Poster session J

August 31, Wednesday, 16:30 – 18:30
Title: The use of pair identity and smooth variation rules to check asymmetric rotor molecules on the HITRAN database

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The concept of families of transitions was introduced by Brown and Plymate¹ to study the structure of variations in collision-broadened half-widths. Several other studies²,³ have used the families of transitions and partner transitions idea to analyze line shape parameters. In 2011, Ma et al.⁴ developed theoretically what they termed pair identity and smooth variation rules. These rules were developed for a-type transitions of water vapor and are applicable under certain constraints to the line position, intensity, half-width, line shift, and temperature dependence of the half-width. Here the pair identity and smooth variation rules are extended to consider other types of transitions. These rules are applied to water vapor transitions on the 2012 HITRAN database⁵. The rules are then tested on other asymmetric rotor molecules on HITRAN.

References:


Title: Modified Complex Robert-Bonamy (MCRB) calculations of H$_2$O transitions broadened by H$_2$ for applications to planetary and exoplanet atmospheres

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Line shape parameters for hydrogen broadening of water vapor are needed to understand remote sensing measurements of planetary and exoplanet atmospheres. In order to address these needs, semiclassical line shape calculations based on the Modified Complex Robert-Bonamy (MCRB) formalism$^{1,2}$ were made. The intermolecular potential for the calculation is comprised of electrostatic, atom-atom (expanded to order 20 and rank 4), induction, and London dispersion terms. The trajectories were determined by numerical integration of the Hamilton’s equations. The average over the Maxwell–Boltzmann distribution of velocities was performed by integration over 35 velocities corresponding to the temperature range 75K – 27000K. The formalism is complex valued yielding the half-width and line shift from a single calculation. The calculations are reported at 7 temperatures from 200 to 700 K. The half-width temperature dependence coefficient $n$ was determined using the relation

$$\gamma(T) = \gamma(T_0)[T_0/T]^n$$

with $T_0=296$K. It will be shown that H$_2$O-H$_2$ is a very off-resonance collision system, which leads to the atom-atom potential having a dominant role. Adjustments to the atom-atom parameters were made to improve the agreement with and structure of the measurements. The calculations are compared with a database of measured H$_2$O-H$_2$ line shape parameters. The rotational, vibrational, and temperature structure are discussed.

References:

Title: Creation of a line list of HDO transitions broadened by CO$_2$ in the 1100-4100 cm$^{-1}$ range


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Precise data including line shape parameters and their temperature dependences will be needed to reduce the remote sensing measurements to be made by the ExoMars Trace Gas Orbiter. For that, high-resolution laboratory absorption spectra of HDO in mixture with CO$_2$ were recorded in the $\nu_1$, $\nu_2$, and $\nu_3$ fundamental bands in the 1100-4100 cm$^{-1}$ region. The spectra were obtained with the Bruker IFS-125HR Fourier transform spectrometer at the Jet Propulsion Laboratory along with two specially built coolable absorption cells with path lengths of 0.2038 m and 20.941 m at various sample gas temperatures (230 - 296 K), pressures and volume mixing ratios. To aid in the analysis of these spectra and to provide line shape data for transitions in the region, modified complex Robert-Bonamy (MCRB) calculations were made. The calculations are compared with the measured line shape parameters determined by a multispectrum nonlinear least squares technique$^1$. The line list began with the 6166 HDO transitions form the HITRAN2012 database$^2$. The measured positions, intensities, and CO$_2$-broadened line shape information was added to these transition followed by the MCRB line shape information. Self-broadening of HDO is also included in the line list. The line list was augmented with H$_2$O and D$_2$O CO$_2$-broadened transitions from the line list of Gamache et al.$^3$

References
H-bonding networks in Sugar Alcohols

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The conformational behaviour of sorbitol and dulcitol has been investigated for the first time using a combination of chirped pulse Fourier transform microwave spectroscopy CP-FTMW (1) coupled with a laser ablation LA source (2). In gas phase isolation conditions, two different conformers have been detected for each polyalcohol, found to be overstabilised by cooperative networks of intramolecular hydrogen bonds between vicinal hydroxyl groups stretching throughout the whole molecule. In accordance with Shallenberger’s old proposal (3), a prerequisite for a compound to be sweet is the presence in its structure of a proton donor (AH)/acceptor (B) system. These two groups form what is called a glucophore, which generally refers to the part of the sweetener interacting with the sweetness receptor. Detailed structural information extracted from our experiments (4) provided information on the orientation of the OH groups with respect to the molecular frame, thus allowing the character of the intramolecular interactions involving these functional groups to be established. In addition, a common structural signature - involving hydroxyl groups in the H-bond - has been characterized and ascribed to the glucophore’s AH and B sites, indicating that anchoring to the sweetness receptor may occurs at this place. Thus, a new window to provide further insight on the linkage between sweetness and structure has been opened by the high resolution reached by our LA-CP-FTMW experiments.

The Torsional Fundamental Band and Rotational Spectra up to 940 GHz of the Ground, First, and Second Excited Torsional States of Acetone

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A new global study of the acetone (CH₃)₂CO spectrum is reported. The new microwave measurements covering the frequency range from 34 GHz to 940 GHz have been carried out using spectrometers in IRA NASU (Ukraine) and PhLAM Lille (France). The far infrared spectrum of acetone has been recorded on the AILES beamline of the synchrotron SOLEIL using a Fourier transform infrared spectrometer coupled to a long path cell. The transitions belonging to the three lowest torsional states as well as to the observed fundamental band associated with the methyl-top torsion mode (ν₁₇=1) have been analyzed using recently developed model for the molecules with two equivalent methyl rotors and C₂ᵥ symmetry at equilibrium (PAM_C2v_2tops program). The dataset consisting of more than 27400 microwave and 1100 FIR line frequencies and including transitions with J up to 90 was fit using a model consisting of 121 parameters and weighted root-mean-square deviation of 0.9 has been achieved. In the presentation the details of this new study will be discussed.

References
Submillimeter wave spectroscopy of dimethylsulfide in the ground, first and second excited torsional states from 150 to 660 GHz

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A new study¹ of the dimethylsulfide ((CH₃)₂S) spectrum is reported. The new measurements have been carried out using the Lille spectrometer in PhLAM laboratory (France) and cover the frequency range from 150 GHz to 660 GHz. The rotational transitions belonging to the three lowest torsional states of the molecule as well as previously published data on the FIR torsional band² have been analyzed using recently developed model for the molecules with two equivalent methyl rotors and C₂ᵥ symmetry at equilibrium (PAM_C2v_2tops program)³. In the presentation the details of this new study will be discussed.

