

Contributed Lectures N

September 8, Saturday, 9:00 – 12:30

Millimeter-wave spectrum of the *ortho*H₂-CO Molecular Complex: New Measurements and Assignments

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The rotational motion of H₂ is only slightly hindered in the H₂-CO complex, and two nuclear spin modifications of H₂ give rise to completely distinct, though overlapping, *para*H₂- and *ortho*H₂-CO spectra. In the cold molecular environment required for efficient formation of the H₂-CO complexes, only the lowest states, i.e., $j_{H_2} = 0$ for *para*H₂ and $j_{H_2} = 1$ for *ortho*H₂ are significantly populated. The IR and MW spectra of *para*H₂-CO resembled Rg-CO (Rg = rare gas) spectra and their analysis was straightforward in the past [1-3]. Those results provided very valuable indirect information about the interaction energy surface and fairly good agreement between experiment and theory was achieved for *para*H₂-CO [4]. However, due to the character of the H₂ motion in *para*H₂-CO, only very limited information about the dependence of the potential on H₂ orientation can be gained from those experimental data. The hydrogen molecule anisotropy of the H₂-CO surface can be much more extensively probed in the *ortho*H₂-CO spectrum. Such IR and MW spectra have been recorded, but have not been assigned due to their complexity.

Very recently the assignments of the most experimental transitions became possible due to the new *ab initio* interaction energy surface for H₂-CO computed on the six-dimensional grid including the dependence on the H-H and C-O separation [5]. The *ortho*H₂-CO complex is again experimentally investigated in a molecular jet expansion using OROTRON intracavity millimeter-wave spectrometer. The vast part of the resulting spectrum has been interpreted by comparison with the theoretical and IR spectra. Altogether 30 transitions of *ortho*H₂-CO were assigned in the frequency range of 80-150 GHz. These results were used to build the empirical pattern of the rotational energy levels.

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Two- dimension study of methanol internal rotation in argon matrix.

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As demonstrated by the recent studies¹, the matrix affects to the height of the internal rotation barriers of methanol isolated in the solid matrix. That is reflected by changes in splitting of the torsional states. This splitting has been considered as one of the possible mechanisms responsible for the appearance of a multiplet structure of some absorption bands in low temperature FTIR spectra of CH₃OH. Since the FTIR spectra show no signs of overall molecule rotation and at the same time there are bands due to internal rotation, we assumed that the axis of rotation (C-O) is fixed relative to the argon atoms. For estimation of argon matrix effect on internal motion in methanol, the configuration including a molecule of methanol and eight argon atoms, initially positioned at the vertices of the cube, was optimized. Then the argon atoms were space-fixed and rotation of methyl and hydroxyl groups with respect to the argon lattice was simulated. In the case of a methyl group rotation by steps of 20° the hydroxyl group position was additionally fixed relative to the matrix, and vice versa. Besides, all other internal parameters of CH₃OH were optimized. It was computed 64 points on potential surface $U = U(\varphi_{OH}, \varphi_{CH_3}) = U(\varphi_{OH} + 2\pi k, \varphi_{CH_3} + 2\pi n / 3)$.

We were looking for potential surface in the form:

$$U(\varphi_{OH}, \varphi_{CH_3}) = \sum_{k,n} A_{k,n} e^{i(k\varphi_{OH} + 3n\varphi_{CH_3})} \quad (1)$$

where $|n, k| \leq 3$. Then we introduced the following new coordinates:

$$s = \varphi_{CH_3} - \varphi_{OH}; \quad t = \frac{I_{CH_3}}{I_{CH_3} + I_{OH}} \varphi_{CH_3} + \frac{I_{OH}}{I_{CH_3} + I_{OH}} \varphi_{OH} \quad (2)$$

where I_{CH_3}, I_{OH} - inertial parameters of CH₃ and hydroxyl groups with respect to C-O bond. Substituting (2) in (1) the potential surface in new coordinates ($U = U(s, t)$) was obtained. The Schrodinger equation for s, t takes the form:

$$C \frac{\partial^2 \Psi}{\partial s^2} + D \frac{\partial^2 \Psi}{\partial t^2} - U(s, t) \Psi + E \Psi = 0 \quad (3)$$

where $C = \frac{\hbar}{2I_{reduce}}; I_{reduce} = \frac{I_{OH} I_{CH_3}}{(I_{CH_3} + I_{OH})}; D = \frac{\hbar}{2(I_{CH_3} + I_{OH})};$ (4)

