideal model systems to study electron correlations in molecular solids. Vibrational spectroscopy is perfectly suited for the investigation of Jahn-Teller distortions in fullerides due to its sensitivity to symmetry reduction. Previous infrared studies [1] indicated the dynamic nature of the distortion down to 28 K; the gradual increase in complexity of the IR pattern on cooling was attributed to temperature-dependent solid-state conformers. We will present the results of extending these measurements on both polymorphs (fcc and A15) down to 10 K. We find that the dynamic nature persists in the whole studied temperature range and we do not observe ferrodistortive ordering. We also compare our results to recent theoretical studies [2,3] which take into account non-linear coupling and yield lower symmetry of the distortion than former estimates. In addition, the possibility of an orbital excitation being responsible for the gradual temperature dependence, predicted by sophisticated ab initio calculations [3], is examined and found to be in qualitative agreement with the experiments. In A15 Cs_3C_{60} a phase transition occurs at the antiferromagnetic Néel temperature [4] which lowers the site symmetry of the C_{60}^{3-} anion, and induces a new infrared line. In the merohedrally disordered fcc crystal where the magnetic ordering temperature lies below our measurement range, we observe a broadening of spectral lines without the appearance of any new features.

[1] G. Klupp, P. Matus, K. Kamarás, A.Y. Ganin, A. McLennan, M.J. Rosseinsky, Y. Takabayashi, M.T. McDonald, K. Prassides: Dynamic Jahn-Teller effect in the parent insulating state of the molecular superconductor Cs_3C_{60}, Nat. Commun. **3,** 912 (2012).
[2] H.S. Alqannas, A.J. Lakin, J.A. Farrow, J.L. Dunn: Interplay between Coulomb and Jahn-Teller effects in icosahedral systems with triplet electronic states coupled to *h*-type vibrations, Phys. Rev. B **88,** 165430 (2013).
[3] S. Naghavi, M. Fabrizio, T. Qin, E. Tosatti: Orbital excitation of a Mott-Jahn-Teller insulator revealed by infrared spectra, this conference.
[4] R. H. Zadik, et al., to be published.

Defects in graphene and the role of Jahn Teller reconstructions.

Jamie WARNER[1]
[1]Department of Materials, University of Oxford, 16 Parks Road, Oxford OX1 3PH, UK

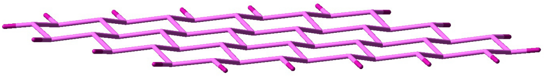
Defects in graphene influence the chemical and electrical properties and therefore their understanding at the atomic level is important. Vacancy defects often involve bond rotations and Jahn Teller reconstructions to form low energy structures that are stable. I will present our latest results on atomic resolution imaging of defects in graphene and show how we can track their dynamics and bond lengths with unprecedented detail. I will discuss the important role of reconstruction in stabilising monovacancies [1]. Imaging is performed using aberration corrected transmission electron microscopy operated at an accelerating voltage of 80kV with monochromation of the electron source to reduce chromatic aberration effects and achieve 80 pm spatial resolution [2].

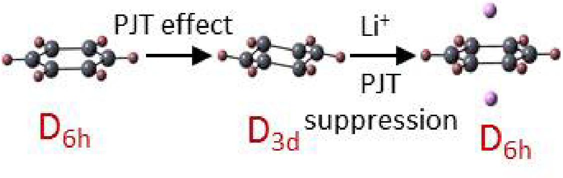
[1] A. W. Robertson et al. ACS Nano, *7*, (2013), 4495–4502
[2] J. H. Warner et al. Science, 337 (2012) 209-212

Silicene: Its different from Graphene

Ayan DATTA
Department of Spectroscopy, Indian Association for the Cultivation of Science (IACS),
Kolkata – 700032, INDIA. E – mail: spad@iacs.res.in

Graphene has emerged as one of the most fascinating areas of research in condensed matter and materials science. However, its heavier analogue, Silicene has generated interest only recently. It is now well – understood that for silicene, even though the electronic structure is similar to that for graphene (zero gap semiconductor), the structural aspects are very different. Silicene, unlike graphene has periodic puckering (buckling) in the six – membered aromatic rings leading to an interesting rippled structure. The effects of such ripples are manifold particularly in its local reactivity to halogens and hydrogens along the more ~sp^3 atoms. The chemistry of silicene to silicane (hydrogenated silicene) is studied in details. Also, a microscopic understanding of the buckling distortion in silicene is provided based of detailed PJT (pseudo Jahn – Teller distortion) analysis between the symmetry breaking normal modes that correspond to the related KS orbitals.





[1] D. Jose, Ayan Datta, *Acc. Chem. Res.* **2014**, *47*, 593.
[2] D. Jose, Ayan Datta, *J. Phys. Chem. C* **2012**, *116,* 24639.
[3] Le Lay, G. and co – workers, *Phys. Rev. Lett.***2012**, 108, 15550.
[4]V. Mohan, A. Datta, *J. Phys. Chem. Lett.* **2010**, 1, 136.

Jahn-Teller-promoted superconductivity in cuprates and iron pnictides

Victor POLINGER
Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195-1700, USA

High T_C superconductivity in hole-doped copper oxides and iron pnictides can be explained as due to their half-filled valence electron shells. In cuprates, hole doping creates Cu^{3+} centers with configuration e^2. In iron pnictides, it creates Fe^{5+} centers with the electron configuration t^3. In such a case the highest-occupied molecular orbitals (HOMO) can be proportionally populated, one electron per orbital, or populated with an orbital disproportionation. In the former case, the high-spin totally symmetric charge distribution cancels any Jahn-Teller coupling and can be treated as the so-called *anti*-Jahn-Teller effect [1, 2]. The low-spin orbital disproportionation is energy beneficial for a low-symmetry distortion. It is twice stronger than the one without doping and, therefore, manifests the *enhanced* pseudo Jahn-Teller effect [2, 3]. Thus, hole doping creates two kinds of sites, with and without Jahn-Teller instability. Transformation of the two sites into one another is spin-forbidden. The two types of holes are in a thermodynamic equilibrium with one another. Relative concentration of the sites with the *enhanced* Jahn-Teller effect drops with doping. At the same time, the two sites have significantly different conductivity. In cuprates, in the *anti*-Jahn-Teller site the hole populates the orbital $3z^2 - r^2$. It is oriented in the apical direction and includes a significant admixture of apical ligands. The extended size of the apical ligands provides high polarizability and low in-plane mobility of these holes (heavy fermions). In the sites with the *enhanced* Jahn-Teller effect the extra hole is in the in-plane orbital $x^2 - y^2$. It extends in the equatorial direction and, therefore, manifests high in-plane mobility. Due to a relatively large resonance integral, it delocalizes over the whole crystal and, therefore, at low doping is difficult to observe. In this model, the $(x^2 - y^2)$-holes provide conductivity and, at a higher level of doping, are responsible for superconductivity. The number of sites with the *anti*-Jahn-Teller effect saturates with doping. Qualitatively, conductivity of the crystal changes as follows. With doping the new holes increase the number of the sites with the *enhanced* Jahn-Teller effect that delocalize over the whole crystal. In the under-doped mode the normal conductivity increases with doping proportional to the number of $(x^2 - y^2)$-holes. When the average distance between the $(x^2 - y^2)$-holes becomes as small as the diameter of Cooper pairs, the $(x^2 - y^2)$-holes become coherent and the sample manifests superconductivity. The *anti*-Jahn-Teller sites with immobile but highly polarizable $(3z^2 - r^2)$-holes serve as mediators in the inter-carrier coupling in the manner of the exciton mechanism of pairing. The longer are the apical ligands, the greater is the arm of the induced dipole moment and, respectively, the higher is the temperature of the superconductive phase transition. In the over-doped mode the relative number of the polarizing holes drops down and the temperature of the superconductive phase transition drops to zero. This explains the bell-shape phase diagram of HTSC.

[1] J.G. Bednorz and K. A. Müller: Possible high T_c superconductivity in the Ba-La-Cu-O system, Z. Physik B – Condensed Matter **64** (1986) 189-193.

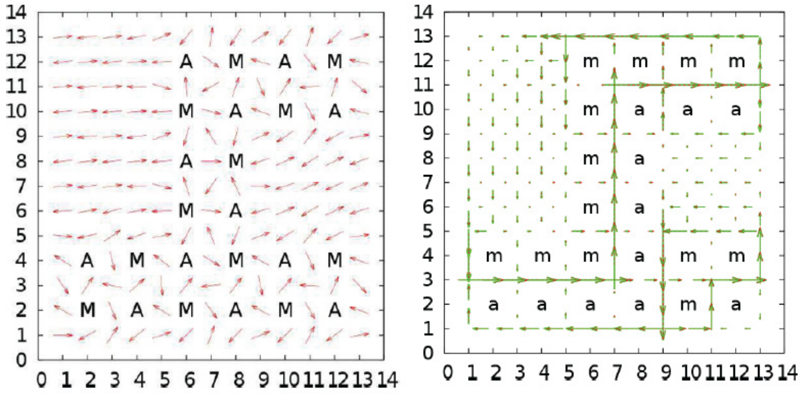
[2] V. Polinger, D. Haskel, and E. A. Stern: Dopant induced enhancement of the Jahn-Teller effect in perovskite cuprates: in: Vibronic Interactions: Jahn-Teller Effect in Crystals and Molecules, Ed. by M. D. Kaplan, and G. O. Zimmerman (Kluwer Academic Publishers, Dordrecht, 2001) 215-220

[3] P. Garcia-Fernandez, I. B. Bersuker, and J. E. Boggs: Orbital disproportionation and spin-crossover as a pseudo Jahn-Teller effect, J. Chem. Phys. **125** (2006) 104102.

Supercurrent generation in Cuprate: Spin-vortex model.

H. KOIZUMI[1], A. OKAZAKI, M. ABOU GHANTOUS[2], M. TACHIKI[3]
[1]Division of Materials Science, U of Tsukuba, Tsukuba 305-8573 Japan
[2]Department of Physics, Texas A & M U at Qatar, Doha, Qatar
[3]Department of Physics, Tohoku U, Sendai 980-8573 Japan

We propose a novel microscopic mechanism of supercurrent generation for cuprate superconductors. It originates from the appearance of the Dirac monopole type singularities due to the spin-vortex formation by itinerant electrons. The core of the spin-vortex is made by the strong hole-lattice interaction of the pseudo Jahn-Teller type; it also provides a superexchange interaction between the spins in the copper d_{x2-yx2} orbitals across the hole, and stabilizes the spin-vortex formation. A quartet of the spin-vortices, the spin-vortex quartet (SVQ), is a stable unit for the construction of the network of the spin-vortices. The supercurrent is generated as a collection of loop currents induced by the spin-vortices, called the "spin-vortex induced loop currents (SVILCs)". The network of the SVQs creates a channel for the supercurrent.



Left: a network of 6 SVQs. Right: The supercurrent generated as a collection of SVILCs. It enters to (1,3) and exits from (13,11).

[1] H. Koizumi, R. Hidekata, A. Okazaki, and M. Tachiki, J Supercond Nov Magn **27** (2014), 121.

O25

Electron-phonon superconductivity in *A*P$_3$P compounds: From weak to strong coupling.

Lilia BOERI[1]
[1]Institute for Theoretical and Computational Physics, TU Graz, Austria

In 2012, Takayama et al. reported the synthesis of a new class of ternary superconductors, *A*Pt$_3$P (*A*=Sr, Ca, La), with an anti-perovskite crystal structure. Early first-principles calculations suggested an exotic mechanism for superconductivity in the La compound, due to the presence of Pt states at the Fermi level, and to the locally non-centrosymmetric crystal structure.[2]
In this work, using first-principles calculations and Migdal-Eliashberg theory, we show that the superconducting critical temperatures, gap magnitudes and thermodynamical properties can be well described by the single-band Migdal Eliashberg theory of superconductivity. The pairing, and hence T_c, increase from La to Ca and Sr due to changes in the electron-phonon matrix elements and low-frequency phonons, while the spin-orbit coupling of Pt plays a marginal role.[3]
Recent penetration depth measurements support our picture, but also indicate that SrPt3P might be the first example of a two-band superconductor with equal gaps but different coherence length parameters within two Fermi surface sheets.[4]

[1] T. Takayama et al., Phys. Rev. Lett. **108**, 237001 (2012).
[2] I.A. Nekrasov, M.V. Sadovskii, JETP Letters **96**, 227 (2012); H. Chen, X.-F. Xu, C. Cao, and J. Dai, Phys. Rev. B **86**,125116 (2012); C.-J. Kang, K.-H. Ahn, K.-W. Lee, and B.I. Min, J. Phys. Soc. Jpn. **82**, 053703 (2013).
[3] A. Subedi, L. Ortenzi, and L. Boeri, Phys. Rev. B **87**, 144504 (2013).
[4] R. Khasanov, A. Amato, P.K. Biswas, H. Luetkens, N.D. Zhigadlo, B. Batlogg, cond-mat/1404.5473.