References
[1] This work was done under support of the Volkswagen foundation.
The Millimeter-Wave Spectrometer with Sub-Doppler Spectral Resolution

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The structure of the millimeter-wave spectrometer with sub-Doppler spectral resolution is presented (Fig. 1). This is an absorption spectrometer with backward wave oscillator (BWO) as a radiation source. To obtain necessary accuracy the frequency of BWO’s output signal is locked to a reference synthesizer of 3.4 – 5.2 GHz by a PLL. The sub-Doppler spectral resolution is achieved by means of Lamb-dip observation using commonly applied approach with double-pass absorbing cell and polarization separation of backward and forward waves (see Fig.1). One of the main new features of the spectrometer is an application of the direct digital synthesizer (DDS) as a reference source for the PLL, which provides frequency stabilization of the BWO. The DDS is capable to operate with two frequency profiles $f_1=50\text{MHz}+\Delta f$ and $f_2=50\text{MHz}-\Delta f$ ($\Delta f$ is a deviation of FM signal). The FM signal is produced by means of periodical (square-wave) switching of the DDS frequency between $f_1$ and $f_2$ values. Both the deviation and the frequency of the modulation are chosen to be matched to the parameters of the observed Lamb-dip. Due to the first harmonic lock-in detection molecular spectra are recorded in the form of the first frequency derivative of a lineshape. An example of obtained spectra is given in Fig. 2 where the hyperfine structure of the 81$E_{1/2} - 73E_{1/2}$ transition of the methyamine molecule is shown. The second derivative (lower plot in Fig. 2) was obtained numerically to improve a contrast of the record. The distance between hf components is of about 154 kHz whereas the width of resolved components is about 26 kHz. At the same time our measurements of $J=1\leftarrow 0$ transition of the CO molecule show that the Lamb-dip width of about 10 kHz may be obtained.

References

Fig. 1: The block-diagram of the millimeter-wave spectrometer with sub-Doppler spectral resolution.

Fig. 2: The hyperfine structure of the 81$E_{1/2} - 73E_{1/2}$ transition of the methyamine molecule.
Perturbations in the rotational spectra of hydrazoic acid

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The microwave spectra of hydrazoic acid, HN₃, have been measured in the frequency region of 95 – 670 GHz. Huge perturbations were observed in the analysed frequencies of the rotational transitions in both the ground state and the exited vibrational states. In accordance with the previous high resolution analyses of azoimide,¹ resonances with crossing of the ground and v₅ rotational level structures were observed. The detail analysis of the transition frequencies required a simultaneous analysis of the ground and v₅ excited rotational transitions along with the infrared v₅ and v₆ high resolution data.²,³ This simultaneous analysis included the effective ground, v₅ and v₆ state diagonal Hamiltonian matrix elements as well as the off-diagonal rotation-vibration (e.g. Coriolis and centrifugal distortion terms) and anharmonic matrix elements interconnecting the ground state with the vibrationally excited rotational structures.

These huge perturbations make the analysis of the 4≤ Kₐ ground and 3≤ Kₐ v₅ state energy levels impossible without the correct involvement of the vibrationally off-diagonal terms of the Hamiltonian.⁴

In the present contribution, the ground and v₅ state rotational transitions were assigned and quantitatively analysed up to Kₐ=8 and Kₐ=7, respectively. In addition to those, the rotational transitions in the v₆ state vibrational excited state were assigned up to Kₐ=5 but these transitions were quantitatively analysed only up to Kₐ=3 probably because further significant resonances with additional vibrational states (e.g. v₅ and v₆) that have not been included in our Hamiltonian so far.

References

A large pulsed-beam high resolution Fourier transform microwave (FTMW) spectrometer is being developed and constructed at the University of Chemistry and Technology Prague. The new FTMW spectrometer is based on the classical Balle-Flygare design and is planned to operate in the low-frequency range (1.2–6 GHz). The Fabry-Perot type cavity, employing 90-cm diameter spherical mirrors, provides Q-values in the range of $10^4$ to $3.10^5$. The spectrometer is operated in the coaxial molecular beam arrangement allowing very high sensitivity as well as sub-Doppler resolution. Transition linewidths under 5 kHz are expected. The very high resolution of this spectrometer makes detailed studies of very large molecules of a biological importance possible and enables measurements of rotational transitions with resolved hyperfine structures.

Reference

Cavity Ring Down spectroscopy of $^{18}$O enriched carbon dioxide in the 6977 -7918 cm$^{-1}$ region

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In the present work, we extend our recent works [1-3] devoted to the study of CRDS spectra of $^{18}$O enriched carbon dioxide in the 5851–6990 cm$^{-1}$ region to the higher range (6977-7918 cm$^{-1}$). The CW-Cavity Ring Down Spectra (CRDS) of $^{18}$O enriched carbon dioxide have been recorded at room temperature and pressure 10 Torr in the 6977-7918 cm$^{-1}$ (1.43-1.26 µm) spectral region with a noise equivalent absorption $\alpha_{\text{min}} \approx 2 \times 10^{-10}$ cm$^{-1}$.

A total of 8671 transitions belonging to 166 bands of eleven CO$_2$ isotopologues were rovibrationally assigned on the basis of the predictions of the effective Hamiltonian models [1-6]. Among the 166 assigned bands, 104 were observed for the first time. All identified bands belong to the $\Delta P=9$-12 series of transitions, where $P=2V_1+V_2+3V_3$ is the polyad number ($V_i$ are vibrational quantum numbers). Most of the new observations concern the $^{16}$O$^{12}$C$^{18}$O, $^{16}$O$^{13}$C$^{17}$O, $^{12}$C$^{18}$O$_2$, $^{17}$O$^{12}$C$^{16}$O and $^{13}$C$^{18}$O$_2$ isotopologues.

The global modeling fits of the line intensities was performed to refine the corresponding sets of the effective dipole moment parameters for the $^{16}$O$^{12}$C$^{18}$O, $^{16}$O$^{13}$C$^{17}$O, $^{12}$C$^{18}$O$_2$, $^{17}$O$^{12}$C$^{16}$O and $^{13}$C$^{18}$O$_2$ isotopologues.