We represented potential function as: $U(s, t) = US(s) + UT(t) + UST(s, t)$, where $US(s) = U(s, 0); UT(t) = U(0, t); UST(s, t) = U(s, t) - U(s, 0) - U(0, t)$. So we solve the (3) using this representation for potential energy and perturbation theory methods. The positions of torsional energy levels, wave functions and transition probabilities were found.

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Spectroscopy of a major complex organic molecule: Mono-Deuterated Dimethyl Ether

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Dimethyl ether is one of the most abundant molecules in star-forming regions. Like other complex organic molecules, its formation process is not yet clearly established. The study of deuteration may provide crucial hints¹.

The mono-deuterated species (CH_2DOCH_3) is still a relatively light molecule; its spectrum is the most intense in the THz domain even at ISM temperatures (100/150 K). Therefore, it is necessary to measure and assign its transitions in this range in order to be able to compute accurate predictions which should allow us to detect it with ALMA, expected to be a powerful tool to observe such isotopic species. In this context, spectra between 50 and 950 GHz were recorded in Lille with a solid-state submillimeter-wave spectrometer.

The starting point of the analysis was the centimeter-wave measurements carried out in 2003 for almost all isotopic species². Results concerning the symmetric conformer of the mono-deuterated species will be presented in the paper. The fits performed with the ERHAM code³ will be discussed. Theoretical developments are in progress in order to treat the case of the asymmetric conformer.

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Spectroscopic Observation of Benzyl-type Radicals using a Technique of Corona Excited Supersonic Expansion

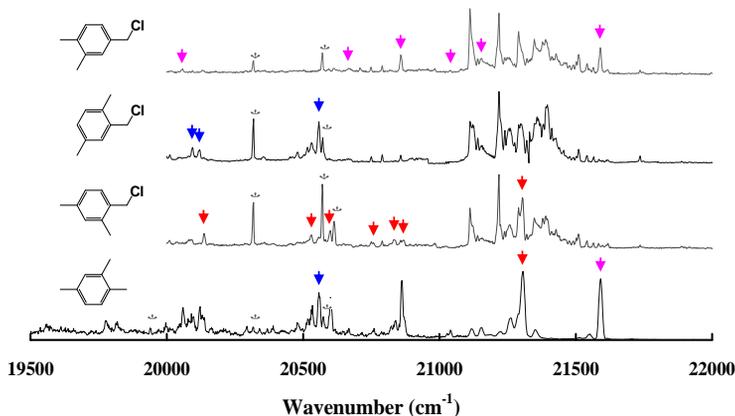
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The benzyl radical, a prototype of aromatic free radical, has been believed to be a key intermediate in aromatic chain reactions and the subject of numerous spectroscopic works. On the other hand, benzyl-type radicals, ring-substituted benzyl radicals have received less attention due to the difficulties associated with the identification of the species and possible rearrangement of substituents at the transition state.

The dimethylbenzyl chlorides were employed as precursors to generate each isomeric dimethylbenzyl radical,¹ from whose spectra we clearly confirmed the assignments of each species in the spectrum observed from polymethylbenzenes. From the analysis of the spectra, we identified the benzyl-type radicals formed in the corona discharge of the precursor and determined the electronic energy and several vibrational modes in the D_0 state to confirm the assignments of bi-substituted benzyl radicals by comparison with an *ab initio* calculation. The origin band shows increased shift to red region due to the synergic effect of two substituents into benzene ring.² The shift of the origin band of the most of the poly-substituted benzyl radicals is comparable to the summation of the contribution of each substituent regardless of the nature of substituent. However, the benzyl-type radicals with substituent at the 4-position always show much smaller shift than others, for which we tried to explain the shift of the origin band using a simple molecular orbital theory. The new model describes well the shift of the origin band of the homo- and hetero-substituted benzyl-type radicals for CH_3 and F substituents.