New interpretation of the role of vibronic interactions in superconductivity

Takashi KATO
Institute for Innovative Science and Technology, Graduate School of Engineering, Nagasaki
Institute of Applied Science, 3-1, Shuku-machi, Nagasaki 851-0121, Japan

The effect of vibronic interactions and electron–phonon interactions [1] in molecules and crystals is an important topic of discussion in modern physics. Phonon-mediated electron–electron interactions via the second-order processes in quantum field theory in physics have been discussed on the basis of the conventional two-electrons Bardeen–Cooper–Schrieffer (BCS) model by many researchers. However, in the calculations of the electron–phonon coupling constants even in the electron pairing processes, in which two electrons finally play an essential role, only independent one electron has been considered in the previous researches. Therefore, we discuss new mechanism of the electron pairing and definitely discuss how the independent one electron is stabilized in energy in view of the second-order processes in vibronic and electron–phonon interactions in quantum field theory. In particular, by comparison with the conventional BCS theory, we suggest new interpretation of the role of electron–phonon interactions in electron pairing in superconductivity. According to our calculated results, two electronic states originating from independent one electron become stabilized because phonon is exchanged between these two electronic states of independent one electron. That is, phonon emitted by an electron is received by the same electron, and as a consequence of this phonon exchange between two electronic states with opposite momentum and spins, this independent one electron becomes stabilized in energy (Fig. 1). Therefore, the vibronic stabilization energy in the opened-shell electronic states can be considered to originate from the second-order processes in the vibronic interactions between two electronic states of independent one electron, in view of our one-electron theory. This may mean that even independent one electron can form a pair via two electronic states with opposite momentum and spins (so called “self electronic state pairing”) without any external applied magnetic or electric field and can behave as a Bose particle (Fig. 1) [2]. However, once the even very small external electric or magnetic field is applied, such electronic state pair is immediately destroyed and behaves as a Fermi particle, as expected. Vibronic stabilization for independent one-electron systems cannot be explained by the conventional BCS theory, on the other hand, those for independent one-electron systems as well as for two-electrons systems can be explained by our one-electron theory. That is, our one-electron theory is more general than the conventional BCS theory. This is the reason why many researchers in the previous researches did not have to consider two electrons with opposite momenta and spins occupying the same orbital at the beginning stage of the electron–phonon interactions, which are needed in the conventional BCS theory. Furthermore, on the basis of this theoretical results, we will also suggest the unified theory, by which the Meissner effects in superconductivity as well as the Lenz’s law in the normal metallic states can be explained in view of Higgs mechanism.

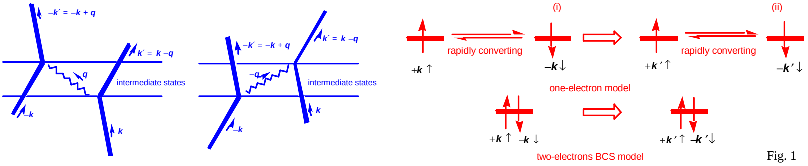


Fig. 1

[1] I. B. Bersuker, The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry; (Plenum: New York, 1984).
[2] T. Kato, Synthetic Metals 181 (2013) 45.

Poster Abstracts

Pseudo Jahn-Teller effect in conjoined structures of benzene and graphene

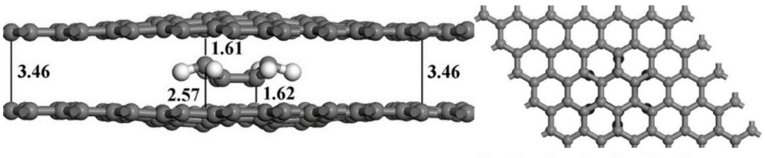
Vadim BOLTRUSHKO, Veera KRASNENKO,
and Vladimir HIZHNYAKOV
Institute of physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

Considering the rapidly growing number of the applications of graphene it may be interesting to study conjoined structures of materials with honeycomb-like carbon structural elements, specifically when mechanism behind their cooperation is the pseudo Jahn-Teller effect (PJTE). The chemical bounds in these conjoined structures are established between the adjoined carbon atoms in parallel C_6 rings by switching off the intra π-bonds to the inter σ-bonds. For the conjoined structures of graphene nanoribbons (GNR) and carbon nanotubes (CNT), as it was found in [1], not all intra-π-bonds may be switched off to inter- σ-bonds in the same way: the rearrangement of different bonds may take place differently. As a consequence, the conjoined C_6 rings are strongly distorted. The vibronic mechanism of the distortion is PJTE.

In this communication we show that the property of rearranging the bonds of π-electrons differently, followed by subsequent different distortions, established in [1], is a common property of the structures with chemically bounded C_6 rings. This opens new possibilities for various applications of these structures, including the opportunity to fabricate the all-carbon devices for information storage gadgets.

In the present study the electronic structure calculations of a benzene molecule, chemically bounded with another benzene molecule (we call the bound state of these molecules as bi-benzene) and with graphene, were carried out, where the bonding and distortions in these structures have been investigated. For a bi-benzene molecule theoretical estimations for energy levels splitting and dissociation barriers of bi-benzene in extended Hückel approximation were performed, taking vibronic interaction into account.

We have found that, in addition to symmetric bi-benzene, three distorted allotropes of this compound molecule may exist. The mechanism of the appearance of the distorted states is PJTE caused by the length-dependence of the overlapping of the wave functions of $2p_z$ electrons. Analogous PJT-induced distortions have been established in conjoined structures of benzene with graphene. We have also found that the non-distorted benzene molecule, placed between two graphene sheets, does not produce a chemically bound state. However, the distorted benzene molecule does form the chemical bounds with two graphene sheets (see Fig. 1). This allows one, by doping with benzene, to change the stack to the hollow ordering of graphite, which should result in the increase of the conductivity and in changing other properties of graphite.



(a) (b)

Fig.1. Bound state of benzene with two graphene sheets in hollow position: (a) side view (distances are shown in Å), (b) top view (benzene molecule is shown as black spheres for better visibility)

[1] V. Krasnenko, V. Boltrushko, M. Klopov, V. Hizhnyakov: Conjoined structures of carbon nanotubes and graphene nanoribbons, Physica Scripta **89** (2014) 044008.

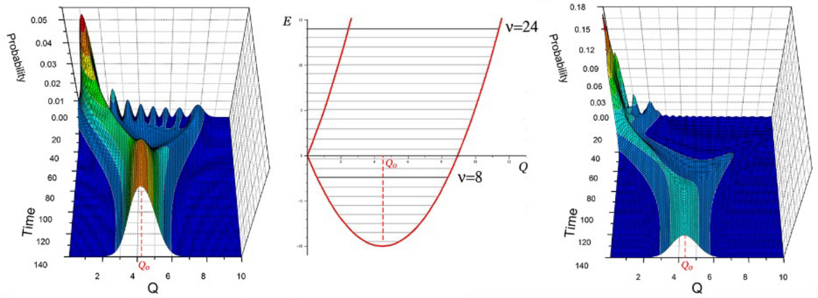
Relaxation through Conical Intersection Caused by Emission of Phonons

Kaja PAE, Vladimir HIZHNYAKOV
Institute of Physics University of Tartu, Tartu, Estonia
e-mail: kaja.pae@gmail.com

We are considering the effect of non-totally symmetric vibrations on the electronic transition from a non-degenerated to the two-fold degenerated electronic state of an impurity centre in solids. Two-fold degenerate electronic state (*E*-representation) interacting with doubly degenerate vibrations (e-representation) is known as $E \otimes e$-problem, which is studied in present survey. In this case the potential energy in the space of configurational coordinates has the famous Mexican hat shape including conical intersection.

We have developed a rigorous quantum mechanical method [1,2] which allows one to calculate the optical spectra of impurity centers in crystals with the JTE in the excited state, taking into account the non-totally symmetric phonons of the bulk. The method works for arbitrary vibronic interaction with a few local modes and weak interaction with phonons.

Rigorous quantum mechanical method enables us to find density matrix which describes the population of the vibronic levels and time evolution of the coherence. Knowing this matrix one can calculate the time dependence of any quantity of the vibronic subsystem. Here we consider the time-dependence of the distribution function of the configurational coordinate in the case of the optical excitation of the centre by a spectrally non-selective short light pulse and also in case of selective light pulse if only one certain vibronic level is excited.



Relaxation in case of spectrally selective excitation. Left: relaxation from vibronic level v=8. Right: relaxation from vibronic level v=24.

Our consideration allows us for the first time to give a rigorous description of the long-time-scale relaxation of the system through the conical intersection, caused by the emission of phonons to the bulk. Several cases of various vibronic interaction strength, phonon interaction strength and optical excitation types (spectrally selective and non-selective) are studied.

[1] Hizhnyakov, V.; Pae, K.; Vaikjärv, T. (2012). Optical Jahn-Teller effect in the case of local modes and phonons. Chemical Physics Letters, 525–526, 64 - 68.
[2] Pae, Kaja; Hizhnyakov, Vladimir (2013). Nonadiabaticity in a Jahn-Teller system probed by absorption and resonance Raman scattering. Journal of Chemical Physics, 138(10), 104103.

Unusual vibronic interaction of molecules in helium-3 probed by Raman scattering

I. TEHVER[1], G. BENEDEK[2,3], and V. HIZHNYAKOV[1]
[1] Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia
[2] Donostia International Physics Center (DIPC), Paseo de Lardizàbal 4, 20018 Donostia/San Sebastian, Spain
[3] Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca,Via Cozzi 53, 20125 Milano, Italy

Inelastic (Raman) scattering of light from pure He liquids is very weak due to small polarizability of helium atoms. However the addition of impurity atoms or molecules may allow one to observe such a scattering, especially if excitation takes place close to the resonance with electronic transition in the impurities. Differently from all other materials, light scattering in quantum liquid helium-3 may involve a unique mechanism - the creation and annihilation of atom excitations across the Fermi level. In the low-energy limit there is a finite density of states (DOS) of quasi-particles and quasi-holes close to the Fermi level. Therefore the DOS of particle-hole excitations in the low-energy limit is strongly enhanced as compared to the DOS of collective excitation of atoms (phonons), also existing in helium-3. This makes possible to observe Fermi excitations in the Raman scattering spectrum.

In this communication we consider resonant Raman scattering (RRS) spectra in helium-3 droplets doped by impurity molecules. The results are applied to a helium-3 droplet doped by one glyoxal molecule. The absorption spectrum of this system at T=0.15 K has been studied experimentally in [1] and theoretically in [1-3]. It was found that Fermi excitations essentially affect the spectrum in the vicinity of the zero-phonon line (ZPL): they cause the disappearance of the dip between the zero-phonon line (ZPL) and the phonon tail (existing in case of helium-4), the 0.5 cm^{-1} broadening and strong asymmetry of the line. The observed decay to the blue tail superimposing the localized spherical vibrational mode at 8 cm^{-1} and extending to ~40 cm^{-1} to the blue side is also attributed to Fermi excitations.

In this communication we present calculations of the first and second order RRS by glyoxal molecule taking into account the creation of both, Fermi excitations and phonons of helium-3. According to our calculations the RRS spectra essentially depend on the excitation frequency. Especially strong changes in the RRS spectra should be observed when excitation frequency is shifted from the blue to the red of ZPL. The simplest spectra of RRS should be observed in case of excitation at the red side on the distance ‰ 40 cm^{-1} of ZPL. In this case the spectrum of the first order of RRS is dominantly determined by the convolution of the hole- and particle-type excitations in the vicinity of the impurity molecule. The contribution of phonons is mainly given by the localized spherical vibration. This should allow one to study by RRS, among other questions, how impurities affect the Fermi excitations in helium-3.

[1] N. Poertner, J.P. Toennies, A.F. Vilesov, G. Benedek, and V. Hizhnyakov, Anomalously sharp phonon excitations in 3He droplets, Europhys. Lett. **88** (2009) 26007-p1 - p6.
[2] G. Benedek and V. Hizhnyakov, Fermi sea excitations in the optical spectrum of a doped 3He droplet Chem. Phys. Lett. **548** (2012) 17-22.
[3] G. Benedek, V. Hizhnyakov, and J. P. Toennies, The response of a 3He Fermi liquid droplet to vibronic excitation of an embedded glyoxal molecule, J. Phys. Chem. (in press).

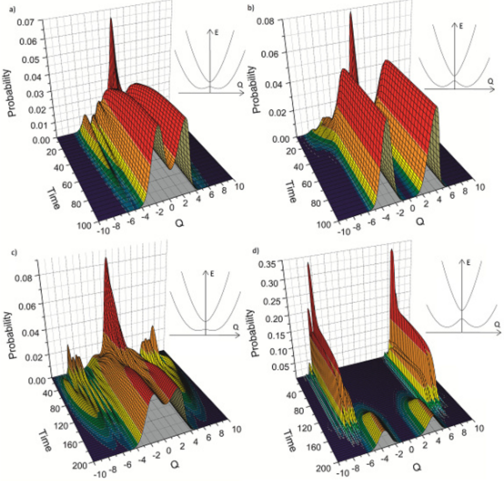
Phonon induced energy relaxation in quasi-degenerate electronic states

Taavi VAIKJÄRV
Institute of Physics, University of Tartu, Estonia

Excited states in molecules and impurity centers in crystals with high symmetry are usually degenerate. The dynamics which occurs in the vicinity of the symmetric configuration is essentially determined by the nonadiabaticity of the electronic and nuclear motion. We present a method which allows one to study theoretically the dynamics of the time evolution of the excited states of these systems. We note that the phonon continuum in the excited state is taken into account.

Our study is based on the recently proposed method [1] of calculation of optical transitions in centers with the Jahn-Teller and pseudo-Jahn-Teller effect in the final state. The time evolution of the states is calculated in the density matrix form using the master equation [2]. The result of this work is calculated evolution of the relaxation process [3]. The method is applicable for calculations for short and intermediate times as well as long times. The most interesting thing to notice is the dependence of relaxation times on the distance of nearest neighbor vibronic states.

