SB01 9:00 – 9:17

Ab initio CALCULATIONS FOR THE GROUP 2 M_2O HYPERMETALLIC OXIDES

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This paper reports the results of our ab initio study of Group 2 M_2O hypermetallic oxides Be_2O, Mg_2O, Ca_2O, Sr_2O, Ba_2O and Ra_2O. They are examples of molecules having metal stoichiometries that exceed normal valence. We find that all molecules have a linear symmetric M-O-M $X^1\Sigma_g^+$ ground electronic state and a low-lying $a^3\Sigma_u^+$ first excited electronic state. We calculate the three dimensional potential energy and dipole moment surfaces so that we can simulate infrared spectra for comparison with experimental spectra. We also calculate the energies of higher excited electronic states and transition moments so that comparisons with observed electronic spectra can be made.

For the heavier members, the extent of the spin-orbit coupling between vibronic levels of the ground singlet state and the first excited triplet state is examined to see if they would make good candidates for looking for a time dependence of the electron to proton mass ratio and of the fine structure constant.

SB02 9:17 – 9:32

APPLICATION OF GENERALIZED EULER SERIES TRANSFORMATION (GET) TO CALCULATIONS OF ROTATION ENERGY LEVELS OF H_2 MOLECULE

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Within semiempirical Effective Hamiltonian (EH) approach parameters of the EH – rotational, centrifugal distortion and resonance coupling constants are declared as free parameter, which have to be determined from measured transition frequencies. The other frequencies, which cannot be measured, can be calculated using these parameters. In the case of low lying states of "heavy" ridged molecules (such as SO2, CO2), semiempirical EH's work satisfactorily providing energy levels close to experimental transition frequencies. But in the case of high vibrational and rotational states that are often strongly perturbed by vibration anharmonicity, centrifugal distortion or Coriolis coupling, applicability of calculation methods, developed for low lying states of "heavy" molecules are under question.

It has long been recognized that the standard power series expansion of the EH in terms of rotational angular momentum operators, which is based on perturbation theory (PT), does show poor convergence in the case of highly excited states (for instance, [13] and references therein). To improve convergence we apply the Generalized Euler Transformation (GET) [4] to the series summation in the calculation of the H2 molecule rotational energy levels. The GET method utilizes an approximation functions to construct the sum and transformed series can be represented as a combination of the approximant, its derivatives with respect of perturbation parameter, and coefficients of initial series. The use of approximants allows to build in additional information into PT series. If approximant reflect the main features of vibration and rotation motion, then the transformed series should have more correct behavior at high degree of excitation.

The GET method combined with different simple approximation functions was used to calculate ground vibrational state energy levels of the H2 molecule. The H2 molecule was chosen because of this molecule exhaustive set of high quality ab initio levels is known [5]. Present calculations allow to make two conclusions. Firstly, the GET gives a possibility to use simple approximation functions in the calculations of rotational energy levels of molecules. This approach doesn't require high orders of PT computations. Secondly, the application of this method (if an approximant was correctly chosen) enable to reach satisfactory prediction for higher energy levels which were not used to fit the parameters of transformed series.

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Results were supported by the funds of Strategic Programme on National Research Tomsk Polytechnic University Competitiveness Enhancement in the Group of Top Level World Research and Academic Institutions
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SB03 9:32 – 9:49