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Gas phase infrared and near infrared spectroscopy of a medium strength hydrogen bond molecular complex at room temperature

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The gas phase spectroscopy of the hydrogen bond complex formed between dimethylamine (DMA) and methanol (MeOH) has been measured with Fourier transform infrared (FTIR) spectrometer. The spectra have been recorded in the 1100 to 14000 cm^{-1} region using long path conventional spectroscopy techniques. The spectra of the MeOH-DMA complex are obtained by spectral subtraction of the monomer spectra from spectra recorded of the mixture. The OH-stretching overtone transitions ($\Delta v = 1 - 3$) and the NH-stretching overtone transitions ($\Delta v = 2, 3$) of the MeOH-DMA complex are obtained in the gas phase at room temperature. The second overtone transitions of the hydrogen bonded OH-stretching and the free NH-stretching in the MeOH-DMA complex are assigned to be at 9370 and 9615 cm^{-1} , respectively. We report the first measurement of the second overtone transitions for a medium strength hydrogen bond complex in the gas phase at room temperature. The measured red shifts of the fundamental, and first and second overtones of the hydrogen bonded OH-stretching transitions are 301, 694, 1162 cm^{-1} , respectively, compared to the corresponding transitions of methanol. We did not observe the NH-stretching fundamental transition because it is expected to be overlapped with the OH-stretching fundamental transition but ~ 6000 times weaker. The enthalpy of hydrogen bond formation for MeOH-DMA in the temperature range of 298 and 358 K is determined to be $-35.8 \pm 3.9 \text{ kJ mol}^{-1}$ by temperature dependent measurements of the OH-stretching fundamental transition band. We complement the experimental results with quantum chemical calculations using the explicitly correlated CCSD(T)-F12a/VDZ-F12 method. The most stable conformer of the MeOH-DMA complex has been found with a nearly linear O-H \cdots N hydrogen bond. The OH- and NH-stretching frequencies and oscillator strengths of the MeOH-DMA complex and the monomers were calculated with an anharmonic oscillator local mode model. The OH-stretching fundamental transition intensity of the MeOH-DMA complex is calculated to be 51 times stronger than that of methanol. We combine our calculated oscillator strength with the measured band intensity to determine the equilibrium constant K_p of MeOH-DMA complexation to be 0.11 atm^{-1} at room temperature.

Spin-orbit transitions of Cl and Br dopants in solid parahydrogen: A quantum Monte Carlo study

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Solid parahydrogen (pH₂) matrices containing open-shell (²P) Cl and Br atoms as substitutional impurities exhibit several infrared (IR) absorption features associated with intermolecular interactions between the halogen atom and nearby pH₂ molecules [1, 2]. These dopant-induced IR absorption features are associated with (i) spin-orbit excitation of the halogen atom and (ii) cooperative excitations in which a single IR photon both triggers spin-orbit excitation of the halogen atom and excites the H–H stretching coordinate of a nearby pH₂ molecule.

In the gas phase, the spin-orbit ground and excited states of Cl and Br atoms have symmetries ²P_{3/2}^o and ²P_{1/2}^o, respectively. The spin-orbit transitions in isolated Cl and Br atoms are therefore electric-dipole-forbidden and acquire IR absorption intensity through electric-quadrupole and magnetic-dipole terms in the atom-field interaction Hamiltonian.

For Cl and Br atoms that are substitutional impurities in solid pH₂, however, the pH₂ matrix crystal field can perturb the electronic wave function of the halogen atom and give the spin-orbit transition some electric-dipole character. The intensities of the Cl and Br impurities' IR absorption transitions therefore provide both a quantitative measure of this perturbation and insight into the role that many-body interactions play in the halogen-doped pH₂ solid.