Here, for example, are presented the time evolutions of configurational coordinates for four different parameters. As we can see, the relaxation process exhibits quite different characteristics depending on the vibrational states excited. This all can be attributed to different dynamics near the pseudo-degeneracy. Still all the systems relax to the two minima of the lower potential energy surface as expected.



[1] K. Pae, T. Vaikjärv, V. Hizhnyakov Program & Abstracts: 20th International Symposium on the Jahn-Teller Effect (2010) 77 – 79.
[2] G. Lindblad, Commun. Math. Phys. **48** (1976) 119.
[3] T. Vaikjärv, V. Hizhnyakov J. Chem. Phys. **140** (2014) 064105.

POSTER

P05

Hemidirected [M(II)L$_4$]^q structures and Jahn-Teller effect.

Martin BREZA[1], Stanislava ŠORALOVÁ[1,2] and Silvia LENÍKOVÁ[1]
[1]Department of Physical Chemistry, Slovak Technical University, Radlinského 9, SK-81237 Bratislava, Slovakia
[2]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Comenius University, Odbojárov 10, SK-83232 Bratislava, Slovakia

Based on crystallographic studies [1], the preferred Pb coordination numbers in lead complexes are 4 for Pb(IV) and 4 and 6 for Pb(II). All Pb(IV) structures in the Cambridge Structural Database have a holodirected coordination geometry in which the lead–ligand bonds are distributed throughout the surface of an encompassing globe (such as tetrahedral PbL$_4$ structures). Pb(II) compounds for low coordination numbers (2-5) are prevailingly hemidirected, *i.e.* the lead–ligand bonds are directed throughout only a part of an encompassing globe and there is an identifiable void in the distribution of lead-ligand bonds (such as pyramidal PbL$_4$ structures) [1]. The stability of the hemidirected Pb(II) structures has been explained by the so-called ‘‘inert-pair effect” of 6s^2 lone-pair electrons. MP2 studies of tetracoordinated Pb(II) complexes [1] show that their stable hemidirected structures have not a tetragonal principal axis (corresponding to C_4 or C_{4v} symmetry point groups) and their symmetry is lower. This symmetry descent cannot be explained by electrostatic repulsion of the Pb lone electron pair.

Alternatively, the stability of less-symmetric hemidirected PbL$_4$ structures might be explained by pseudo-Jahn–Teller effect [2]. The role of relativistic effects might be studied on a series of similar metal complexes with various central atoms of the same group of the periodic table.

In order to test the above mentioned hypotheses we have performed B3LYP and MP2 calculations of [ML$_4$]^q complexes in their ground singlet spin states, M = Pb, Sn or Ge in +II and +IV oxidation states, L= F$^-$, Cl$^-$, Br$^-$, OH$^-$, SH$^-$, H$_2$O, NH$_3$ or PH$_3$, q being the charge of the complex. We have optimized their geometries within various symmetry groups and analyzed their imaginary vibrations and excited electron states from the point of view of the Jahn-Teller effect.

Our results indicate that the stable [M(II)L$_4$]^q hemidirected structures of lower symmetry are a consequence of the pseudo-Jahn-Teller effect. On the other hand, the problem of the stability of the high-symmetric [M(IV)L$_4$]^q holodirected structures of T_d, D_{2d} or S_4 symmetry point groups cannot be explained by excited states of too high energies for an effective pseudo-Jahn-Teller interaction.

This work was supported by Science and Technology Assistance Agency of Slovak Republic under the contract No. APVV-0202-10 and by Slovak Grant Agency VEGA under the contract No. 1/0327/12.

[1] L. Shimoni-Livny, J.P. Glusker, Ch.W. Bock: Lone Pair Functionality in Divalent Lead Compounds, Inorg. Chem. **37** (1998) 1853-1867.

[2] M.Breza, L.Bučinský, S.Šoralová, S.Biskupič: On the origin of the hemidirected geometry of tetracoordinated lead(II) compounds, Chem. Phys. **368** (2010) 14–19.

Pseudo-Jahn-Teller effect in charged bis((μ_2-diphenylamido)-diphenylamido-zinc(II))

Ingrid PUŠKÁROVÁ[1] and Martin BREZA[1]
[1]Department of Physical Chemistry, Slovak Technical University, SK-81237 Bratislava, Slovakia

Binuclear transition metal complexes such as bis((μ_2-diphenylamido)-diphenylamido-zinc(II)), $[Zn(NPh_2)_2]_2$ (Fig. 1) [1] are possible products of the reaction of diphenylamine-type antioxidants with transition metals. We have investigated the optimal geometry and electronic structure of neutral as well as charged forms of this compound in the lowest spin state at DFT level of theory using hybrid B3LYP functional and cc-pVDZ basis sets for all atoms. Unlike the neutral and cationic forms, the anionic form of C_i symmetry is unstable and its stable structure is of C_1 symmetry. This symmetry descent may be explained by a pseudo-Jahn-Teller effect. QTAIM (Quantum Theory of Atoms-in-Molecule) analysis [2] indicates no Zn-Zn bonding in all the systems under study. Zinc and nitrogen atomic volumes and charges imply that the stable C_1 anionic structure seems to be more reactive than the C_i symmetry one as well as than the neutral and cationic forms.

This work was supported by Science and Technology Assistance Agency of Slovak Republic under the contract No. APVV-0202-10 and by Slovak Grant Agency VEGA under the contract No. 1/0327/12.

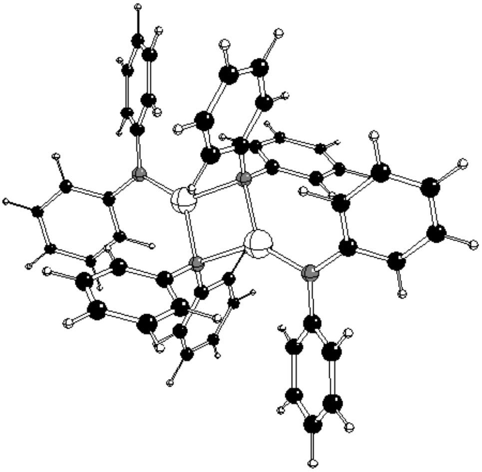


Fig. 1 Optimized structure of $[Zn(NPh_2)_2]_2$ (Zn - white, C - black, N - grey, H - small white).

[1] M.A. Putzer, A. Dashti-Mommertz, B. Neumuller, K. Dehnicke: Synthesis and crystal structures of the zinc amido complexes of $[Zn(NPh_2)_2]_2$ and $[Zn(NPh_2)_2(THF)_2]$, Z. Anorg. Allg. Chem. **624** (1998) 263-266.
[2] R. F. W. Bader, Atoms in Molecules: A Quantum Theory, (Clarendon Press, Oxford, 1990**).**

Theoretical Analysis of the Pseudo Jahn-Teller Instability of Single Six-Member Silicene Clusters

J J. CASTRO [1], J.R. SOTO [2], and B. MOLINA [2]
[1]Departamento de Física, CINVESTAV del IPN, Apdo. Post. 14-740, 07000, México D.F., México
[2]Departamento de Física, Facultad de Ciencias, Universidad Nacional Autónoma de México, Apdo. Post.70-646, 04510,
México D. F., México

The structure and electronic properties of silicene, the 2D analog of graphene has been the subject of great theoretical and experimental interest. It has been theoretically predicted that unlike graphene, the ground state of silicene presents a buckled structure, whose origin is the puckering distortion on the individual six-member rings. This distortion arises from the instability of the D_{6h} planar structure towards a D_{3d} buckled structure and has been attributed to the pseudo Jahn-Teller effect. However, in our opinion, the treatment found in the literature is still incomplete since it lacks a quantification of the vibronic coupling intensity by a proper calculation of the excited states[1]. In this work we present a theoretical analysis of the instability of the 2D - D_{6h} non-degenerate ground state hexasilabenzene cluster towards a 3D structure with D_{3d} symmetry. The analysis is based on the modeling of the pseudo Jahn–Teller effect through the linear vibronic coupling between the ground and the lowest excited state which leads to a puckering distortion of the more symmetric cluster [2]. The model, which has been used to study similar structural transitions in a hexagonal gold ring system [3], determines the coupling constants and predicts simultaneously the APES behavior for the ground and the excited state for values of the symmetrized coordinate around the maximum symmetry point. We discuss the effects on Raman, IR and UV-vis spectra. The study is based on a scalar relativistic DFT and TDDFT calculations in the Zero Order Regular Approximation (ZORA) using hybrid and meta-hybrid functionals.

We are thankful with the computer facilities of the Dirección General de Cómputo y de Tecnologías de Información y Comunicación (DGTIC-UNAM) and with the GENERAL COORDINATION OF INFORMATION AND COMMUNICATIONS TECHNOLOGIES (CGSTIC) at CINVESTAV for providing HPC resources on the Hybrid Cluster Supercomputer “Xiuhcoatl”.

[1] D. Jose, A. Datta, Understanding of the Buckling Distortions in Silicene, Journal of Physical Chemistry C, 116 (2012) 24639-24648.
[2] I.B. Bersuker, The Jahn-Teller Effect, Cambridge University Press, 1st edn, 2006.
[3] J.R. Soto, B. Molina, J.J. Castro, Nonadiabatic structure instability of planar hexagonal gold cluster cation Au_7 and its spectral signature, RSC Advances, 4 (2014) 8157-8164.

High-order *(A + E) × (a + e)* JT/PJT effect and its influence on photoelectron spectra in trigonal systems: PH_3^+ as a case study

Swarnendu BHATTACHARYYA[1], Zuyang DAI[2],
and Wolfgang DOMCKE[1]
[1]Technische Universität München, D-85747 Garching, Germany.
[2]Department of Physics and Key Laboratory of Low-Dimensional Quantum Physics, Tsinghua University, Beijing, 100084, China.

XY_3 systems, having doubly degenerate electronic states and doubly degenerate vibrational modes, exhibit the $E \times e$ Jahn-Teller (JT) effect. In addition, a nearby nondegenerate electronic state (A) is vibronically coupled with the E state by pseudo-JT (PJT) coupling. The symmetric bending mode (umbrella mode) modulates both the A-E energy gap as well as the PJT coupling and is therefore an important tuning mode. We have developed an $(A + E) \times (a + e)$ three-state three-mode JT/PJT model which includes all three large amplitude bending modes of XY_3 systems. Computational invariant theory has been employed to derive the expansion of the elements of the diabatic potential-energy (PE) matrix to arbitrary polynomial orders. PH_3^+ have been chosen as a case study for this advanced JT/PJT model. In fact, all the trihydride cations of the elements of group 15 are potential applications of the theory [1]. Adiabatic *ab initio* PE surfaces have been calculated at the CASSCF/MRCI/cc-pVTZ level using the Molpro quantum chemistry package [2]. A dense grid of data points along all the three vibrational coordinates has been generated to resolve the complexity of the PE surface. The parameters of the polynomial expansion up to 8th order have been obtained by fitting the eigenvalues of the diabatic PE matrix to the *ab initio* data. Data points having energies up to 7 eV from the planar reference geometry have been included in the non-linear fitting procedure. The resulting analytic diabatic PE surface has been employed to simulate the first two bands of the photoelectron spectrum of phosphine.

[1] J. Yang, J. Li, Y. Hao, C. Zhou and Y. Mo, J. Chem. Phys. 125, 054311 (2006).

[2] MOLPRO, a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles; see http://www.molpro.net

Infrared Absorption Spectra of Jahn-Teller Systems: Application to the Transition Metal Trifluorides MnF_3 and NiF_3

Padmabati MONDAL[1] and Wolfgang DOMCKE[2]
[1]Institut für Physikalische und Theoretische Chemie, Goethe Universität Frankfurt, Germany
[2] Department of Chemistry, Technische Universität München, 85747 Garching, Germany

The theory for the calculation of vibronic absorption spectra within a Jahn-Teller (JT) active electronic state from first principles has been developed. The infrared absorption spectra of the $^5E'$ ground state, the low-lying $^5E''$ excited state of MnF_3 and the $^4E'$ state of NiF_3 have been computer and analyzed. Dipole moment derivative have been determined by linear-plus-quadratic expansion of nuclear dipole moment functions in the JT-active coordinates. Electronic transition dipole moments have been taken into account in the Condon approximation in the diabatic representation. The initial and final vibronic states have been expanded in a product of diabatic electronic states and vibrational basis functions. The effect of spin-orbit coupling on the vibronic infrared spectra of these molecules in their JT-active electronic states has been investigated, employing the Breit-Pauli spin-orbit operator. The effect of temperature on the vibronic infrared spectra has also been explored. These results represent the first theoretical study of vibronic infrared spectra of JT-active states in transition metal compounds [1] .

[1] P. Mondal and W. Domcke: Infrared Absorption Spectra of Jahn-Teller Systems: Application to the Transition Metal Trifluorides MnF3 and NiF3, J. Phys. Chem. A **118** (2014) 3726.