References
The CO2 absorption spectrum in the 2.3 µm region by high sensitivity CRDS: Rovibrational lines and continuum

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The absorption of carbon dioxide is very weak near 2.3 µm which makes this spectral window of particular interest to study the lower atmosphere of Venus in the 25–40 km altitude range and measure abundances of carbon monoxide, carbonyl sulfide, water vapor, sulfur dioxide and hydrofluoric acid [1,2]. This implies the accurate characterization of carbon dioxide absorption which is the main source of opacity in the window. This opacity results from the contributions of the local absorption lines absorption due to the rovibrational transitions of the monomer and of the “continuum” absorption.

In this work, we use the Cavity Ring Down Spectroscopy (CRDS) technique for a high sensitivity characterization of the CO2 absorption spectrum in two spectral intervals of the 2.3 µm window: 4248-4257 and 4295-4380 cm⁻¹ which were accessed using a Distributed Feed Back (DFB) diode laser and a Vertical External Cavity Surface Emitting Laser (VECSEL) as light sources, respectively. The achieved sensitivity (noise equivalent absorption, αₘₙₙ, on the order of 5×10⁻¹⁰ cm⁻¹) allowed detecting numerous new transitions with intensity values down to 5×10⁻³⁰ cm/molecule. The rovibrational assignments were performed by comparison with available theoretical line lists in particular those obtained at IAO Tomsk using the global effective operator approach. Hot bands of the main isotopologue and ¹⁶O¹²C¹⁸O bands were found to be missing in the HITRAN database while they contribute importantly to the absorption in the region. Additional CRDS spectra of a CO2 sample highly enriched in ¹⁸O were recorded in order to improve the spectroscopy of the ¹⁶O¹²C¹⁸O isotopologue. As a result about 700 lines of ¹⁶O¹³C¹⁸O, ¹⁶O¹²C¹⁷O, ¹⁷O¹²C¹⁸O, ¹²C¹⁸O₂ and ¹³C¹⁸O₂ were newly measured.

CO2 continuum was also determined from in flow CRDS experiments at different pressures between 250 Torr and 750 Torr where pure CO2 and synthetic air were alternatively passed through the high finesse cell keeping the pressure constant. After subtraction of the monomer contribution, absorption coefficients normalized with density have been retrieved between 4320 and 4380 cm⁻¹. They increase from ~2×10⁻⁸ cm⁻¹ Amagat⁻² near 4330 cm⁻¹ to 4.5×10⁻⁸ cm⁻¹ Amagat⁻² around 4380 cm⁻¹ corresponding to the centre of a CIA band. These values show a good agreement with the ones derived from [3] despite big difference in densities.

References
High resolution spectroscopy on alkali-alkaline earth molecules

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The mixed alkali-alkaline earth molecules have recently attracted the interest of the scientific community due to possible applications in the field of cold and ultracold molecules. The combination of alkaline and alkaline earth atoms leads to molecules which have permanent electric and magnetic dipole moments and thus offer manipulation of their states by external fields. Several ab initio calculations have been published on various combinations of group IA and group IIA atoms from which $^2\Sigma^+ – ^2\Sigma^+$ transitions in the near infrared are expected.

Experimentally, not so much is known about the molecular electronic states but for a few molecules. We have successfully recorded the near infrared spectrum of LiSr and KCa. The molecules were created in a heatpipe and their thermal emission was recorded via a high resolution Fourier transform spectrometer.

The assignment of the dense spectrum was facilitated by tuning a diode laser to a molecular line of the emission spectrum, resulting in the observation of light induced fluorescence consisting of P-R-doublets and a simple, short vibrational progression.

We used the rotational constants from ab initio-calculations for a first guess of the rotational quantum numbers. Then we proceeded to take into account more lines from higher rotational and vibrational levels.

For KCa, we have used laser induced fluorescence to assign the vibrational band heads of transitions from $v' \leq 2$ to $v'' \leq 3$ in the $^2\Sigma^+ – ^1\Sigma^+$ system. The resulting vibrational constants predicted other, moderately higher bandheads which can be observed in the emission spectrum.

For LiSr, we are able to describe the rovibrational spectrum up to $N = 70$ of the $v = 0$ and $v = 2$ levels of the $^1\Sigma^+$ and $^2\Sigma^+$ states. Furthermore, in LiSr perturbations due to couplings between the $^2\Sigma^+$ state and the $^1\Pi$ state have been observed and will be used to investigate the $^2\Sigma^+_{1/2} – ^1\Pi_{1/2}$ and $^2\Sigma^+_{1/2} – ^1\Pi_{3/2}$ couplings quantitatively.

We will report on the status of the investigations.

References

High Resolution Terahertz-Spectra of the $\nu_2$-Bending Mode of Linear C$_3$ and its $^{13}$C-isotopomers

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Short carbon chains are fundamental for the chemistry of stellar and interstellar ambiances: They are omnipresent throughout the interstellar medium, they likely participate in the formation of long carbon chains and they are products in photo-fragmentation processes of larger species.

Triatomic carbon, C$_3$, exhibits a mid-infrared $\nu_3$ antisymmetric stretching mode and a $\nu_2$-bending vibration at 1.9 THz. The spectroscopic investigation of the $\nu_2$-band is challenging as high resolution radiation sources in the terahertz frequency region became commercially available only recently.

In our experiments we used a frequency multiplier chain at 1.8-1.9 THz driven by a 10 GHz synthesizer from Virginia Diodes Inc. to study C$_3$ molecules produced in a laser ablation source. The carbon chain molecules were cooled to rotational temperatures below 20K in an adiabatically expanding supersonic helium jet. $^{13}$C-enriched samples were used in order to study the isotopomers of linear C$_3$. Improved molecular parameters for $^{12}$C$^{12}$C$^{12}$C and for the singly $^{13}$C-substituted species $^{13}$C$^{12}$C$^{12}$C and $^{12}$C$^{13}$C$^{12}$C were derived, which will foster their future interstellar detections.

In addition doubly and triply substituted $^{13}$C-species were studied to derive an experimental equilibrium structure of C$_3$. All results were found in excellent agreement with a recent ab initio study by Schröder and Sebald (2016) [1].