To better understand these many-body interactions, we perform quantum Monte Carlo simulations of Cl-doped and Br-doped solid pH₂ matrices. Our results demonstrate how the morphologies of the halogen atoms' trapping sites control the IR intensities of their spin-orbit transitions and provide a basis for understanding the coupling between the dopants' electronic degrees of freedom and the nuclear motion of the surrounding pH₂ molecules.

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Towards traceability in CO₂ spectroscopic line parameter measurements using tunable diode laser absorption spectroscopy

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Tunable diode laser absorption spectroscopy (TDLAS) is a measurement technique with exceptionally high spectral resolution in the range of 10^{-4} cm⁻¹ and therefore is highly interesting for accurate measurements of molecular spectral line parameters, like line strengths or pressure broadening coefficients¹. Based on such data TDLAS enables absolute measurements and traceability, which ensures reliability and comparability of results.

We are aiming at traceable line parameter measurements by means of TDLAS^{2,3}. Such spectroscopic line parameters are frequently measured by Fourier-transform infrared spectroscopy (FTIR) or other broadband techniques to derive data for a whole manifold of lines. Results are collected in databases that are typically used for concentration determinations. A recent project, e.g., aims at traceable spectral line data for atmospheric monitoring using traceable FTIR spectroscopy⁴. FTIR provides extremely wide spectral coverage, however at the price of a limited spectral resolution of 10^{-2} to 10^{-3} cm⁻¹. TDLAS-based high resolution spectral anchor points are beneficial in order to validate and increase the reliability of FTIR measurements.

We have measured the strength of a number of CO₂ lines between 2 and 3 μm employing TDLAS. Traceability of the measured line strength values requires traceability of all input parameters, namely the gas temperature and pressure, the concentration and isotopic composition of the measured species in the gas sample, the optical path length, as well as the line area. Thus we discuss the question of traceability in case of each of these parameters. We present the retrieved line strength values together with an uncertainty assessment referring to the ISO-GUM, identifying critical parameters influencing the accuracy of the resulting line strength. Finally, we compare the measured line strength values to literature data. This work was initiated within the framework of the European project MACPoll⁵, devoted to air pollutant and gas purity measurements.

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Quantum Simulations of Helium Clusters with Open Shell and Ionic Dopants

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Many experiments on pure and doped helium clusters result in the production of a broad distribution of charged fragment ions after electron impact or laser ionisation. These ion yield distributions can exhibit distinct stability patterns. We use the diffusion quantum Monte Carlo (DMC) technique to study these stability patterns and structural features of helium clusters with open shell atomic and molecular dopants, which can also arise from photodissociation processes. Recent experiments addressed the photodissociation of CH_3I inside helium clusters. Simulations of these processes require reliable many-body potentials which we construct from high level ab initio CCSD(T) calculations for several electronic states mixed by spin-orbit coupling and including non-additive interactions arising from induction. For small clusters numerically exact calculations of rovibrational properties are used to establish the quality of our potential surfaces.

We present steps towards the modelling of the photodissociation $\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}$ inside helium droplets. Potential energy curves have been calculated for several electronic states of $\text{I}^q\text{-He}$, $q=-1,0,+1,+2$ with the CCSD(T) method and effective core potentials and are used for the construction of many body models for mixed clusters of the type $\text{I}^q\text{@He}_n$ which have been observed as photofragments ($q=0$) and in electron impact ionisation experiments ($q=-1,+1,+2$). The potential models include non additive induction effects and spin-orbit mixing. Stability patterns computed with the DMC technique indicate the existence of soft shells for $q=-1,0$ and a pronounced shell closure at $n=16$ for $q=+2$ in excellent agreement with recent experiments. The accuracy of our many body potential model is illustrated by calculations for the experimentally well known Ar^+He_n clusters.

Three-dimensional potential energy surfaces for the weak van der Waals interaction between a helium atom and a CH_3 radical in several geometries ranging from planar to pyramidal have been computed by RCCSD(T) calculations with large diffuse basis sets and fitted to a compact analytical form which reproduces all ab initio interaction energies with in 0.05 cm^{-1} . The assembly of these building blocks for a global potential energy function will eventually allow dynamical studies of fragmentation and product size and energy distributions.