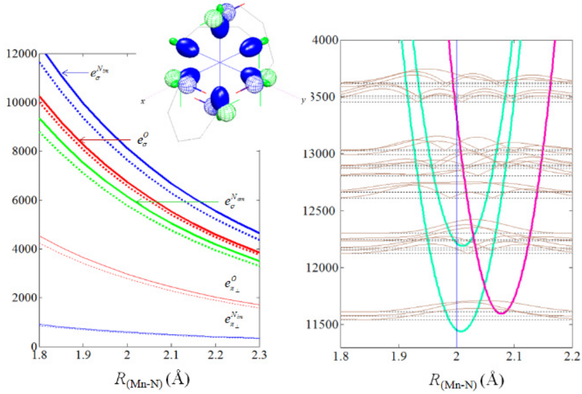
The vibrational chemistry of the spin-crossover phenomena. New case studies.

Marilena FERBINTEANU[1] and Fanica CIMPOESU[2]
[1]University of Bucharest, Faculty of Chemistry, Inorg. Chem. Dept., Dumbrava Rosie 23, Bucharest 020462, Romania
[2]Institute of Physical Chemistry, Splaiul Independentei 202, Bucharest 060021, Romania

The spin crossover phenomena, known for a limited series of configurations, d^4-d^7 of transition metal complexes is a challenging subject both for academic studies, being due to subtle balance of ligand field, spin-orbit and vibronic couplings, and also for application purposes in the frame of spintronics desiderata [1]. Having as primary goal the magnetic anisotropy of compressed vs. elongated Mn(III) octahedral complexes, we serendipitously entered the field of spin conversion identifying systems with unusual spin behavior [2], obtaining systems similar to those initially discovered by G. Morgan et al.[3]

Taking the challenge we advanced deeper into the topic, with models and calculations. Thus, we determined the bond-length dependence ligand field parameters and with this advent we explicitly modeled the interplay of the vibrational factors into the electronic levels, simulating the details of the spin crossing mechanisms (Synopsis1).

Aside the Mn(III) complexes from ours [4] and Morgan's synthetic outcome [5], we considered also classical prototypes of Fe(II) spin transition, identifying the electronic and vibrational factors of the cooperativity and hysteresis.



Synopsis. a) the scheme of lone pairs determining the ligand field parameters and their variation with the bond length. b) The reaction coordinate dependence of all low-lying states of the Mn(III) complexes.

[1] A. Hauser, Top. Curr. Chem. **234** (2004) 155–198.

[2] S.Wang, M. Ferbinteanu, C. Marinescu, A. Dobrinescu, Q.-D. Ling, W. Huang, Inorg. Chem. **49** (2010) 9839-9851.

[3] G. G. Morgan, K. D. Murnaghan, H. Müller-Bunz, V. McKee, C. J. Harding, Angew. Chem. Int. Ed. **45** (2006) 7192-7195.

[4] S. Wang, W.-R. He, M. Ferbinteanu, Y. -H. Li ,W. Huang, Polyhedron **52** (2013) 1199–1205.

[5] B. Gildea, L. C. Gavin, C. A. Murray, H. Müller-Bunz, C. J. Harding, G. G. Morgan, Supramolecular Chemistry **7-8** (2012) 640-652.

Pseudo Jahn-Teller effect in coordinated ketene molecule induced by the orbital charge transfers

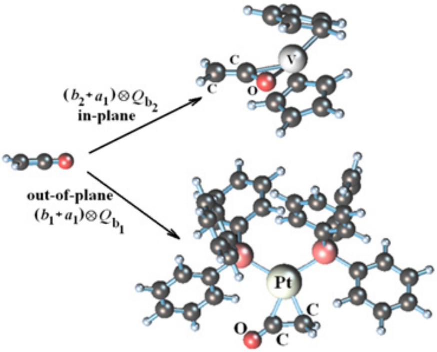
Natalia GORINCHOY
Institute of Chemistry, Academy of Sciences of Moldova, Kishinev, Republic of Moldova
§E-mail: ngorinchoy@yahoo.com

To date, a number of complexes with ketenes was synthesized and structurally characterized. It was found that ketenes bind to transition-metal centers in two fashions, via the η^2-(C-O) mode and the η^2-(C-C) one. Moreover, in the first case the ketene molecule undergoes the in-plane distortion of the b_2-type, while the η^2-(C-C) coordination mode leads to the out-of-plane distortion (b_1-type) of ketene [1]. In order to reveal the factors which determine the preference of the ketene π-system to adopt one or another coordination mode, and to clarify the origin of distortions, we used the approach outlined in [3] which is based on an approximate evaluation of the Jahn-Teller and the pseudo Jahn-Teller effects in systems with fractional charges that occur due to the orbital charge transfers (OCTs). According to this approach, the curvature of the adiabatic potential (AP) of coordinated molecule in the Q direction can be estimated as follows:

$$K_Q^{\text{coord}} = K_Q^{\text{free}} - \Delta q_i \,(|f_Q^{(i,j)}|^2/\Delta_{\text{ij}}),$$

where K_Q^{free} is the curvature of the AP of free molecule, Δq_i is the OCT to or from ith molecular orbital, $f_Q^{(i,j)}$ is the PJT vibronic coupling constant between the interacting MOs, and Δ_{ij} is the energy gap between them.

As the examples, two complexes with ketene were considered, VCp_2-H_2C_2O (I) and $Pt(PPh_3)_2$-H_2C_2O (II), in which its free molecule planar configuration of C_{2v} symmetry undergoes the b_2-type and b_1-type distortions, respectively (Figure). The values of K_Q^{free}, Δq_i and Δ_{ij} were obtained from *ab initio* calculations, and the corresponding vibronic constants $f_Q^{(i,j)}$ were calculated by considering the distortions of the molecule in the low-lying $^3A_2$ and $^3A_1$ excited states.



It is shown that the curvature of the AP of coordinated ketene respectively in the b_2 (in I) and b_1 (in II) directions becomes negative in both complexes, that explains the origin of the geometry of coordination of the molecule. The η^2-(C-O) coordination and the in-plane distortion of ketene in the complex (I) is due to the PJTE induced by the back donation to its LUMO $3b_2$ (π_{CO}*). The η^2-(C-C) coordination mode, as well as the out-of-plane distortion of the molecule in the complex (II) is caused by two charge transfers: from the HOMO $2b_1$(π_{CC}) to the metal d_{z2}-AO, and from the d_{xz}-AO of Pt to the vacant $3b_1$(π_{CC}*) MO of ketene, thus being the result of diorbital metal-ketene interaction.

[1] D. B. Grotjahn, L. S. B. Collins, M. Wolpert, G. A. Bikzhanova, H. C. Lo, D. Combs, and J. L. Hubbard, J. Am. Chem. Soc. **123** (2001) 8260–8270; P. Hofmann, L. A. Perez-Moya, O. Stelgelmann, and J. Riede, Organometallics **11** (1992) 1167-1176.

[2] N. N. Gorinchoy, I. I. Balan, I. B. Bersuker: Jahn-Teller, pseudo Jahn-Teller, and Renner-Teller effects in systems with fractional charges, Comput. & Theoret. Chem. **976** (2011) 113-119.

Jahn-Teller effect in C_{60}^{3-} studied by infrared spectroscopy in solution

Judit HORVÁTH, Gyöngyi KLUPP, and Katalin KAMARÁS
Institute for Solid State Physics and Optics, Wigner Research Centre for Physics,
Hungarian Academy of Sciences, Budapest, Hungary

Fulleride anions show an inherent Jahn-Teller effect which has been proven for mono- and dianions in the gas phase [1,2]. Near-infrared data for most fulleride anions in solution are known [3] and indicate that the Jahn-Teller distortion in the solvated molecular species is dynamic and depends on solvent polarity. However, vibronic spectra in the infrared range are much less reported because of technical difficulties caused by solvent absorption and air-sensitivity of the samples.

The infrared spectrum of C_{60}^{3-} is particularly interesting because most solids containing trivalent fullerides are metallic [4] and the screening by conducting electrons obscures the details of the vibronic bands. We will present a comparison of the infrared spectra of conducting K_3C_{60}, the expanded Mott insulator Cs_3C_{60} [5], and solvated C_{60}^{3-} in tetrahydrofurane and benzonitrile. Solvated ions exhibit a considerable broadening of the $T_{1u}(4)$ band, indicating a dynamic Jahn-Teller effect. Details of these dynamics will be deduced from temperature-dependent measurements.

[1] S. Tomita, J.U. Andersen, E. Bonderup, P. Hvelplund, B. Liu, S. Brondsted Nielsen, U.V. Pedersen, J. Rangama, K. Hansen, O. Echt: Dynamic Jahn - Teller effects in isolated C_{60}^- by near-infrared spectroscopy in a storage ring, Phys. Rev. Lett. **94** (2005) 053002.
[2] U. Kadhane, J.U. Andersen, E. Bonderup, B. Concina, P. Hvelplund, M.B. Suhr Kirketerp, B. Liu, S. Brondsted Nielsen, S. Panja, J. Rangama, K. Støchkel, S. Tomita, H. Zettergren, K. Hansen, A.E.K. Sundén, S.E. Canton, O. Echt, J.S. Forster: Near-infrared photoabsorption by C_{60} dianions in a storage ring, J. Chem. Phys. **131** (2009) 014301.
[3] C.A. Reed, R.D. Bolskar: Discrete fulleride anions and fullerenium cations. Chem. Rev. **100** (2000) 1075-1120.
[4] K. Kamarás, G. Klupp: Metallicity in fullerides. Dalton Transactions **43** (2014) 7366-7378.
[5] G. Klupp, P. Matus, K. Kamarás, A.Y. Ganin, A. McLennan, M.J. Rosseinsky, Y. Takabayashi, M.T. McDonald, K. Prassides: Dynamic Jahn – Teller effect in the parent insulating state of the molecular superconductor Cs_3C_{60}. Nat. Commun. **3 (2012)** 912.

Interplay between isotope localization and second order Jahn-Teller effect

Naoya IWAHARA[1], Tohru SATO[2,3], Kazuyoshi TANAKA[2],
and Liviu F. CHIBOTARU[1]
[1]Theory of Nanomaterials Group, Katholieke Universiteit Leuven,
Celestijnenlaan 200F, B-3001 Leuven, Belgium
[2]Department of Molecular Engineering, Graduate School of Engineering, Kyoto University,
Kyoto 615-8510, Japan
[3]Unit of Elements Strategy Initiative for Catalysts & Batteries, Kyoto University,
Kyoto 615-8510, Japan

This is a continuation of the work on isotope-substituted dynamical Jahn-Teller system [1]. In the previous work [1], we have shown (1) the mechanism of the localization of the vibronic wave functions by isotope substitution and that (2) the degeneracy of the vibronic levels of the linear $E \times e$ problem remain double degenerate upon arbitrary isotope substitution on the reasons similar to time reversal symmetry in which the role of spin is played by orbital pseudospin. The degeneracy is lifted by the quadratic (even order) vibronic coupling. In this work, we address the interplay between the isotope effect and quadratic vibronic coupling. To this end a $E \times e$ system X_3 with quadratic vibronic coupling is considered in detail. By isotope substitution of $X_3 \rightarrow X_2Y$, the ground level of the localized state in each potential well varies and one of them ($\phi = 0$) is obtained to be different from the others ($\phi = 2\pi/3, 4\pi/3$) by Δ. These levels split into three through the tunneling between the wells:

$$E_{A(1)} \approx -\Gamma/(1-S)+2\Delta/(3-3S), \quad E_B = -\Gamma/(1-S), \quad E_{A(2)} = 2\Gamma/(1+2S)+\Delta/(3+6S).$$

We found that Δ is negative for $W_E < \omega_E/\sqrt{10}$, while it becomes positive with increase of W_E ($> \omega_E/\sqrt{10}$). Therefore *with increase of* W_E, *the order of lowest vibronic levels is inverted from* $E_{A(1)} < E_B$ *to* $E_B < E_{A(1)}$. The inversion is observed in the exact solution of the pseudorotational Hamiltonian (Fig. 1(a)). The pseudorotational A state is localized at $\phi = 0$ for small W_E, while at $\phi = 2\pi/3$ and $4\pi/3$ for large W_E (Fig. 1(b)).

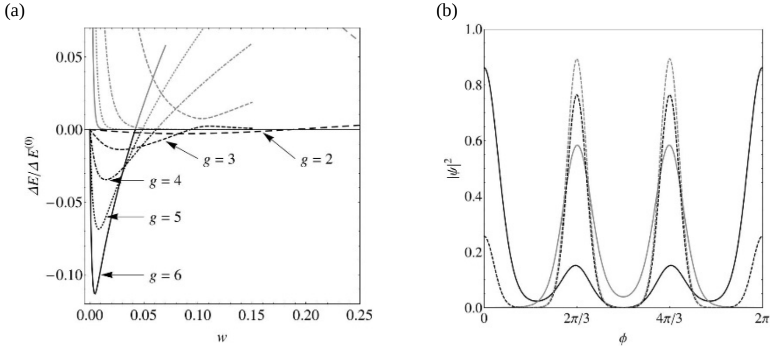


Figure 1. (a) Pseudorotational levels ΔE for various g ($=V_E/\sqrt{\hbar\omega_E^3}$) and w ($=W_E/\omega_E^2$). $\Delta E = E_{A(1)}-E_B$ (black), $E_{A(2)}-E_B$ (gray) and $\Delta E^{(0)}$ is the first pseudorotational excitation energy without W_E. (b) Densities of $A(1)$ (black) and B (gray) states for $g = 3$, $w= 0.029$ (solid) and 0.111 (dashed).