TOWARDS A COMPREHENSIVE LINE LIST FOR HOT CHROMIUM HYDRIDE

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Chromium Hydride (CrH) is a molecule of astrophysical importance as well as of theoretical and experimental interest. Under the widely accepted classification of Kirkpatrick et al [1], CrH abundance is a key parameter in the identification and characterisation of L-type brown dwarfs and could also be used to help distinguish brown dwarfs, planets and stars having similar masses and luminosity profiles. Given the astrophysical importance of CrH and that at present there is no accurate or complete line list for this molecule, as part of the ExoMol project we aim to bridge this gap [2]. From a theoretical perspective CrH is a challenging system because, in common with other transition metal hydrides, its spectra is determined by many, heavily interacting electronic states dissociating to various dissociation limits. Relativistic effects such as spin-orbit are also very important. In this work we present potential energy curves, dipole moment curves and various coupling curves between low lying states (up to approximately 20,000 cm^{-1}) produced using the Multi Reference Configuration Interaction (MRCI) method as implemented in the *ab initio* quantum chemistry package MOLPRO. For the ground state of $^6X\,S^+$ we compare and contrast the use of different Gaussian basis functions and the knock-on effects on the spectroscopic constants obtained from potential energy curves. Energy, dipole moment and coupling curves are then used to produce rovibronic spectra employing the in-house program Duo. *Ab initio* results obtained using MOLPRO for the A-X $^6S^+$ electronic transition are presented and refined by fitting the corresponding potential energy curves to the available experimental data.

This work was supported by the ERC under Advanced Investigator Project 267219.

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SB04 9:49 – 10:01

THEORETICAL INVESTIGATION OF THE LOW-LYING ELECTRONIC STURCTURE OF LACL MOLECULE BY AB-INITIO METHODS

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Monohalides lanthanum LaX (X=F,Cl,Br,I) have received considerable attention in the experimental field [1,2] as theoretical [3] primarily upon detection in astrophysics environment as lanthanum chloride LaCl molecule, which occurs in gas phase at high temperature [4,5]. By using the ab-initio quantum methods as the CASSCF/MRCI methods, the theoretical electronic structure of the LaCl molecule has been investigated. These methods have been performed for 26 singlet and triplet electronic states in the representation $^{2s+1}\Lambda^{(\pm)}$. All calculations have been performed via the quantum software MOLPRO [6]. Calculated potential energy curves (PECs) are also ploted. Spectroscopic constants including the harmonic vibrational wavenumber $\omega_e(cm^{-1})$, the relative electronic energy $T_e(cm^{-1})$ referred to the ground state, and the equilibrium internuclear distance $R_e(Å)$ have been predicted for all of the singlet and triplet electronic states situated below 24 000 cm^{-1}. Spin−orbit effects have also been taken into consideration and calculated for the 47 components in the representation $\Omega^{(\pm)}$.

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SB05 10:01 – 10:18

DETECTABLE ORGANOSULFUR COMPOUNDS

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Highly correlated ab initio methods are used for the spectroscopic characterization of ethyl mercaptan ($CH_3CH_2{}^{32}SH$, ETSH) and dimethyl sulfide ($CH_3{}^{32}SCH_3$, DMS) and various isotopologues considering them on the vibrational ground and excited torsional states. Since both molecules show non-rigid properties, torsional energy barriers and splittings are provided.

Equilibrium geometries and equilibrium rotational constants are calculated by means of a composite scheme based on CCSD(T) calculations that accounts for the extrapolation to the complete basis set (CBS) limit and core-correlation effects. The ground and excited states rotational constants are then determined using vibrational corrections obtained from CCSD/cc-pVTZ force-field calculations, which are also employed to determine anharmonic frequencies for all vibrational modes. CCSD(T) and CCSD force fields are employed to predict quartic and sextic centrifugal-distortion constants, respectively. Equilibrium rotational constants are also calculated using CCSD(T)-F12.

The full-dimensional anharmonic analysis does not predict displacements of the lowest torsional excited states due to Fermi resonances with the remaining vibrational modes. Thus, very accurate torsional transitions are calculated by solving variationally two-dimensional Hamiltonians depending on the CH_3 and SH torsional coordinates of ethyl mercaptan or on the two methyl torsions of dimethyl-sulfide. For this purpose, vibrationally corrected potential energy surfaces are computed at the CCSD(T)/aug-cc-pVTZ level of theory.

For ethyl mercaptan, calculations show large differences between the gauche (g) and trans (t) conformer spectral features. Interactions between rotating groups are responsible for the displacements of the g-bands with respect to the t-bands that cannot therefore be described with one-dimensional models. Our accurate spectroscopic data should be useful for the analysis of the MW and FIR spectra of ETSH and DMS recorded, at low temperatures, either in laboratory or in the interstellar medium.