We present first results for CO^+ ions in helium clusters. He-CO^+ is an interesting astrophysical collision system but its interest for helium cluster studies is the similarity of the CO^+ rotational constant with the one of neutral CO. Our present understanding of rotation inside helium clusters relies on studies of molecules where changing the molecule implies changing dynamical parameters and the interaction potential. The CO/CO^+ case allows to study the specific effect of changing only the interaction energy. We have computed accurate ab initio surfaces for the two lowest electronic states of He-CO^+ to predict rovibrational spectroscopic and collisional properties. A many-body model using these surfaces is used to study larger CO^+He_n clusters.

Core-mass nonadiabatic corrections to molecules: H_2 , H_2^+ and isotopologues

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Non-adiabatic corrections, which are important for accurate calculations of rovibrational states of light molecules, can be incorporated in a single surface picture through coordinate-dependent vibrational and rotational reduced masses. We present a compact method for their evaluation and relate in particular the vibrational mass to a well-defined nuclear core mass. The use of these masses in the nuclear Schrödinger equation yields numerical data for the corrections of much higher quality than can be obtained with optimized, constant masses, typically better than 0.1 cm^{-1} . We demonstrate the method for H_2 , H_2^+ and some isotopologues. Isotopic asymmetry does not present any particular difficulty.

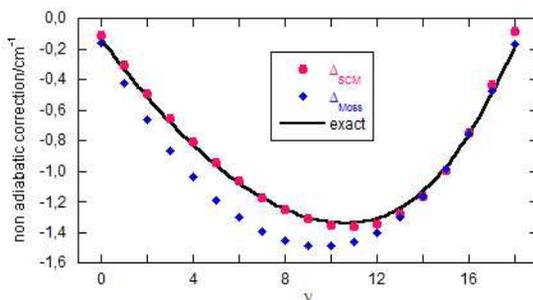


Fig. 1: Non-adiabatic corrections to the vibrational states of H_2^+ : Exact data by Wolniewicz, Moss masses and present model.

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Line mixing effects in CO₂ spectra modelled by an Energy-Corrected Sudden approach

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The important role played by the carbon dioxide CO₂ in the terrestrial and planetary atmospheres has initiated numerous spectroscopic studies of this molecule. One of features related to its infrared absorption spectra modelling is the important line overlapping due to the small value of the rotational constant and occurring in the Q-branches even at low pressures and in all the branches at elevated pressures. As a result, the spectral intensity exhibits a significant deviation from the simple sum of Lorentzian lines corresponding to the isolated lines, and its reliable modelling requires including of line-mixing effects.

From the theoretical point of view, the description of line interference is based on the notion of the relaxation matrix which diagonal elements (real and imaginary parts) correspond to the half-widths and shifts of individual lines whereas the off-diagonal elements describe the intensity transfer between the lines. Since the calculation of these off-diagonal elements by quantum-mechanical methods from the interaction potential represents a very time-consuming computational task, they are commonly modelled with dynamical scaling laws, such as, for example, the Energy-Corrected Sudden (ECS) approach proposed by De Pristo et al. [1] for the Q-branches of isotropic Raman scattering in the framework of the impact approximation (frequency-independent relaxation matrix). This model ensures a more realistic dynamics with respect to the models of instantaneous collisions (such as Infinit-Order Sudden approximation) via a corrective “adiabaticity factor” introducing the final duration of collisions and provides a good description of overlapped lines near their centres.

In the far spectral wings, however, the role of photon is no more negligible and the relaxation matrix becomes essentially dependent on the photon frequency (so-called non-Markovian matrix). Such a non-Markovian model of the relaxation matrix has developed a decade ago [2,3] and successfully applied to the high-density Raman scattering spectra of N₂ [3,4] and CO₂ [5,6].

In the present work we adapt and apply this ECS model to infrared absorption spectra of pure CO₂. For the considered low-pressure spectra we focalise our modelling of the Q-branches where the impact approximation is valid and the non-Markovian effects are negligible.

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