[1] N. Iwahara, T. Sato, K. Tanaka, and L. F. Chibotaru: “Mechanisms of localization in isotope-substituted dynamical Jahn-Teller systems”, EPL **100** (2012) 43001 1-6

Zeeman interaction and Jahn-Teller effect in Γ_8 multiplet

Naoya IWAHARA, Liviu UNGUR, and Liviu F. CHIBOTARU
Theory of Nanomaterials Group, Katholieke Universiteit Leuven,
Celestijnenlaan 200F, B-3001 Leuven, Belgium

Magnetic compounds with strong magnetic anisotropy have attracted wide attention because they often show single-molecular magnet behavior. The magnetic anisotropy is manifested in the Zeeman interaction, $H_{zee} = -\boldsymbol{\mu}\cdot\mathbf{B}$, and in the zero-field splitting which are described by *pseudospin S* when spin-orbit interaction and crystal field effects are concomitantly present [1]. As S increases, the magnetic moment $\boldsymbol{\mu}$ becomes nontrivial, i.e., it is not merely proportional to $\boldsymbol{S}$ for $S \geq 3/2$. In cubic systems the $S = 3/2$ pesudospin corresponds to the Γ_8 multiplet, encountered as ground state in many compounds, such as ReF_6, TcF_6, Cs_2ZrCl_6:Np^{4+}, etc. Since the fourfold degenerate Γ_8 state couples to the Jahn-Teller e and t_2 modes, the low-energy properties must be described by concomitant treatment of the Zeeman interactions and the Jahn-Teller effect (JTE). Recently the theoretical methodology for the unique definition of the pseudospin Hamiltonian from *ab initio* wave functions has been proposed and applied to many compounds [2,3]. In the present work, we study the effect of JT distortions and dynamics on the Zeeman interaction in the Γ_8 multiplet and explain relevant experimental data by applying the *ab initio* methodology for the derivation of pseudospin Hamiltonians.

The vibronic reduction of the parameters (g, G) in the Zeeman interaction are simulated diagonalizing the $\Gamma_8 \times (e + t_2)$ dynamical JT Hamiltonian. We find that the dynamical JTE modifies not only the absolute values but also the signs of these parameters with respect to pure electronic multiplet (Figure 1 a). With the dynamical JTE the Zeeman interaction remains symmetric, while freezing of JT dynamics changes the Zeeman interaction corresponding to Γ_8 into the Zeeman interaction corresponding to low symmetry Kramers doublet. The parameters of the Zeeman interaction and the magnetic axes change with the direction of the JT deformation (Figure 1 b, c).

The Zeeman pseudospin Hamiltonian and the parameters of JT effect of Cs_2ZrCl_6:Np^{4+} derived from the *ab initio* methodology reproduces experimental data.

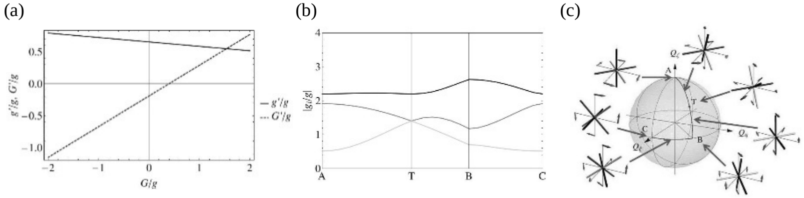


Figure 1. The parameters of Zeeman Hamiltonian for (a) $\Gamma_8 \times t_2$ dynamical JTE (g', G') and (b) static JTE with respect to pure electronic case (g, G). (c) Magnetic axes for different static JT distortions.

[1] A. Abragam and B. Bleaney: “Electron Paramagnetic Resonance of Transition Ions”, Claredon Press, Oxford, 1970

[2] L. F. Chibotaru and L. Ungur: “Ab initio calculation of anisotropic magnetic properties of complexes. I. Unique definition of pseudospin Hamiltonians and their derivation”, J. Chem. Phys., **137** (2012) 064112 1-22

[3] L. F. Chibotaru: “Ab initio methodology for pseudospin Hamiltonians of anisotropic magnetic complexes”, Adv. Chem. Phys. **153** (2012) 397-519

The Jahn-Teller effect in the ethane and the 2-butyne radical cations.

U. JACOVELLA[1], C. LAUZIN[1], B. GANS[2], M. GRÜTTER[3],
and F. MERKT[1]

[1]Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093 Zurich, Switzerland
[2]Institut des Sciences Moléculaires d'Orsay, Univ Paris-Sud, F-91405 Orsay, France
[3]Department of Dynamics at Surfaces, Max Planck Institute for Biophysical Chemistry,
37077 Göttingen, Germany

The ethane radical cation ($H_3C\text{-}CH_3^+$) and the 2-butyne radical cation ($H_3C\text{-}C{\equiv}C\text{-}CH_3^+$) are subject to the Jahn-Teller (JT) and pseudo-Jahn-Teller (PJT) effects. These two cations are structurally similar in that they have two equivalent methyl rotors. However, the internal rotation is expected to be much more hindered in the ethane cation. The experimental information on their energy level structures is so far limited to that contained in low-resolution (~50 cm^{-1}) photoelectron spectra [1-3].

We present high-resolution (~0.4 cm^{-1}) pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of ethane and 2-butyne in the region of the origin band and of transitions to low-lying vibrational levels of the cations with partially resolved rotational structure. From these spectra, we have derived new information on the cations, which reveals a completely different behavior, particularly concerning the strength of the JT, PJT and spin-orbit coupling and the role of internal rotation.

The rotational structure observed in the photoelectron spectrum of 2-butyne indicates a weak JT effect and an observable spin-orbit splitting of ~12 cm^{-1} between the two components $E_{3/2}$ and $E_{1/2}$ of the $\tilde{X}^+\ {}^2E_{2(d)}$ ground state, which is in agreement with the results of recent *ab-initio* calculations [4]. It also reveals spectral patterns that we attribute to an almost free internal rotation.

The vibrational level structure observed in the photoelectron spectrum of ethane shows much stronger JT and PJT effects as has been predicted in Ref. [5], which completely quench the spin-orbit coupling. In the vicinity of the ionization threshold, several isomers resulting from the ionization of the e_g and a_{1g} orbitals have been predicted ab initio [6,7]. The relevant potential energy surfaces come very close in several regions and most probably result in a triple conical intersection in addition to the conical intersection associated to the $(E\otimes e)$-JT effect. The rovibrational structure observed in the PFI-ZEKE photoelectron spectra confirms the existence of at least two isomers and provides information on their structures.

[1] P. Carlier, J.E. Dubois, P. Masclet and G. Mouvier, J. Electron Spectrosc., **7**, (1975) 55-67.
[2] H. Xu, U. Jacovella, B. Ruscic, S.T. Pratt and R.R. Lucchese, J. Chem. Phys., **136,** (2012) 154303.
[3] J. W. Rabalais and A. Katrib, Mol. Phys., **27, (**1974) 923.
[4] S. Knecht and M. Reiher, ETH Zürich, private communication (2014).
[5] T. S. Venkatesan and S. Mahapatra, J. Chem. Phys., **123**, (2005) 114308.
[6] A. Ioffe and S. Shaik, J. Chem. Soc., Perkin Trans. 2, **8**, (1993) 1461-1473.
[7] H. M. Sulzbach, D. Graham, J. C. Stephens and H. F. Schaefer III, Acta. Chem. Scand, **51**, (1997) 547-555.

Molecular Structure of [n]Cycloparaphenylene Radical Cation

Takahiko KOYAMA[1], Tatsuhisa KATO [1, 2], Eiichi KAYAHARA [3], and Shigeru YAMAGO [3]
[1] Department of Interdisciplinary Environment, Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan
[2] Institute For Liberal Arts and Sciences, Kyoto University, Kyoto 606-8501, Japan
[3] Institute for Chemical research, Kyoto University, Uji 611-0011, Japan

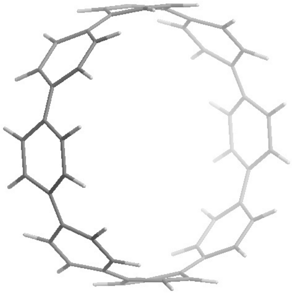


Fig. 1 Molecular model of [8]CPP.

[n] Cycloparaphemylene ([n]CPP : n=6, 8, 10, and 12) is a hoop-shaped π-conjugated oligomer consisting of n para-linked phenylene rings, as shown in Fig.1. Since [n]CPP is the smallest structural unit of armchair (n, n)-carbon nanotube, the oligomers gained much attention and their synthesis has recently developed.[1] On the other hand, radical cations of π-conjugated oligomers such as poly-p-phenylenes and polythiophenes have played an important role as a constituent of charge-transporting layer in organic electronics. Because CPPs can be regarded as an end-free, cyclic version of poly-p-phenylenes, the electronic and molecular structures of their radical cations are of great interest.

A radical cation and a dication of [8]CPP were prepared and isolated as hexahaloantimonate salts by one- and two-electron chemical oxidation by $NOSbF_6$ [2]. Although neutral [8]CPP exhibited the torsional structure around the bond of adjacent phenylene rings, which was proved by the X-ray crystallographic analysis[3], dication species showed the coplanar arrangement of all paraphenylene units forming a belt-like structure with the smaller dihedreal angle between the neighboring paraphenylene units than that observed in neutral form [2]. The instability of the cylindrical D_{6h} structure is the feature peculiar to [n]CPP.

The electron spin resonance (ESR) spectra of [6], [8], [10], [12]CPP radical cations were measured in CH_2Cl_2 solution, which exhibited the equally split multiplets due to ^1H hyperfine coupling, indicating that the spin and charge were delocalized over the benzene rings in all CPP cases. The electron nuclear double resonance (ENDOR) spectra of [6] and [8]CPP were also measured in CH_2Cl_2 solution. The dynamics with respect to the instability of the cylindrical D_{6h} structure was reflected in ESR and ENDOR spectra.

[1] (a) U. H. F. Bunz et al.: para-Connected Cyclophenylenes and Hemispherical Polyarenes; Building Block for Single-Walled Carbon Nanotubes?, *Angew. Chem. Int. Ed.*, **51** (2012) 7094-7101. (b) E. Kayahara et al. : Selective Synthesis of [6]-, [8]-, and [10]cycloparaphenylenes, *Chem. Lett.*, **42** (2013), 621- 623.
[2] E. Kayahara et al. : Isolation and Characterization of the Cycloparaphenylene Radical Cation and Dication, *Angew. Chem. Int. Ed.*, **52** (2013) 13722-13726.
[3] (a) J. Xia and R. Jasti: Synthesis, Charaterization, and Crystal Structure of [6]Cycloparaphenylene, *Angew. Chem. Int. Ed.*, **51** (2012) 2474-2476. (b) J. Xia et al. : Gram-scale synthesis and crystal structures of [8]-and [10]CPP, and the solid-state structure of C_{60}@[10]CPP, *Chem. Sci.*, **3** (2012), 3018- 3021.

P17

Pseudo Jahn-Teller effect in [6]cycloparaphenylene

Yuichiro KAMEOKA[1], Tohru SATO[1,2], Takahiko KOYAMA[3],
Kazuyoshi TANAKA[1], and Tatsuhisa KATO[3,4]
[1]Department of Molecular Engineering, Graduate School of Engineering, Kyoto University,
Nishikyo-ku, Kyoto 615-8510, Japan
[2]Unit of Elements Strategy Initiative for Catalysts & Batteries, Kyoto University,
Nishikyo-ku, Kyoto 615-8510, Japan
[3]Department of Interdisciplinary Environment, Graduate School of Human and Environmental
Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
[4]Institute for Liberal Arts and Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

[*n*]Cycloparaphenylenes ([*n*]CPPs) are π-conjugated cyclic molecules which consist of *n* paraphenylenes. They can be regarded as basic units of armchair carbon nanotubes, and therefore their structure and physical properties have attracted much attention. It has been experimentally shown that the structures of [*n*]CPPs are not cylindrical but twisted with respect to the neighboring paraphenylene units[1]. This deformation can be ascribed to the pseudo Jahn-Teller (PJT) effect [2]. We discuss the origin of the PJT effect in [6]CPP [3].

The PJT potential for mass-weighted normal coordinate of deformation mode Q_α is expressed as,

$$E(Q_\alpha)=E_0+1/2(K_{0,\alpha}-K_{v,\alpha})\,Q_\alpha^2,$$

where $K_{0,\alpha}$ is the quadratic vibronic coupling constant. $K_{v,\alpha}$ is positive and this term can give rise to an instability depending on the magnitudes of $K_{0,\alpha}$ and $K_{v,\alpha}$.

Within the orbital approximation, $K_{v,\alpha}$ is expressed in terms of orbital vibronic coupling constants (OVCCs) [4]. By calculating the OVCCs, we clarify that the coupling of highest occupied molecular orbital (HOMO) and a certain unoccupied σ orbital is the main source of the PJT instability of cylindrical [6]CPP. Analysis of orbital vibronic coupling density (OVCD) [5], the integrand of OVCC, shows the reason of the strong coupling of deformation mode and overlap between π-type HOMO and σ-type molecular orbital.

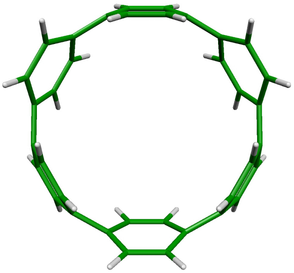


Figure 1. The structure of [6]CPP.