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SB06 10:18 – 10:35

AN UPDATE OF THE CO_2 LINE-MIXING DATABASE AND SOFTWARE AND ITS TESTS IN THE 2.1 AND 4.3 μm REGIONS

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An update of the former version of the database and software for the calculation of CO_2-air absorption coefficients taking line-mixing into account [1] is described. In this new edition, the data sets were constructed using parameters from the 2012 edition of the HITRAN database and recent measurements of line-shape parameters. Among other improvements, speed-dependent profiles can now be used if line-mixing is treated within the first order approximation. This new package is tested at various pressure, temperatures and CO_2 concentration conditions, using laboratory spectra measured in the 2.1 and 4.3 μm spectral regions. Further tests using laboratory and atmospheric spectra are thus required to further evaluate the performances of this updated package.

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SB07 10:35 – 10:52

HOW TO FILL SPECTROSCOPIC DATABASES WITH ACCURATE LINE SHAPE PARAMETERS ? THE EXAMPLES OF H_2O AND CO_2

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The algorithms that add H_2O and CO_2 line shape information to spectroscopic databases are discussed. The selection of data uses a rather sophisticated scheme that determines and eliminates outliers in the measurement database. Once filtered, the algorithm follows a structure that adds the best available data to each transition. The current algorithm for water vapor considers the air- broadened half-width, γ, and line shift, δ, the temperature dependence of the air-broadened half- width, and the self-broadened half-width, and the associated errors. Currently there are data for $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, $HD^{18}O$, $HD^{17}O$, $D_2{}^{16}O$, $D_2{}^{18}O$, and $D_2{}^{17}O$. The carbon dioxide algorithm follows a similar procedure which adds the half-width and its temperature dependence for both air- and self-broadening and the air-induced line shift with the corresponding errors. Data are available for $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{17}O$, $^{16}O13C^{18}O$, $^{16}O13C^{17}O$, $^{12}C^{18}O_2$, $^{17}O^{12}C^{18}O$, $^{12}C^{17}O_2$, $^{13}C^{18}O_2$, $^{17}O^{13}C^{18}O$, $^{13}C^{17}O_2$, and $^{14}C^{16}O_2$. The current algorithm can generate data for the half-width and the line shift for any vibrational transition for J"$\leq$200 for temperatures in the range 150-2000 K for CO_2-air and CO_2-CO_2 collisions.

SB08 11:22 – 11:39

AB INITIO/FCF SIMULATIONS OF VIBRATIONALLY RESOLVED PHOTODETACHMENT AND POTOELECTRON SPECTRA OF REACTIVE SPECIES INCLUDING SOME CRIEGEE INTERMEDIATES

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Abstract: Employing state-of-the-art *ab initio* and Franck-Condon factor calculations, vibrationally resolved photodetachment and/or photoelectron spectra of a number of reactive species have been simulated. The simulated spectra obtained have been used to assist assignments of available experimental spectra. In some cases, comparisons between simulated and observed spectra confirm the assignments of the molecular carriers, the electronic states and vibrational structures involved. However, in other cases, such comparisons revise and/or cast doubt on the original assignments. The photodetachment spectra of CCl_2^- [1,2] and AlH_2^- [3], and the photoelectron spectra of some Creigee intermediates, CH_3CHOO [4] and $(CH_3)_2COO$, which are of importance in atmospheric chemistry, are selected to demonstrate the reliability and predictive power of this spectrum simulation technique.