Vibronic Spectroscopy of Jet-Cooled Chlorofluorobenzyl Radicals Generated in Corona Discharge: Mechanism and Spectroscopy

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Although ring-substituted benzyl radicals, so called benzyl-type radicals are believed to play a key role in understanding the delocalization of π electrons over the benzene ring, the spectroscopic observations have been very limited due to the difficulties associated with the production from precursors and observation of spectra. Recently, we have applied the technique of corona excited supersonic expansion to produce vibronically excited but jet-cooled benzyl-type radicals from corona discharge of precursors using a pinhole-type glass nozzle developed in this laboratory. Stable precursor molecules such as chlorofluorotoluenes and chlorofluorobenzyl chlorides were used for the production of jet-cooled chlorofluorobenzyl radicals¹-⁵, in which the methyl C-H and C-Cl bonds are preferentially dissociated in corona discharge to produce chlorofluorobenzyl radicals. The visible vibronic emission spectra were recorded in the D₁→D₀ transition of the radicals using a long-path monochromator. From the analysis of the vibronic emission spectra observed from the different precursors, we can propose the mechanism of the formation of chlorofluorobenzyl radicals as well as the displacement reaction of Cl in the benzene ring by methyl H atom. In addition, the red-shift of the electronic transition energies with substituent positions was discussed to identify the behavior of π electrons over the benzene ring. The negligible contribution of substituent at the 4-position to the red-shift is explained by adapting the concept of node in the Hückel’s molecular orbitals. The large red-shift of the 2,5-disubstituted benzyl radicals is attributed to the orientation effect of substituents. The anti-parallel alignments change the molecular plane available for delocalized π electrons to be elongated one which reduces the translation energy of electrons.

References

Dynamic polarizabilities of polar molecules: Density functional theory versus quantum defect Green’s function

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Dynamic polarizability of molecules is of great interest in the study of phenomena related to atmospheric optics, plasma diagnostics, propagation of laser radiation in molecular gases etc. Recent versions of packages for quantum chemical ab initio calculations (e.g. Gaussian09) contain built-in procedures for calculation of dynamic polarizabilities. A number of different basis sets were tested for the molecular hydrogen as simplest benchmark. As an efficient technique for more complex molecules, the semi-analytical method of reduced-added Greens function in quantum defect approximation (QDT GF) can be used. In the present report we compare various density functional theory (DFT) methods in calculation of the dynamic polarizability of fluoroborylene (BF) up to the first electronic resonance, with the QDT-GF results. The DFT calculations were performed using AUG-cc-pV5Z basis set in the Gaussian09 package with the following methods taken: M11, wB97, HSEH1PBE, HISSbPBE; HFS; M06L, B97D (Pure stand alone functionals); B3PW91, mPW1PBE, BHandH, M06, M06HF, M062X.

As it can be seen from the result of our comparison given in Fig 1, the discrepancy between some methods of calculation increases as the frequency approaches the first resonance. Given the fact that different methods give different values of the resonance energies, the QDT-GF method could be considered as most reliable since it uses the experimental values of the resonance energies.

Fig. 1: Ratio of DFT-to-QDT-calculated polarizabilities of BF molecule: (a) Parallel component (the first resonance at \( \omega = 0.298 \) a.u.); (b) Perpendicular component (the first resonance at \( \omega = 0.233 \) a.u.)

References
OSCILLATOR STRENGTHS FOR RYDBERG STATES IN CaF and NaHe

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With the help of a semi-analytical procedure the oscillator strengths for Rydberg electronic transitions in CaF and NaHe molecules are calculated which account for the effects of l-coupling (due to dipole potential of the core) [1,2]. Such effects result in non-zero oscillator strength values for some transitions which are forbidden in the widely used atom-like model of molecular Rydberg states. For the allowed transitions we also report the difference between the atom-like calculations and the calculations which take into account the dipole moment of the molecular core in the frame of one-channel theory.

This work was supported by Grant of the Ministry of Education and Science of RF under Project №1122.

References
Global ab initio potential energy surface for the isomerising HCN-HNC system

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A new global purely ab initio potential energy surface for the HCN-HNC isomerising¹ system is presented. We show that this PES is a significant improvement on the previous ab initio global PES² as well as the global potential fitted to the observed energy levels³.

This surface was built from 1856 points calculated using MOLPRO with aug-cc-pCV6Z basis set at the all electrons MRCI level of theory. These points were fitted to 272 parameters of analytical form of PES the same as used in ². The ab initio points were reproduced by this surface with an accuracy of 2.58 cm⁻¹.

The vibrational energy levels were calculated using the DVR3D program suite. At first, a purely BO PES was used for the comparison with experimental energy levels. For HNC vibrational band origins we obtain an order of magnitude improvement comparison with available experimental data, 19 levels were calculated with an accuracy 3.43 cm⁻¹ for the energies up to 7200 cm⁻¹. In HCN we obtained 2.25 cm⁻¹ accuracy for the energies up to 15000 cm⁻¹ (50 levels). When we used BODC and relativistic correction of ¹ this standard deviation reduced to 1.6 cm⁻¹.

The comparison with the previous global PES of HCN/HNC²,³ shows an improvement of one or two orders of magnitude with ab initio results² and comparable accuracy with the fitted PES of³ for the low lying energies and an order of magnitude improvement for the energies between 10 000 cm⁻¹ and 14 000 cm⁻¹.

Further improvement of the global PES will be presented at the conference. In particular BODC and relativistic surface are now being calculated as well as aug-cc-pCV5Z basis set points for the extrapolation to complete basis set.

References

Overview of hot and room T water line lists for H$_2^{16}$O, H$_2^{17}$O, H$_2^{18}$O, D$_2$O, HDO

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We present here an overview of 5 new water line lists including the main isotopologue and H$_2^{17}$O, H$_2^{18}$O, D$_2$O, HDO. All the calculations were performed using DVR3D$^1$. For all line lists we used \textit{ab initio} dipole moment surface from (DMS)$^2$.

The H$_2^{16}$O line list, POKAZATEL, includes all the transitions involving energies up to 40 000 cm$^{-1}$ and J up to 72 and is designed for high temperature applications. We created potential energy surface (PES) using Varandas-type analytical form and using two different data sets. The final PES was obtained by fitting to experimental energy levels up to ~ 40 000 cm$^{-1}$ and rotational excitations up to J=5. Extension to rotational quantum numbers up to 72 covers all the bound state rotational excitations. Our PES is the most accurate global water PES available.

This linelist is now complete and involves all the bound states up to dissociation and consists of 15 billion lines$^4$.

Hot line lists for two isotopologues of water, H$_2^{17}$O and H$_2^{18}$O, also are presented. We cover energies up to 30000 cm$^{-1}$ and J up to 50. We fit Born-Oppenheimer (BO) mass-independent PES to the available experimental data for H$_2^{16}$O and fix BO diagonal correction, mass-dependent surface to its \textit{ab initio} value. For the fit we used data for J=0, 2, 5 rotational states.