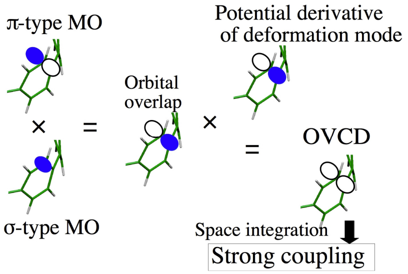


Figure 2. Schematic diagram of OVCD analysis.

[1] U. H. F. Bunz, *et al.*: *para*-Connected Cyclophenylenes and Hemispherical Polyarenes: Building Blocks for Single-Walled Carbon Nanotubes?, Angew. Chem. Int. Ed. **51** (2012) 7094-7101.
[2] I. B. Bersuker: Pseudo-Jahn-Teller Effect-A Two-State Paradigm in Formation, Deformation, and Transformation of Molecular Systems and Solids, Chem. Rev. **113** (2013) 1351-1390.
[3] Y. Kameoka, *et al.* Pseudo Jahn-Teller origin of distortion in [6]cycloparaphenylene, Chem. Phys. Lett. **598** (2014) 69-74.
[4] I. B. Bersuker: The Jahn-Teller Effect, (Cambridge University Press, Cambridge, 2006) 27-31.
[5] T. Sato, *et al.*: Vibronic coupling density and related concepts, J. Phys.: Conf. Ser. **428** (2013) 012010.

Vibronic Interaction and Mechanochemical Reactivity

Naoki HARUTA[1], Tohru SATO[1, 2], Kazuyoshi TANAKA[1],
and Michel BARON[3]
[1]Department of Molecular Engineering, Graduate School of Engineering,
Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
[2]Unit of Elements Strategy Initiative for Catalysts & Batteries,
Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
[3]Université de Toulouse, Mines-Albi, CNRS UMR 5302, Centre Rapsodee,
Campus Jarlard, 81013 Albi Cedex 09, France

Dibenzophenazine, which is a basic structure in pharmaceutical and functional materials, has been mechanochemically synthesized from diamine and dione by a ball-milling method with high yield [1] (Fig. 1). This method receives a great deal of attention because it is a green synthesis method without organic solvents.

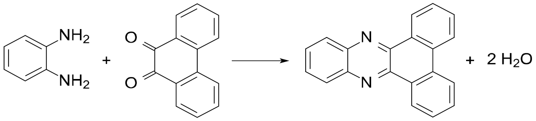


Fig. 1 Mechanochemical synthesis of dibenzophenazine from diamine and dione.

In this study, we theoretically investigated the reaction mechanism in the mechanochemical synthesis of dibenzophenazine using the concept of vibronic coupling density (VCD) [2-4]. This analysis enables us to predict its experimentally observed reactive sites that cannot be explained by the conventional frontier orbital theory (Fig. 2). Furthermore, on the basis of the symmetry of the VCD distributions, we found that the reaction path depends on the conformation of diamine: C_2-diamine or C_s-diamine. The most stable C_2-diamine favors the stepwise formation of the intermolecular bonds, while the unstable C_s-diamine favors the concerted formation of the intermolecular bonds. This difference originates from the difference of their vibrational modes. The concerted mechanism can be possible mechanochemically because mechanochemical conditions increase the amount of energetically unstable diamines.

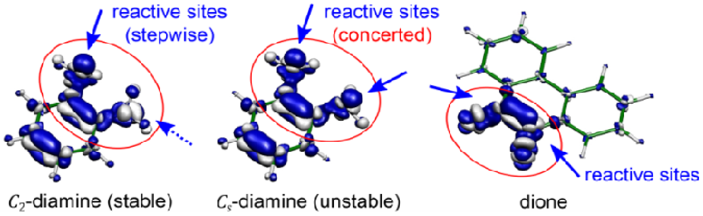


Fig. 2 Vibronic coupling densities of diamine and dione.

[1] L. Carlier, M. Baron, A. Chamayou, G. Couarraze: Use of co-grinding as a solvent-free solid state method to synthesize dibenzophenazines, Tetrahedron Lett. **52** (2011) 4686–4689.
[2] T. Sato, K. Tokunaga, K. Tanaka: Vibronic Coupling in Naphthalene Anion: Vibronic Coupling Density Analysis for Totally Symmetric Vibrational Modes, J. Phys. Chem. A **112** (2008) 758–767.
[3] T. Sato, N. Iwahara, N. Haruta, K. Tanaka: C_{60} bearing ethylene moieties, Chem. Phys. Lett. **531** (2012) 257–260.
[4] N. Haruta, T. Sato, K. Tanaka, M. Baron: Reaction mechanism in the mechanochemical synthesis of dibenzophenazine: application of vibronic coupling density analysis, Tetrahedron Lett. **54** (2013) 5920–5923.

P19

Vibronic interactions and their role in the formation of Cooper pairs in superconductivity

Takashi KATO
Institute for Innovative Science and Technology, Graduate School of Engineering, Nagasaki Institute of Applied Science, 3-1, Shuku-machi, Nagasaki 851-0121, Japan

In the Jahn-Teller Conferences 2008 held in Heidelberg, Germany [1], and 2010 held in Fribourg, Switzerland [2], we have predicted the mechanism of the formation of Cooper pairs and their role in the occurrence of supercurrents. In the previous works [3,4] as well as in these conferences [1,2], we suggested that in the microscopic sized materials with large HOMO-LUMO gaps ($\Delta E_{\mathrm{HOMO\text{-}LUMO},N}$) such as benzene (**6an**), naphthalene (**10ac**), and anthracene (**14ac**) (Fig. 1), the Cooper pairs are formed by the stable spin singlet states as a consequence of large HOMO-LUMO gaps (about 5~10 eV) formed by the quantization of the orbitals by nature, and by strong attractive Coulomb interactions (about 70~80 eV) between two electrons with opposite momentum and spins occupying the same orbitals via the positively charged nuclei at room temperatures. Furthermore, by analogy with the supercurrents in the microscopic sized materials such as **6an**, **10ac**, and **14ac**, we predicted that the macroscopic sized materials with large $\Delta E_{\mathrm{HOMO\text{-}LUMO},N}$ values, in which the valence bands are completely occupied by electrons, and which have been considered to be insulator in the textbooks of the solid state physics and chemistry, such as very pure diamond crystals, can exhibit high temperature superconductivity at the temperatures in the order of 10^4~10^5 K (Fig. 2) [1-4]. On the other hand, it was reported in the recent experimental research [5] that the Cooper pairs have been observed at about 70~80 eV in photoemission spectrum at room temperatures in the neutral **6an**, **10ac**, **14ac**, and coronene molecules. Furthermore, in 2012, Esquinazi et al. reported that the virgin graphite powder treated by water or exposed to the hydrogen plasma can exhibit superconductivity at much higher temperatures than room temperatures (~10^4 K) (Fig. 2) [6]. In this conference, we will show that our prediction [1-4] can be well confirmed by the recent experimental research [5], and our previous theory can be reasonably applied to the explanation of the mechanism of the occurrence of the granular room temperature superconductivity in carbon materials [6]. Furthermore, from these experimental results [5,6], we can conclude that the vibronic interactions destroy the electron pairs formed by the attractive Coulomb interactions, and reform electron pairs by forming small energy gap ($\Delta(0)_{\mathrm{BCS}}$) (like Jahn–Teller effects), by which, the electron pairing states become stable at low temperatures in the macroscopic sized superconductivity.

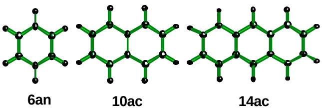


Fig. 1

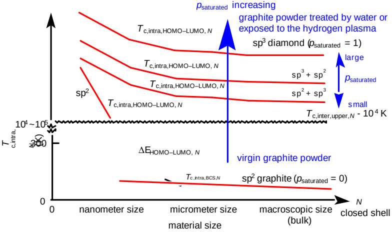


Fig. 2

[1] T. Kato, Jahn-Teller Conference 2008 (Heidelberg, Germany).
[2] T. Kato, Jahn-Teller Conference 2010 (Fribourg, Switzerland).
[3] T. Kato, Chemical Physics 345 (2008) 1.
[4] T. Kato, Chemical Physics 376 (2010) 84.
[5] R. Wehlitz, et al. Physical Review Letters 109 (2012) 193001.
[6] P. Esquinazi, et al. Advanced Materials 24 (2012) 5826.

Pseudo Jahn-Teller instability of Nb^{5+} in $KNbO_3$ under high pressure

Victor POLINGER
Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195-1700, USA

In $KNbO_3$, similar to barium titanate, lowering temperature results in ferroelectric phase transitions, from the high-symmetry cubic to tetragonal phase at 708 K, tetragonal to orthorhombic at 498 K, and orthorhombic to rhombohedral phase at 263 K. Correspondingly, as it follows from neutron-diffraction measurements, position of Nb changes with temperature from the body-centered position in high-temperature cubic phase to off-center shifted in the directions [100], [110], and [111]. These temperature changes of the crystal structure are well described by Bersuker's vibronic theory of ferroelectricity in cubic perovskites [1]. In his approach the off-center instability is due to the pseudo Jahn-Teller hybridization of the highest-occupied molecular orbitals (HOMO, mostly oxygen AOs), with the lowest unoccupied molecular orbitals (LUMO, mostly transition-metal AOs). The observed sequence of ferroelectric phase transitions follows from the temperature averaging of the off-center motion of the transition metal over different saddle points between the wells. This model was supported by the experimental discovery of the persistent presence of the trigonal displacement of the transition metal in the direction [111] at high temperature well above the cubic-to-tetragonal phase transition. The XAFS technique allows accurate measurement of the trigonal displacement of Nb in potassium niobate under high pressure [2]. Shown below in Fig.1, the experimental results of [2] do not show any significant difference of the pressure-induced shift of Nb at $T = 77$ K and $T = 300$ K.

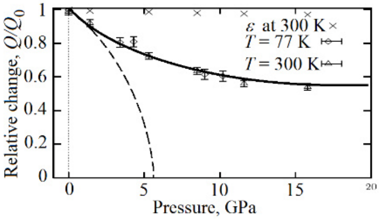


Fig. 1. Pressure-induced relative change of the off-center displacement of Nb in potassium niobate under ambient pressure at $T = 77$ K and 300 K.

In this work the off-center displacement of Nb in $KNbO_3$ is explained in terms of the pseudo Jahn-Teller effect, following the basic idea introduced in [1]. The fundamental reason of the magnitude drop of the off-center displacement of Nb is the pressure-induced increase of the energy gap between the Jahn-Teller-hybridized HOMO and LUMO. The latter is due to the increase of the energy stabilization of the populated oxygen HOMO due to a greater overlap under ambient pressure of the populated oxygen HOMO with excited orbitals of the same symmetry t_{1u} and t_{2u}. However, as distinguished from the experimental observation, just this mechanism gives a too-fast drop of the off-center shift to zero, see the broken graph in Fig.2. A better fit (solid graph in Fig.2) is achieved under assumption of a non-linear dependence of the size of the oxygen octahedron $[NbO_6]$ with pressure. At about 5 GPa the oxygen octahedron manifests an increasing rigidity with respect to its decrease in size. Further decrease in size of the unit cell under increasing hydrostatic pressure is due to a drop of the dimensions of the 8-coordinated cube of potassium atoms.

[1] I.B. Bersuker: On the origin of ferroelectricity in perovskite-type crystals, Phys. Lett. **20** (1966) 589-590.
[2] A.I. Frenkel, F.M. Wang, S. Kelly, R. Ingalis, D. Haskel, E.A. Stern, and Y. Yakoby: Local structural changes in $KNbO_3$ under high pressure, Phys. Rev. B **56** (1997) 10 869 – 10 877.

Percolation features of Cooperative Jahn-Teller systems: Ising EFT framework

E. A. MOUJAES[1] and Michel ABOU GHANTOUS[2]
[1]Department of Physics, Federal University of Rondônia, 76900-900, Porto Velho, Brazil
[2]Department of Physics, Texas A and M University at Qatar, PO Box 23874, Doha,Qatar

Elastic exchange between two nearest Jahn-Teller (JT) centers in two or three dimensional dense crystals, can give an ordered macroscopic distortion known as the cooperative JT effect (CJTE) [1]. A very diluted JT crystal doesn't show this effect. In the dynamic JT effect (DJTE), tunneling between different equivalent distorted wells has a pronounced infuence on the CJTE. We investigate this phenomenon using a progressive increase in the concentration of these centers in the JT crystals, based on a bond percolation vector spin analogy technique within the framework of effective field theory (EFT) [2,3]. Mean field theory (MFT) was extensively used in previous studies of CJTE; however it neither includes correlation between JT centers in the lattice due to the complexity of the distortion field in the crystal nor the effect of tunneling between wells. We resort to an alternative procedure, by describing a JT center as a pseudo-spin S , induced to represent the degenerate JT-distorted states, where two nearest JT centers interact via an elastic exchange described by an Ising type spin interaction. The DJTE is considered to be similar to an elastic transverse field term in the Hamiltonian portraying the effect of tunneling between equivalent wells in the adiabatic potential energy surface (APES). We will be particularly discussing $S = 1$, $S = 3/2$ and $S = 5/2$ spin cases, where $2S + 1$ wells in the APES are present, and what JT systems they actually represent, with a percolative mechanism [4,5] applied to the interactions between different JT centers. The different lattices are distinguished by their coordination numbers. Strong tunneling effects can suppress the CJTE and lead to a new state of criticality. Generalizations to higher spin systems will be obtained using a scaling technique. For the relevant distortions, we determine single site correlations, the macroscopic average distortion describing a structural phase transition and the elastic isothermal susceptibility as a function of temperature. The critical bond percolation threshold and the critical tunneling parameter are also obtained.