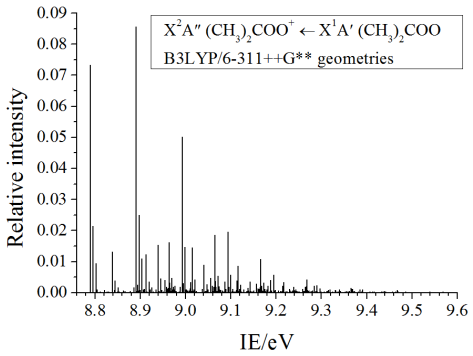

Figure: Computed Franck-Condon factors (FCFs) of the $\tilde{X}^2A''$ $(CH_3)_2COO^+$ + e ← $\tilde{X}^1A'$ $(CH_3)_2COO$ ionization, obtained using the UCCSD(T)-F12/CBS//B3LYP/6-311++G** computed AIE_0 value of 8.79 eV and the B3LYP/6-311++G** geometries and harmonic vibrational frequencies. The major vibrational progression is the 14a′ mode, which is essentially symmetric $(C)_2COO$ skeletal stretching (unpublished work).

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SB09 11:39 – 11:51

COMPUTATION OF VIBRATIONAL ENERGY LEVELS OF TRIATOMIC MOLECULES BY SUMMING DIVERGENT SERIES OF THE RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY

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The perturbation theory is widely used to calculate the energy levels and the wave functions of molecules. The condition for the applicability of the quantum mechanical theory is the convergence of the corresponding series. Practical calculations show, however, that, in many cases, the series diverge and it is necessary to apply special summation methods. A number of authors (see, for example, [1–3]) proposed earlier to use different methods for summing divergent series in order to determine the vibrational and vibrational–rotational energy levels of molecules, and it was shown that their application significantly improved the calculated results.

The results of testing the known methods of Padé, Padé–Borel, Padé–Hermite and the moments method by the example of calculations of vibrational energy levels of the water molecule are presented in [4]. It was shown that these methods are well suited for calculating the energy levels in spite of the divergence of the series caused by the Fermi and Darling–Dennison anharmonic resonances. Currently the calculations for HDO molecule and other triatomic molecules of the C_{2v} and C_S symmetries (SO_2, H_2S, F_2O, HOF, HOCl and DOCl), analysis of the corresponding perturbation theory series and structure of the energy function in the complex plane were made in [5]. Also the computation of energy levels of CO_2 (linear molecule) and O_3 (C_{2v} and D_{3h} symmetries are possible) were carried out.

Results obtained by the summation of divergent series within the framework of Rayleigh–Schrödinger perturbation theory for wide range are quite satisfactory. So, if the potential function parameters are selected correctly, this method allows describing numerically the spectra even in the cases of extremely rapid divergence of series.

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SB10 11:51 – 12:03

AB INITIO CALCULATIONS OF H_2F^+.

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A*b initio* calculations were performed using a multi-reference configuration interaction (MRCI) method with aug-cc-pCVnZ (n=5 and 6) basis sets and basis set extrapolation to CBS limit. We construct a potential energy surface (PES) by fitting 1370 points lying at energies less than 16 000 cm^{-1} above the minimum. The fit reproduces the *ab initio* points with a standard deviation less than 1 cm^{-1}. This Born-Oppenheimer (BO) surface was augmented with a full relativistic correction, a quantum electrodynamic (QED) correction, and an adiabatic correction(BODC). Each of these corrections was found to contribute significantly to the improved accuracy.

The vibrational J=0 energy levels and rovibrational levels up to J=4 have been calculated using DVR3D program suite [1]. Levels belonging to the ground vibrational state and all three fundamental bands are known experimentally and have been compared to our calculated ones. The accuracy of ab initio calculations of about 0.1cm^{-1} was achieved. It corresponds to the accuracy achieved earlier for water molecule [2], which is isoelectronic to H_2F^+. The accuracy of our calculations is almost 2 orders of magnitude higher, than that of the recent ab initio calculations of [3].

We conjecture that the energy levels of closed-shell molecules with roughly the same number of electrons as H_2F+ and water, such as NH_3, CH_4 and H_3O^+, could be calculated to this accuracy using an analogous procedure. This means that ab initio calculations are capable of predicting transition frequencies with an accuray only about a factor of five worse than high resolution experiments.