We also present new room temperature line lists for D$_2$O and HDO. These are created using the methodology of Lodi-Tennyson$^3$ for calculating uncertainties. For the uncertainties characterisation four subsidiary linelists are computed using two PESes and two DMSes. These linelists are suitable for inclusion in HITRAN.

\textbf{References}


Carbon monoxide: subwavenumber accuracy for energy levels and sub percentage accuracy for intensities from *ab initio* theory and experiment

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The *ab initio* calculation of transition intensities and of vibrational and rovibrational levels of CO are presented. These calculations extend up to 30000 cm\(^{-1}\) and \(v=16\) for vibrations and 40 000 cm\(^{-1}\) and \(J=116\) for rotational levels. Unprecedented accuracy for energy levels is achieved – better than 0.1 cm\(^{-1}\). The *ab initio* accuracy for intensities for bands up to 0-6 at the percent and subpercent level is also achieved.

We used all electron MRCI calculations with the highest available basis set in the MOLPRO package. The aug-cc-pCV6Z results are extrapolated to the complete basis set limit (CBS). First and second order relativistic corrections and adiabatic corrections are also included. The accuracy of the pure rotational energy levels within the first 16 vibrational states is three orders of magnitude better than the best published results.

For calculating intensities we used all electron MRCI calculations with different size extensivity corrections and with the biggest available basis set. These results are significantly better than the previous ab initio calculations, for example for 0-6 band, we provide the sub percentage accuracy using purely ab initio calculations of the dipole moment curve. Comparison with the experimental intensities\(^1,2\) will be presented. New experimental measurements of intensities are made for first three bands 0-1, 0-2, 0-3 of CO. The details of experiment will be presented and their comparison with new ab initio calculations will be given.

The *ab initio* model for CO was used to assist the construction of a high accuracy model for CO\(_2\) intensities\(^3\).
High resolution stimulated Raman spectroscopy from collisionally populated states after optical pumping. Acetylene isotopologues.

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We demonstrate a variation of a sequential pump-probe, double resonance stimulated Raman technique in which the optical pumping of population is combined with the naturally occurring process of vibration-to-vibration (V-V) collisional energy transfer. A fraction of the vibrational population initially promoted by the pump stage to the $v_2=1$ excited state of $^{12}\text{C}_2\text{H}_2$ and $^{12}\text{C}_2\text{D}_2$, ends up reaching other excited states for which the collisional energy transfer is energetically favourable. After this, the probe (spectroscopy) stage is used to register high resolution spectra of transitions departing from these states. The technique, schematically depicted in Figure 1, requires the optimization of sample pressures and pump-probe delays in order to maximize the amount of population transferred to the excited states one wishes to observe while minimizing the impact of competing processes (molecular diffusion or V-T energy transfer) and still maintain the relatively low pressures necessary to obtain high resolution spectra.

Fig. 1: Scheme of the pump-collisional relaxation-probe technique.

Ro-vibrational transitions belonging to the $Q$ branch of the $v_2=3 \leftrightarrow v_2=2$ band in $^{12}\text{C}_2\text{H}_2$ and $^{12}\text{C}_2\text{D}_2$ have been assigned and analysed. Accurate term values for the $v_2=3$ state of both isotopologues have been determined for the first time. Intense lines due to $\Delta J=0$ transitions in the $v_2$ fundamental band of $^{13}\text{C}^{12}\text{CH}_2$ and $^{13}\text{C}^{12}\text{CD}_2$, present in the samples in natural abundance, have been also identified in the investigated spectral range. Finally, the $v_2+2v_4+v_5 \ (^{1}\Pi_u) \leftarrow 2v_4+v_5 \ (^{1}\Pi_u) \ Q$ branch observed in the spectrum of $^{12}\text{C}_2\text{H}_2$ has been analyzed, yielding a center term value for the $v_2=1$, $v_4=2$, $v_5=1$ state slightly different from the one reported in the literature.
Development and Validation of an Analytical Method for the Determination of Ferrocyanide Ions in Salts

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Abstract
A simple and rapid method of ferrocyanide ion in salts has developed using high-performance liquid chromatography with photodiode array detector. Ferrocyanides such as calcium ferrocyanide, potassium ferrocyanide and sodium ferrocyanide are authorized additives used as anti-caking agents in salts. They were extracted as ferrocyanide anions using 20 mM NaOH solution. The chromatographic separation of ferrocyanide ions was carried out on AG11-HC (4 mm × 50 mm) guard column and AS11-HC (4 mm × 250 mm) analytical column. The mobile phase consisted of 200 mM NaClO₄ and 20 mM NaOH. The eluent was monitored at a wavelength of 221 nm. The method was validated by measuring analytical parameters, which include linearity, accuracy, precision, LOD, LOQ and measurement uncertainty. The recoveries of ferrocyanide ion from spiked samples at levels of 1, 5, 10 ppm were more than 90% with RSDs less than 5%. The proposed method has been proven to be suitable for the extraction and determination of ferrocyanide ions in salts by HPLC.

Fig. 1: Chromatogram of ferrocyanide ion in salt.

References
Pure rotation spectrum of CF$_4$ in the $v_3 = 1$ state using THz synchrotron radiation

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Spherical-top tetrahedral species like CH$_4$, SiH$_4$, CF$_4$, … possess no permanent dipole moment. Therefore, probing their pure rotation spectrum is very challenging since a very weak dipole moment can be induced by centrifugal distortion and/or rovibrational interaction. If some $Q$ branch lines have been recorded thanks to microwave techniques, $R$ branch lines in the THz region have been poorly explored until recently. In two previous studies, we have reported the pure rotation THz spectrum of cold and hot band lines of methane$^{1,2}$ recorded at the SOLEIL Synchrotron facility. Here, we present the first recorded THz spectrum of the $R$ branch of CF$_4$, a powerful greenhouse gas, in its $v_3 = 1$ state. This Fourier transform spectrum covers the $R(20)$ to $R(36)$ line clusters, in the 20–36 cm$^{-1}$ spectral range. It was recorded thanks to a 150 m multiple path cell at room temperature. We could estimate the vibration-induced dipole moment value and also include the recorded line positions in a global fit of many CF$_4$ transitions.