POSTER

[1] I.B. Bersuker, V.Z. Polinger, Vibronic interactions in molecules and crystals, Springer-Verlag, Berlin, Heidelberg, NY, (1989).
[2] A. El Atri, and M. Saber, Phys. Stat. Sol. B **184**, 187 (1994).
[3] C.Z. Yang, and J.L. Zhong, Phys. Stat. Sol. B **153**, 323 (1989).
[4] P. J. Flory, J. Am. Chem. Soc. **63**, 3083 (1941).
[5] D. Stauffer, Introduction to percolation theory (1st ed.), London: Taylor and Francis, (1985).

Jahn-Teller effect in $^4T_{2g}$ excited state of Mn2+:MgO

N.M. AVRAM[1,2], C.N. AVRAM[1], and E.-L. ANDREICI[1]
[1]Department of Physics, West University of Timisoara, Bd.V.Parvan No.4, 300223 Timisoara, Romania
[2]Academy of Romanian Scientists, Independentei 54, 050094-Bucharest, Romania

The aim of this paper is the estimations of the electron-vibrational constants, Huang-Rhys parameters, and Jahn-Teller stabilization energy, in $^4T_{2g}$ excited state of Mn^{2+} doped in MgO crystal, using two methods of calculations.

First method is based on the exchange charge model of crystal field [1] and has been applied to determine the dependence of the crystal field strength 10*Dq* on interionic distances *R*, between the Mn^{2+} impurity ion and O^{2-} ligands, in cubic MgO: Mn^{2+}. The obtained results were extrapolated by the power law and was shown that 10*Dq* depends on *R* as $1/R^n$, with $n = 6.2135$, deviations from the value $n = 5$ (predicted by the simple point charge model of crystal field), explained by the covalent and exchange effects. The second method is based on Ham reduction [2] of the spin-orbit splitting of $^4T_{2g}$ excited state, described by the effective second-order spin-Hamiltonian. In addition, an alternative method of determining the Jahn-Teller stabilization energy based on the harmonic approximation and geometrical consideration of the adiabatic surfaces of the potential energy of the ground and excited electronic states is described. The obtained results are compared between them and with experimental data.

[1].B.Z.Malkin,"Crystal field and electron-phonon interaction in rare-earth ionic paramagnets", in : Spectroscopy of Solids Containing Rare-Earth Ions, Edited by A.A. Kaplianskii and B.F. Macfarlane, (North Holland, Amsterdam, 1987) 13-50.

[2]. M.G.Brik, N.M.Avram, C.N.Avram, "Jahn-Teller effect for 3d ions (orbital triplets in a cubic crystal field), in The Jahn-Teller Effect, Eds.H.Koppel, D.R.Yarkony, H.Barentzen, (Springer-Verlag, Heidelberg, 2009)347-370.

P23

Ab initio quantum study of nonadiabatic S_1-S_2 photodynamics of s-*trans*-butadiene.

Adrian KOMAINDA[1], Bojana OSTOJIĆ[2], and Horst KÖPPEL[1]
[1]Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany
[2]Institute of Chemistry, Metallurgy, University of Belgrade, Studentski trg 14-16, 11 000 Belgrade, Serbia

We present a quantum dynamical approach for the nonadiabatic dynamics of s-*trans*-butadiene in the two lowest singlet excited states [1]. In our calculations the coupled $1B_u$ and $2A_g$ states are considered, which represent the lowest dipole-allowed electronic transition and the dipole-forbidden state with substantial double-excitation character [2], respectively. For the quantum dynamical calculations we use the multi-configuration time-dependent Hartree method (MCTDH) with up to eight nuclear degrees of freedom. The underlying potential energy surfaces were obtained with the CASPT2 and -MRCI methods, where different CAS spaces have been compared. With all CAS spaces applied we confirm the ultrafast electronic population decay, proceeding on a time scale of 30-40 fs. In this work for the first time out-of plane vibrations were included in fully quantal calculations. The usage of these modes considerably increases the complexity of the computed electronic absorption spectrum. We achieve a very good agreement with the experimental result [3] and are able to explain its vibronic structure, which is a main reason for the diffuseness. Less phenomenological broadening is needed than in previous studies [4] and large out-of-plane displacements are obtained at a time scale of 120 fs. The results are compared with these of a preliminary study on s-*cis*-butadiene.

[1] A. Komainda, B. Ostojić, H. Köppel: Ab Initio Quantum Study of Nonadiabatic S_1-S_2 Photodynamics of s-*trans*-Butadiene, J. Phys. Chem. A **163** (2013) 51-59.
[2] J. H. Starcke, M. Wormit, J. Schirmer, A. Dreuw: How much double excitation character do the lowest excited states of linear polyenes have, Chem. Phys. **329** (2006) 39-49.
[3] D. G. Leopold, R. D. Pendley, J. L. Roebber, R. J. Hemley, V. Vaida: Direct absorption spectroscopy of jetcooled polyenes. II. The $1B_u$ – $1A_g$ transition of butadienes and hexatrienes, J. Chem. Phys. **81** (1984) 4218-4229.
[4] R. P. Krawczyk, K. Malsch, G. Hohlneicher, R. C. Gillen, W. Domcke: $1B_u$ – $2A_g$ conical intersection in *trans*-butadiene: ultrafast dynamics and optical spectra, Chem. Phys. Lett. **320** (2000) 535-541.

Vibronic coupling and quenching of the excitonic splitting in the *ortho*-cyanophenol dimer

Sabine KOPEC[1], Philipp OTTIGER[2], Samuel LEUTWYLER[2],
and Horst KÖPPEL[1]
[1]Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229,
D-69120 Heidelberg, Germany
[2]Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3,
CH-3012 Bern, Switzerland

In a joint experimental-theoretical investigation, we study the interplay between excitonic splitting and vibronic coupling in hydrogen-bonded molecular dimers. The experimental analysis is based on high-resolution resonant two-photon ionization spectroscopy. The underlying data for the theoretical investigation are potential energy surfaces obtained at the RI-CC2/aug-cc-pVTZ level; they are used for the dynamical analysis in the framework of a multi-mode vibronic coupling approach [1].

The vertical electronic Davydov splitting exceeds the observed excitonic splitting by a factor of 10-40. We recently explained this discrepancy by considering the quenching of the excitonic splitting through the excitation of vibrational modes in the electronic transition. Two different approaches based on the Fulton-Gouterman model have been employed and found to reconcile theory and experiment [2,3].

The analysis of the vibronic structure of the excitation spectrum requires improved vibronic coupling models beyond the Fulton-Gouterman model [1]. For the *ortho*-cyanophenol dimer as a representative example, we display the vibronic spectrum obtained from a multi-mode vibronic coupling analysis, and discuss the assignment of vibrational modes to gain insight into the vibronic coupling mechanism.

[1] W. Domcke, D. R. Yarkony, H. Köppel, editors: Conical Intersections: Electronic Structure, Dynamics and Spectroscopy, (World Scientific, Singapore, 2004).
[2] P. Ottiger, S. Leutwyler, H. Köppel: Vibrational quenching of excitonic splittings in H-bonded molecular dimers: The electronic Davydov splittings cannot match experiment, J. Chem. Phys. **136** (2012) 174308-13.
[3] S. Kopec, P. Ottiger, S. Leutwyler, H. Köppel: Vibrational quenching of excitonic splittings in H-bonded molecular dimers: Adiabatic description and effective mode approximation, J. Chem. Phys. **137** (2012) 184312.

Tunneling splittings in vibronic energy levels of CH_3F^+ (X^2E) studied by ZEKE and *ab initio* calculation

Shuming GAO, Zuyang DAI, Wei SUN, Hua LI, Jia WANG,
and Yuxiang MO
Department of Physics and State Key Laboratory of Low-Dimensional Quantum Physics,
Tsinghua University, Beijing 100084, China

The energy levels of CH_3F^+ (X^2E), which show strong vibronic coupling effect (Jahn-Teller effect), have been measured up to 3500 cm^{-1} above the ground vibrational state using one-photon zero-kinetic energy photoelectron spectroscopic method [1]. Theoretical calculations have also been performed to calculate the spin-vibronic energy levels using a diabatic model and *ab initio* adiabatic potential energy surfaces including the energy gradients and derivative couplings between the adiabatic surfaces [2]. The calculations showed that the tunneling splittings of the vibrational energy levels occur due to the deep potential energy wells formed by the Jahn-Teller deformation. The calculated spin-vibronic energy levels are in good agreement with the experimental data. For example, the energy splitting for the first excited vibrational energy level is calculated as 111 cm^{-1} that is confirmed by the experimental value. The experimental spectrum was assigned based on the fundamental vibrational modes calculated at the energy minimum. The fundamental vibrational modes related to the H-C-F bending, H-C-H bending, C-F stretching and C-H stretching vibrations have been observed.

[1] S. Gao, Z. Dai, W. Sun, H. Li, J. Wang, Y. Mo: Tunneling splittings in vibronic energy levels of CH_3F^+ (X^2E) studies by high resolution photoelectron spectroscopy and *ab initio* calculation, J. Chem. Phys. **139** (2013) 064302.

[2] J. Dillon, D.R. Yarkony, M.S. Schuurman: On the construction of quasidiabatic state representations of bound adiabatic state potential energy surfaces coupled by accidental conical intersections: Incorporation of higher order terms, J. Chem. Phys. **134** (2011) 044101.

Diabatic Hamiltonian matrix for the three lowest singlet states of H_3^+

Saikat MUKHERJEE and Satrajit ADHIKARI
Indian Association for the Cultivation of Science, Kolkata - 700032, INDIA
Email: pcsm2@iacs.res.in

We present [1] the adiabatic Potential Energy Surfaces (PESs) and Non - Adiabatic Coupling terms (NACTs) for the three lowest singlet states ($1^1A'$, $2^1A'$ and $3^1A'$) of H_3^+ [2] in the hyperspherical coordinate system for a fixed hyperradius, ρ = 5, 10 and 15 Bohr as functions of the hyperangles, θ and φ using the MRCI level of methodology by *ab initio* quantum chemistry package (MOLPRO). It is interesting to observe the semi-circular seam of Conical Intersections (CIs) between the two lowest states. We employ our beyond Born - Oppenheimer theory [3,4] for the three state sub-Hilbert space and perform Adiabatic to Diabatic Transformation (ADT) to obtain ADT angles by plugging the NACTs in the ADT equation for constructing single-valued, continuous, smooth and symmetric 3x3 Diabatic PESs.

[1] S. Mukherjee and S. Adhikari, J. Chem. Phys. (submitted, 2014).
[2] L. P. Viegas, A. Alijah and A. J. C. Varandas, J. Chem. Phys. **126** (2007) 074309.
[3] S. Mukherjee, S. Bandyopadhyay, A. K. Paul and S. Adhikari, J. Phys. Chem. A **117** (2013) 3475.
[4] A. K. Paul, S. Ray, D. Mukhopadhyay and S. Adhikari, J. Chem. Phys. **135** (2011) 034107.

P27

Sodium trimers: What high resolution spectroscopy can teach us about Jahn-Teller and pseudo Jahn-Teller states

Wolfgang E. ERNST
Institute of Experimental Physics, Graz University of Technology, Graz, Austria

Probably the most detailed experimental data on any metal trimer are available for the Na_3 molecule. High resolution laser spectroscopy involving multiple resonance excitation and ionization schemes [1] allowed the assignment of rotational states in many vibronic levels of electronically excited Jahn-Teller (JT) and pseudo Jahn-Teller (PJT) states [2,3]. By evaluating the Coriolis splitting of individual rotational levels in a series of pseudorotational bands, the pseudorotational quantum numbers could be identified that provide insight into the vibronic coupling phenomena that are either of JT or PJT character [4]. Details of the shape of potential surfaces below and above the potential crossings can be extracted [5] via a fit of the precise level energies to either a model Hamiltonian [6] or the classical JT and PJT formalism [7].

The electronic $X\ ^2E'$ ground state of Na_3 is a case of linear and quadratic JT coupling with a barrier too low for resolving the tunneling splitting via laser measurements. Microwave absorption detected via resonant two-photon ionization provided a new way to explore the rotational, fine, and hyperfine structures in the ground state [8]. Together with a theoretical approach based on a Hamiltonian including tunneling, fine structure, and hyperfine interaction from the three coupling nuclei, the well resolved microwave spectra could be interpreted in terms of upper and lower limits for the Fermi contact interaction of the unpaired electron with the three Na nuclei, the barrier height to free pseudorotation, and an upper limit for the permanent electric dipole moment [8].

A summary of the experimental results will be shown at the poster, many of which have not been fully exploited for a full picture of this model trimer. New ab initio calculations should be able to provide electron spin densities at the coupling nuclei, barrier heights for pseudorotation, and details of excited state potentials near degeneracies.