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SB11 12:03 – 12:20

THE STATIONARY POINTS ON THE POTENTIAL ENERGY SURFACES OF $(SO_2)_2$ AND $(CH_2F)_2$ DIMERS STUDIED BY COUPLING DISPERSION-CORRECTED DFT-D3 THEORY AND COLLISION-INDUCED BROADENING OF RO-VIBRATIONAL LINES

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Thermodynamic and spectroscopic properties of molecular complexes are of fundamental interest in physics, chemistry and biology. For many reasons, measuring these properties is an expensive and time-consuming task. On the other hand, thanks to the huge progresses made in computer hardware resources and the development of efficient algorithms, quantum chemistry has become a powerful tool to access thermodynamic and spectroscopic information. Nowadays Kohn-Sham Density Functional Theory (DFT) is the working option for systems composed of hundreds to thousands of atoms. Nevertheless, standard DFT in general fails to correctly describe the long range London dispersion interactions, in particular the correct $-C_6/R^{-6}$ dependence of the interaction energy on the intermolecular separation R. One method of low numerical complexity, to include dispersion correlation effects into DFT is the DFT-D3 scheme [1].

In this contribution, the dimers of difluoromethane (CH_2F_2, HFC-32) and sulfur dioxide (SO_2) are investigated by coupling tunable diode laser (TDL) infrared spectroscopy and quantum chemical calculations adopting the DFT-D3 approach. Specifically, the dissociation energies of $(CH_2F_2)_2$ and $(SO_2)_2$ dimers are determined experimentally from the broadening of the ro-vibrational lines of the corresponding monomers perturbed by He, Ne, Ar, N_2 and O_2 collision partners. The interaction energies and structures of the stationary points on the potential energy surfaces of the two dimers is investigated theoretically DFT-D3. The computations, performed by using the Turbomole quantum chemistry package, are carried out employing various D3-corrected density functionals (BLYP, TPSS, B3LYP, PBE0, TPSSh and PW6B95) in conjunction with Becke's and Johnson's damping function [2]. The obtained results show that (i) collisional broadening cross sections can be profitably used for determining the dissociation energies of homo-dimers; (ii) DFT including dispersion corrections, and the DFT-D3 approach in particular, can reach the accuracy of highly correlated wavefunction methods for dissociation energies; (iii) the interplay between experimental spectroscopic techniques and state-of-the-art theoretical approaches lead to a deep insight into the characterization of the potential energy surfaces of hydrogen-bonded- and van der Waals- complexes.

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SB12 12:20 – 12:37

THEORETICAL VIBRATIONAL FINGER-PRINTS FOR MEDIUM-SIZED MOLECULES: THE ROLE OF BAND POSITION AND INTENSITIES

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The information required for predicting and/or analyzing spectra in the field of vibrational spectroscopy are vibrational frequencies and the corresponding intensities. While the former are univocally defined, the definition of the latter depends on the technique considered: infrared (IR), vibrational circular dichroism (VCD) and Raman. For an accurate comparison between simulated and experimental vibrational spectra, it is necessary to go beyond the double-harmonic approximation, by the inclusion of mechanical anharmonic effects on vibrational energies, i.e., anharmonic shifts, as well as anharmonic effects on intensities (electric or electric/magnetic), allowing to take into account overtones and combination bands, which have null intensities at the harmonic level.

We are actively developing a comprehensive and robust computational protocol, set within a perturbative vibrational framework [1,2], aimed at a quantitative reproduction of the spectra of medium-to-large molecular systems. In particular, recently introduced general formulation of a second-order perturbation theory for vibrational averages and transition properties allows fully anharmonic simulation of IR, Raman and VCD spectra. In these work advantages of the direct comparison between computed and experimental spectra, considering both band positions and their relative intensities, which define the overall spectra pattern, will be discussed for examples of medium sized, closed- and open-shell, chiral and achiral molecules.

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[2] V. Barone, M. Biczysko, J. Bloino, Phys. Chem. Chem. Phys. **16**, 1759 (2014)