![Graph](image-url)

**Fig. 1:** The $R(35)$ and $R(36)$ line clusters, compared to the simulation.

References

Intracavity spectroscopy of metal monohydrides

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We describe a cavity ring-down spectroscopy (CRDS) experiment used to record absorption spectra of weak visible bands of NiH and NiD produced in a discharge source, in order to establish absorption linestrengths not available from earlier laser-induced fluorescence studies. Zeeman patterns have also been recorded in this intracavity experiment. Transition-metal mono-hydrides are short-lived radicals that can be produced at modest temperatures (<400 °C) via an electrical discharge, but at low steady-state concentrations. Spectra of FeH and CrH are strong in the spectra of cool stars. Spectral inversion can assess metal abundances in these remote environments, but only if line positions and intensities are known from laboratory work. The strongest stellar lines are extremely weak at laboratory temperatures with T<1000 K. Cavity-enhanced spectroscopy makes it possible to determine $\alpha(\nu)$ absorbances for some of the rather weak lines. CRDS, which is usually associated with trace detection of stable molecules, gives sensitivities comparable to (and sometimes better than) those we achieve with fluorescence detection with our sputter source. Our NiH/NiD absorption data will be compared with literature results to illustrate some of the strengths and weaknesses of this approach.

By coupling an optical frequency comb in the near IR into a high finesse optical cavity (rather than a single mode tuneable laser), Doppler-limited absorption spectra can be recorded over an entire band, rather than measuring one line at a time with CRDS. The Vernier strategy\textsuperscript{1} we have chosen to use retains high sensitivity, and reduces recording times to the order of a few minutes. Preliminary results on CrH will be presented.

Fig 1. Cartoon of the experimental set-up, and example of isotope structure revealed by CRDS in NiH (after baseline removal to attenuate etalon effects from the optical cavity). Note that $^{64}$NiH was not observed in laser induced fluorescence spectra.

References
High-resolution infrared and millimetre-wave spectroscopy of HC$_3$N: accurate ro-vibrational analysis of its states below 1000 cm$^{-1}$

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HC$_3$N is the simplest cyano-polyynes and is a widespread constituent of many extraterrestrial environments, including star-forming regions, evolved star surroundings, and planetary atmospheres. The observation of its rotational and infrared spectral features, in the ground and vibrationally excited states, thus provides important astrophysical insights.

To improve the spectroscopic knowledge of HC$_3$N, we have undertaken a thorough re-investigation of its vibrational spectrum together with a general revision and integration of the available pure rotational data. Here we present the results obtained for the low-lying levels with $E_{\text{vib}} < 1000$ cm$^{-1}$.

We identified 14 bands by FTIR spectroscopy: they include the ones already studied by Arié et al.$^1$ plus 6 new bands. The very weak $\nu_4$ stretching fundamental has been detected for the first time. More than 3500 infrared lines have been assigned and analysed by taking into account both $l$-type resonance effects among bending sub-levels and the ro-vibrational perturbations originated by further accidental near-degeneracies. About 1100 pure rotational transitions belonging to 13 vibrational states have been included in the analysis. Most of these latter data were taken from earlier works (see, Refs.$^{2-4}$), but we also performed new measurements in selected frequency regions ($\nu_{\text{max}} \sim 1.1$ THz) in order to improve the determination of high-order distortion constants and to accurately study the resonance effects on the most perturbed levels.

References
Investigation of Selective Reflection Spectra by an Optical $L \sim \lambda/2$-thick Cell filled with Rb atomic vapor

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Selective reflection (SR) of a laser radiation from the interface of a dielectric surface and a resonant atomic vapour which form sub-Doppler spectra is known to be an efficient spectroscopic tool for studies of high-density vapour, atom-surface interaction etc.\textsuperscript{1} We have studied experimentally and theoretically SR spectra of a laser radiation from a Rb vapour nano-cell with a thickness $L \sim \lambda/2$ ($\lambda = 795$ nm being the laser wavelength tuned to the $^{87}$Rb $D_1$ line). The laser radiation line-width is 1 MHz. A special Rb nano-cell with a large area of $L \sim \lambda/2$ has been fabricated. In Fig. 1(a) the upper curve shows SR experimental spectrum for the thickness $L = \lambda/2 + 30$ nm, and curve $D(-)$ shows its derivative, while the lower curve shows SR spectrum for the thickness $L = \lambda/2 - 30$ nm and curve $D(+)\textsuperscript{2}$ shows its derivative (the line-width $\sim 40$ MHz). As we see there is a change of the SR spectrum slope sign while crossing the thickness $L = \lambda/2$.

\textbf{Fig. 1:} (a) SR experimental spectra for $^{87}$Rb $D_1$ line, $1 \rightarrow 1', 2'$ transitions (excited levels are labeled with prime) at $L = \lambda/2 + 30$ nm and $\lambda/2 - 30$ nm, curves $D(-)$ and $D(+)\textsuperscript{2}$ show their derivatives; (b) SR spectra as given by theory, $\Gamma_{nat} = 2\pi \times 5.75$ MHz.

The applications are 1) magnetic-field controlled tunable locking of laser frequency to atomic resonance line\textsuperscript{1}, 2) 40 MHz - resonances can serve as frequency references for the Rb transitions, 3) in strong external magnetic fields these resonances (we use $D(+)\textsuperscript{2}$ resonances) are strongly shifted, thus can be used as tunable frequency references for molecular lines of Cs\textsubscript{2}, Rb\textsubscript{2}, K\textsubscript{2} etc. The theory describes the experiment very well.

Research conducted in the scope of the International Associated Laboratory IRMAS (CNRS-France & SCS-Armenia).

References

ExoMol: New molecular line lists for exoplanets and other hot atmospheres


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Fundamental molecular data play a key role for spectral characterization of astrophysical objects cool enough to form molecules in their atmospheres (cool stars, exostellar planets and planetary discs) as well as in a broad range of terrestrial applications. However, at elevated temperatures, the laboratory data for a number of key species is absent, inaccurate or incomplete. The ExoMol project is providing comprehensive line lists for all molecules likely to be observable in exoplanet atmospheres in the foreseeable future; a huge undertaking which will mean providing in excess of a hundred billion spectral lines for a large variety of molecular species. The line lists for a number of key atmospheric species currently available from ExoMol (www.exomol.com) include: CaH, MgH, BeH, SiO, HCN/HNC, CH₄, KCl, NaCl, PN, PH₃, H₂CO, AlO, NaH, CS, HNO₃, CaO, SO₂, H₂S, HOH, SO₃, and VO. The line lists currently being constructed include those for AlH, C₂, C₃, PO, PS, PH, SiH, CrH₂TiH, C₂H₄, CH₃Cl and C₂H₂. We will present examples of molecular spectra computed using the ExoMol line lists. The ExoMol project is supported by the ERC under Advanced Investigator Project 267219.