[1] W. E. Ernst and S. Rakowsky: Rotational Structure of the B-X Systems of Na_3 from High Resolution Resonant Two Photon Ionization Spectroscopy, Can. J. Phys. **72** (1994), 1307-1314, special issue in honor of G. Herzberg's 90th birthday.
[2] W. E. Ernst and S. Rakowsky: Rotational Analysis of Pseudorotational Bands of Na_3, Ber. Bunsenges. Phys. Chem. **99** (1995), 441-446, special issue on Molecular Spectroscopy and Molecular Dynamics.
[3] D. T. Vituccio, O. Golonzka and W. E. Ernst: Optical-Optical Double Resonance Spectroscopy of the A-X and B-X Systems of Na_3, J. Mol. Spectrosc. **184** (1997), 237-249.
[4] W. E. Ernst and S. Rakowsky: Integer Quantization of the Pseudorotational Motion in Na_3 B, Phys. Rev. Lett. **74** (1995), 58-61.
[5] W. E. Ernst and O. Golonzka: Vibronic Interactions in Sodium Trimers, Physica Scripta **T112** (2004), 27-32.
[6] N. Ohashi, M. Tsuura, J. T. Hougen, W. E. Ernst, and S. Rakowsky: Effective Rotation-Pseudorotation Hamiltonian for X_3-Type Molecules: Application to the B-X Transition of Na_3, J. Mol. Spectrosc. **184** (1997), 22-34.
[7] I. B. Bersuker, The Jahn-Teller Effect, Cambridge University Press, Cambridge (UK), 2006.
[8] L. H. Coudert, W. E. Ernst, and O. Golonzka: Hyperfine Coupling and Pseudorotational Motion Interaction in Na_3, J. Chem. Phys. **117** (2002), 7102-7116.

Vibronic interactions in quartet state alkali trimers: Low resolution spectroscopy accompanied by quantum chemistry calculations

Wolfgang E. ERNST[1] and Andreas W. HAUSER[2]
[1]Institute of Experimental Physics, Graz University of Technology, Graz, Austria
[2]Dep. of Chemical & Biomolecular Engineering, University of California, Berkeley, USA

The formation of alkali trimer molecules in high-spin (quartet) states was observed for the first time in an experiment with alkali-doped superfluid helium droplets. Atoms and molecules deposited on nanometer size helium droplets of 0.4 K temperature form aggregates that may be bound by very low energy and would not survive at room temperature. Laser excitation spectra of the $2^4E'$- $1^4A_2'$ transition of Na_3 on helium droplets could be analyzed and linear and quadratic Jahn-Teller interaction parameters were determined for the $2^4E'$ state [1].

Excitation spectra of the same transition in K_3 and Rb_3 revealed the increasing influence of relativistic effects when heavy atoms are involved [2]. Since the formation of alkali trimers in high-spin states has not been achieved in the gas phase, the spectroscopic resolution is limited due to the interaction of the molecules with the helium host. Therefore, the analysis of experimental spectra needs to be accompanied by good *ab initio* calculations. Adiabatic potential energy surfaces of the $1^4A_2'$ lowest quartet state and the $2^4E'$ excited state of K_3 and Rb_3 were obtained by applying second-order multireference Rayleigh-Schrödinger perturbation theory. Both trimers show a typical $E\otimes e$ Jahn-Teller distortion in their $2^4E'$ state, which was analyzed in terms of relativistic Jahn–Teller effect theory. Linear, quadratic, and spin-orbit coupling terms were extracted from the *ab initio* results and used to generate simulated spectra for a direct comparison with experimental results [3]. A summary of these studies including new calculations for Cs_3 is given in ref. [4] showing the increasing dominance of spin-orbit coupling over the Jahn-Teller effect.

Adiabatic potential energy surfaces of the heteronuclear trimer molecules K_2Rb and KRb_2 in their 3^4A_1 and 4^4B_2 states were calculated that correspond to the two branches of the $E\otimes e$ Jahn-Teller distorted $2^4E'$ state of homonuclear trimers and show conical intersections at obtuse (KRb_2) or acute (K_2Rb) isosceles geometries. Vibronic spectra are predicted and compared to laser-induced fluorescence spectra obtained in helium droplet isolation spectroscopy [5]. Calculated vibronic energy levels could also be compared with an analysis of femtosecond photoionization experiments on homo- and heteronuclear alkali trimers [6].

[1] J. Higgins, W. E. Ernst, C. Callegari, J. Reho, K. K. Lehmann, G. Scoles and M. Gutowski, Spin Polarized Alkali Clusters: Observation of Quartet States of the Sodium Trimer, Phys. Rev. Lett. **77** (1996), 4532-4535.

[2] G. Auböck, J. Nagl, C. Callegari, and W. E. Ernst, Observation of Relativistic $E\otimes e$ Vibronic Coupling in Rb_3 and K_3 Quartet States on Helium Droplets, J. Chem. Phys. **129** (2008), 114501.

[3] A. W. Hauser, G. Auböck, C. Callegari, and W. E. Ernst, Relativistic Jahn-Teller effects in the quartet states of K_3 and Rb_3: A vibronic analysis of the $2^4E' \leftarrow 1^4A_2'$ electronic transitions based on ab initio calculations, J. Chem. Phys. **132** (2010), 164310.

[4] A. W. Hauser, G. Auböck and W. E. Ernst, "Jahn-Teller Effect and Spin-Orbit Coupling in Heavy Alkali Trimers", in: *Vibronic Interactions and the Jahn-Teller Effect : Theory and Applications*, (eds. Mihail Atanasov, Claude Daul, Philip Tregenna-Piggott), Springer Series: *Progress in Theoretical Chemistry and Physics Vol. 23, Chapter 16,* Springer 2012, p. 301-316.

[5] A. W. Hauser and W. E. Ernst, Homo- and heteronuclear alkali metal trimers formed on helium nanodroplets: I. Vibronic spectra simulations based on ab initio calculations, PCCP **13** (2011), 18762-18768.

[6] C. Giese, F. Stienkemeier, M. Mudrich, A. W. Hauser and W. E. Ernst, Homo- and heteronuclear alkali metal trimers formed on helium nanodroplets: II. Femtosecond spectroscopy and spectra assignments, PCCP **13** (2011), 18769-18780.

Phonon-assisted electron-hole relaxations on Sb(111) and Bi(111) in iHAS measurements

P. KRAUS[1], F. APOLLONER[1], Ch. GÖSWEINER[1], G. BENEDEK[2]
and W. E. ERNST[1]
[1]Institute of Experimental Physics, Graz University of Technology, Graz, Austria
[2]Donostia International Physics Centre (DIPC), San Sebastián/Donostia, Spain

Recently, a strong Kohn-like anomaly was found in the phononic dispersion relation of Bi_2Se_3 [1]. The supposed nesting vectors connect spin-opposing states on both of the sides of the Dirac cone which are non-equivalent. Thus the electron needs to undergo a non-adiabatic transition to make the softening of the phononic mode possible. This is even more problematic, since transitions that break the adiabatic approximation are not accessible by standard DFPT methods. Recent studies on the (111) surfaces of the semimetals antimony and bismuth revealed deep and narrow strongly pronounced features [2]. The positions of those apparent sudden phonon softenings correspond to an electronic relaxation between the opposite sides of the inner Rashba-split cone [3].

The necessary helicity of 1 which the electron needs to complete this transition can be supplied by a phonon. The helicity exchange between a phonon and an electron is only possible in materials with a strong spin-orbit interaction. The extremely high spin-orbit interaction on the Bi(111) surface has recently been demonstrated by the peculiar ability of inelastic helium atom scattering (iHAS) to measure sub-surface phonon modes. Since HAS is completely surface sensitive and only able to detect changes in the electronic charge density above the surface, the phononic movements of the sub-surface nuclear layers must communicate to the electron density at the surface. The high electron-phonon interaction constant of Bi(111) has been estimated to a value of 1.3 [2], which renders this deep phonon radar possible.

Complete measurements of the anomalies found in Sb(111) and Bi(111) will be presented and compared with the relevant electronic data.

[1] X. Zhu, L. Santos, R. Sankar, S. Chikara, C. Howard, F. C. Chou, C. Chamon, and M. El-Batanouny: Electron-phonon coupling on the surface of the topological insulator Bi_2Se_3 determined from surface-phonon dispersion measurements, Phys. Rev. Lett. **107** (2011), 186102.
[2] Tamtögl, P. Kraus, M. Mayrhofer-Reinhartshuber, D. Campi, M. Bernasconi, G. Benedek, and W. E. Ernst: Surface and subsurface phonons of Bi(111) measured with helium atom scattering, Phys. Rev. B **87** (2013),035410 and Phys.Rev. B **87** (2013) 159906(E).
[3] J.H. Dil: Spin and angle resolved photoemission on non-magnetic low-dimensional systems, J. Phys.: Condensed Matter **21** (2009), 403001.

Geometric phase effects in multidimensional quantum dynamics near conical intersections

Loïc JOUBERT-DORIOL[1,2], Ilya G. RYABINKIN[1,2],
and Artur F. IZMAYLOV[1,2]
[1]Department of Physical and Environmental Sciences, University of Toronto at Scarborough, Toronto, ON, M1C 1A4, Canada.
[2]Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto, ON, M5S3H6, Canada

The adiabatic representation provides a natural framework for fully quantum simulations of non-adiabatic processes with on-the-fly evaluation of electronic surfaces and non-adiabatic couplings. However, in the presence of conical intersections (CIs) between electronic surfaces adiabatic wave-functions acquire the geometric phase (GP) that gives rise to additional interference in the nuclear wave-function. The purpose of this work is to understand when and how the GP affects the non-adiabatic dynamics in multidimensional systems. Our analysis relies on a transformation of the N-dimensional linear vibronic coupling Hamiltonian model to a subsystem-bath representation, where all non-adiabatic effects are confined in a two-dimensional subspace (the branching space), and the remaining (N-2) modes constitute a bath that does not couple electronic states. We identify and quantify GP effects by comparing dynamics with and without GP.

1) In low energy dynamics, two parts of a wave-function tunneling through different paths (red and blue arrows on Fig. 1) acquire opposite phases and resulting in destructive interference that can completely freeze the population transfer. This effect can survive even in the presence of bath modes.

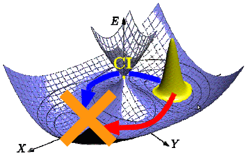


Figure 1

2) In interstate conversion processes (red arrow on Fig. 2), the GP compensates for the repulsion potential at the CI due to the diagonal Born-Oppenheimer correction and enhances the transition probability for parts of a wave-function experiencing central collision with the CI.

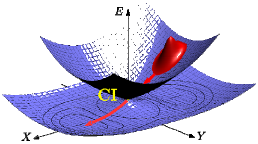


Figure 2

AUTHOR INDEX

Jt2014 Sponsors

Springer Spektrum

COHERENT.

Radiant Dyes Laser

Newport.
Experience | Solutions

PFEIFFER VACUUM

TOPTICA
PHOTONICS

TDK

Das Land
Steiermark
→ Wissenschaft und Forschung

WKO
Wirtschafts- und Standortentwicklung
STEIERMARK

STADT
GRAZ
BÜRGERMEISTERAMT

XXIInd International Symposium on the Jahn-Teller Effect, Graz 2014

	Sunday 17.08	Monday 18.08	Tuesday 19.08	Wednesday 20.08	Thursday 21.08	Friday 22.08
08:30						
09:00		9:00 - 9:45 Bersuker (**Rev1**) 9:45 - 10:30 Hizhnyakov (**Rev2**)	9:00 - 9:45 Wrachtrup (**Rev4**) 9:45 - 10:35 Bin Zhang, Clougherty 25 min each	9:00 - 9:45 Miller (**Rev6**) 9:45 - 10:30 Yuxiang Mo (**Rev7**)	9:00 - 9:45 Bridges (**Rev8**) 9:45 - 10:30 Garcia-Fernandez(**Rev9**)	9:00 - 9:45 Warner (**Rev11**) 9:45 - 10:15 Datta
10:00		**Coffee Break**	**Coffee Break**	**Coffee Break**	**Coffee Break**	10:15 - 10:40 Polinger **Coffee Break**
11:00		11:00 - 11:25 Aichhorn 11:25 - 11:55 Atanasov 11:55 - 12:20 Sorantin	11:15 - 12:30 Gudkov, Kugel, Neville 25 min each	11:00 - 11:30 Wilkinson 11:30 - 12:20 Leveque, Mai 25 min each	11:15 - 12:30 Moreno, Bussmann-Holder, Morgan, 25 min each	11:15 - 11:45 Koizumi 11:45 - 12:35 Boeri, Kato 25 min each
12:00		12:30 - 14:00 **Lunch**	12:30 - 14:00 **Lunch**		12:30 - 14:00 **Lunch**	
13:00				**13:00** **Departure for Conference Excursion:** **Stift Vorau, Science Museum Pöllau**		
14:00		14:00 - 14:45(**Rev3**) Nimrod Moiseyev 14:45 - 15:15 Auböck	14:00 - 14:45 Stanton (**Rev5**) 14:45 - 15:15 Okumura		14:00 - 14:45 Jansen (**Rev10**) 14:45 - 15:10 Tosatti	
15:00		15:15 - 16:05 de Vivie, Matsika 25 min each	15:15 - 16:05 Zlatar, Daul 25 min each		15:10 - 15:40 Dunn 15:40 - 16:05 Sato	
16:00	16:00 **Registration Desk opens**	**Coffee Break**	**Coffee Break** 16:30 - 17:45 Opalka, Perry, Adhikari 25 min each		**Coffee Break** 16:30 - 17:00 Chibotaru	
17:00		**Public Lecture** **Prof. K. A. Müller**			17:00 - 17:50 Arcon, Kamaras 25 min each	
18:00	18:00 **Welcome Reception**		18:00 **Posters**		18:00 **Posters**	
19:00		19:00 **Reception at City Hall**		19:00 **Conference Dinner**		