References
The millimeter-wave spectrum and Coriolis interaction in the ground and excited vibrational states of methoxyisocyanate

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The detection of CH\textsubscript{3}NCO in the Orion\textsuperscript{1} and Sgr B2(N)\textsuperscript{2} interstellar clouds motivated us to study another isocyanate, the methoxyisocyanate (CH\textsubscript{3}ONCO) as a possible candidate for the ISM. It has been synthesized by the flash vacuum pyrolysis of N-Methoxycarbonyl-O-methylhydroxylamine (MeOC(O)NHOMe) at a temperature of 500°C. The Lille's DDS fast-scan solid-state spectrometer has been used to obtain the spectrum in the frequency range 75 - 330 GHz.

In the recorded spectrum we found the effects of perturbations even in the ground vibrational state. The lowest excited vibrational mode $v_{21}$ is predicted by \textit{ab initio} calculations to have the energy of 59 cm\textsuperscript{-1}. Because of relatively low energy difference and different symmetry species of the C\textsubscript{s} symmetry point group for the ground (A') and $v_{21}$ excited states (A''), $a$- and $b$-type Coriolis interactions are possible. In the same manner, the $v_{21}$ state is coupled to $2v_{21}$, $2v_{21}$ to $3v_{21}$ etc. We found that in the frequency range of the experiment, the series of the $a$-type ground state rotational transitions with $K_a \geq 9$ cannot be fitted within experimental accuracy using standard Watson’s Hamiltonian for an isolated state. We successfully fitted the ground state transitions with $K_a < 14$ and $v_{21}$ excited state transitions with $K_a < 5$ to a model that accounts for $a$- and $b$-type Coriolis interactions. For the transitions of $v_{21}$ state with higher $K_a$ values, the interaction with $2v_{21}$ state should be taken into account. The analysis is in progress, the latest results will be presented.

References

Ultra accurate measurements of the S(2) 2–0 transition frequency of D₂ and ab initio calculations of collisional effects

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Constant improvement in theoretical determination of the dissociation and ionization energies of H₂ and its isotopologues¹,² gives predictions of the transition frequencies with uncertainty at the level of 10⁻³ cm⁻¹ for the first overtone band (2–0)³. Such prognosis open a way for testing relativistic, and quantum electrodynamic effects. At this level of accuracy the uncertainty of the H₂ (or HD and D₂) line position determination in the Doppler limit becomes affected by the line-shape effects⁵ including its asymmetry. First approach for overcoming this difficulty is measuring the spectra at low pressures, where collisional effects are negligible⁵. However, it is experimentally challenging due to extremely low intensities of the quadrupole transitions. Another strategy is recording spectra at higher pressures when the collisional influence on the spectral line shapes is described in a more advanced way. Here we present our preliminary results for very weak S(2) transition of D₂ in the 2–0 band, using ab initio calculations to take into account the collisional effects on the line shape. The transition has been measured with the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) assisted by an optical-frequency comb⁶,⁷, using experimental setup described in Ref. [8]. The line positions at high pressures, were measured with sub-MHz accuracy.

Furthermore, we extended our experiments to a wide range of temperatures. We compare results from the experiment with ab initio quantum scattering calculations, where we obtain the generalized spectroscopic cross sections. The real and imaginary parts provide the speed-dependent collisional broadening γ(v) and shifting δ(v). The velocity-changing collisions, are described by hard-sphere approximation of the ab initio potential. The line shape originating from this approach is called the speed-dependent billiard-ball profile (SDBBP)⁹.

References
Exponentially correlated basis set for calculation of QED corrections in the hydrogen molecule

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Today's most popular approach to computational chemistry involves an expansion of the molecular wavefunction in a Gaussian basis set. It is so due to the simplicity of integration algorithms and their straightforward extensibility to large systems. However, Gaussians have wrong asymptotic properties. When QED corrections to electronic energy are considered, it can lead to poor convergence or even wrong results. Calculating them require a well-optimized and mathematically adequate basis set. Our goal is to construct such a set and use it to calculate $\alpha^6$ corrections for the $\text{H}_2$ molecule. We use basis functions of the form:

$$\psi = \exp(-t r_{12} - u(r_{1A} + r_{1B}) - w(r_{2A} + r_{2B}) - y(r_{1A} - r_{1B}) - x(r_{2A} - r_{2B}))$$

(subscripts 1, 2 denote electrons and A, B - nuclei)

They comprise of all possible correlation terms, satisfy Kato’s condition and decay properly at large distances. It facilitates the calculation of expectation values of such operators as Dirac’s delta and negative powers of interparticle distances. The main problem with the application of this basis are difficult two-center integrals. The algorithm$^1$ being developed by us involves a Taylor expansion of them in the internuclear distance $r$. It is completely general in terms of the variational parameters $t$, $u$, $w$, $y$, $x$ and $r$. Due to the quality of basis functions we are able to obtain high accuracy results in relatively small bases. The most recent results and developments will be presented.

References

Near Infrared Heterodyne Spectroradiometer for Column and Vertical Profile measurements of GHGs

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Greenhouse gases (GHG), among which most important are CO₂, CH₄, and N₂O, are subject to monitoring from spacecraft, in situ measurements, and ground-based remote observations. One of the problem limiting development of ground networks, such as TCCON, is relatively expansive and complex Fourier transform spectrometers used for GHG monitoring, and necessity of highly skilled personnel for their maintenance. We propose a compact, lightweight and low cost instrument that provides precise in situ GHG measurements by means of tunable diode laser spectroscopy technique (TDLS) and simultaneous spectroradiometric sounding of the atmospheric column. As local oscillators the instrument uses distributed feedback (DFB) diode lasers with precisely controlled radiation frequency, modulated by pumping current. Wavelengths in the range 1.6 – 1.65 microns are chosen, so that at least one unsaturated line of GHG is covered by each laser. LO frequency is ramping around the contour of a selected spectral line, and stabilized using an off-axis multipass reference cell. Radiation of Sun passed through the atmosphere is coupled with LO signal in a single mode optical fiber. Backend data treatment is reduced to digital square detection of a noise produced by phase-decoupled mixing of sunlight with LO. Not only the resulting spectral resolution ~10⁸ allows highly accurate measurements of GHG column, but also provides a unique opportunity to retrieve vertical profiles of some component and to estimate vertical profile of wind velocity up to 30-50 km. CH₄ and CO₂ column measurements were performed using developed heterodyne spectroradiometer as well as methane vertical profile was retrieved.

Due to relatively low cost of the instrument’s production and maintenance, existing ground networks of GHG monitoring and sounding may substantially expanded, which in turn may result in new insight into climate change problem.
Infrared Spectra and Cross Section Data of 1,1,1,2-Tetrafluoroethane: Results From a Coupled Experimental and \textit{Ab Initio} Investigation

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The medium resolution (up to 0.2 cm$^{-1}$) gas-phase infrared spectra of 1,1,1,2-tetrafluoroethane (C$_2$H$_2$F$_4$, HFC-134a) were investigated up to 6500 cm$^{-1}$. In addition to the vibrational assignments carried out in terms of fundamentals, overtones and combination bands, accurate absorption cross section data were determined and compared to the available literature values.

The vibrational assignments were guided and supported by high-level calculations, where the harmonic data, obtained at CCSD(T) level and employing several correlation consistent basis sets, were combined with DFT fully analytic cubic and quartic force constants, and quadratic and cubic electric dipole terms, to include anharmonicity on frequency and intensity predictions, respectively. Additional calculations were carried out by using cubic and quartic semi-diagonal force constants yielded by MP2 and B2PLYP methods.

Details of the experimental work and of the calculations will be presented and discussed together with the preliminary results.
Benchmarking DFT Analytic Force Fields for Anharmonic Infrared Spectra

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In the present contribution we report the computations of the anharmonic data for infrared spectra by means of fully analytic calculation of force fields obtained by density functional theory (DFT) and a recently developed recursive formulation of the response theory¹. The results thus obtained were compared with the available accurate experimental data for a selected set of halomethanes. In addition, by combining the analytic cubic and quartic terms at DFT level with the harmonic parts obtained by calculations carried out at MP2 and CCSD level, we computed anharmonic corrections to frequencies and intensities, as well as other spectroscopic parameters (centrifugal distortion terms, rotation-vibration constants, Fermi and Darling-Dennison interaction constants). A suite of programs (ARIES) were developed to compute, within the framework of VPT2 approach, all these required parameters. The corresponding results will be presented and discussed.

References

DFT Methods for Calculations of Sextic Centrifugal Distortion Constants: a Benchmark Study

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In the present contribution we extend our previous investigation on the performances of DFT methods for the calculation of sextic centrifugal distortion constants. By including more functionals and basis sets in the analysis we benchmarked their predictions with respect to the accurate experimental values for a selected set of molecules of both atmospheric and astrophysical relevance. Comparing the results of this extensive study with those obtained by calculations carried out at MP2 and CCSD levels of theory, we demonstrate that DFT methods can yield an accuracy almost comparable to that offered by the formers (which are computationally more demanding). Besides, the performances given by hybrid approaches, where the harmonic parts are computed at higher level of electronic correlation, are presented and discussed. The overall good agreement found in this extensive study confirms the reliability of DFT methods to compute sextic centrifugal distortion constants for more complex systems.
Electronic structure and spectroscopy of HBr and HBr$^+$

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We report preliminary ab initio electronic structure calculations of HBr and HBr$^+$. The computations were carried out employing the MRD-CI package, with a basis set of cc-pVQZ quality augmented with s-, p- and d-type diffuse functions. In a first series of calculations, without inclusion of spin-orbit splitting, potential energy curves of about 20 doublet and quartet electronic states of HBr$^+$, and about 30 singlet and triplet (valence and Rydberg) states of HBr were computed. This exploratory step provides a perspective of the character, shape, leading configurations, energetics, and asymptotic behavior of the electronic states. The calculations taking into account spin-orbit are currently being performed. Our study focuses mainly on the Rydberg states and their interactions with the repulsive valence states and with the bound valence ion-pair state. In particular, the current calculations seek to provide information that might be relevant to the interpretation of recent REMPI measurements$^1$ dealing with the interaction between the diabatic E$^1$$\Sigma^+$ Rydberg state and the diabatic V$^1$$\Sigma^+$ ion-pair state (which together constitute the adiabatic, double-well, B$^1$$\Sigma^+$ state). Several new states of both HBr and HBr$^+$ are reported.

References

Combination Differences of CH$_5^+$: From Lines to States without a Model

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CH$_5^+$ is a prototype of a floppy molecule for which the quantum states have eluded an analytical description so far. Therefore, the reconstruction of its quantum states relies on methods as e.g. the search for accumulations of combination differences of rovibrational transitions. Using the high-resolution data and methodology of Asvany et al.$^1$, this reconstruction has been improved by using the properties of kernel density estimators.

Two new combination difference sets have been discovered, and the known ones completed, allowing not only to reconstruct more parts of the ground state levels, but also some vibrationally excited states of CH$_5^+$.

Fig. 1: Energy scheme of a set of reconstructed states of CH$_5^+$. The horizontal lines denote states, the vertical lines indicate the energies of peaks in the CD spectrum. The vibrationally excited states have been independently reconstructed by means of the different peaks (short horizontal lines), trusted states are marked by end-to-end lines.

References

Title: Spectroscopic Study of \textit{n}-Propyl Cyanide and Astronomical Detection of its Vibrationally Excited States

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We have recorded laboratory rotational spectra of \textit{n}-propyl cyanide (\textit{n}-PrCN) at frequencies up to 500 GHz and are presently carrying out a comprehensive analysis on the ground state and several vibrational states for both the gauche and anti conformers of this species. Rotational constants were already available for the first four lowest vibrational states (Hirota\textsuperscript{[1]}), facilitating the laboratory analysis, but from a too limited data set to give the accuracy required for useful predictions for astronomical purposes. Extensive data is already available for the ground state and is summarised in Belloche et al\textsuperscript{[2]}. However, new measurements of high \textit{K} and high \textit{J} states should be useful.

Ground-state, \textit{n}-PrCN has previously been detected (Belloche et al\textsuperscript{[2]}) in the star-forming Sagittarius molecular cloud (specifically in the Northern Sgr B2(N) hot molecular core). The quantum-leap in sensitivity and spatial resolution of the new Atacama Large Millimetre Array (ALMA) affords the possibility of detecting many more new species in the interstellar medium. Some lines of vibrationally excited \textit{n}-PrCN, both gauche and anti, have been identified in ALMA data we obtained for Sgr B2(N) between 84.0 and 114.4 GHz in its Early Science Cycles 0 and 1.

We will give some examples, both of the laboratory spectra under analysis and of the astrophysical detection. The ultimate goal of this work is to contribute to the understanding of the chemical processes and physical conditions that lead to the build-up of molecular complexity in star and planet forming regions.

References
Synchrotron Spectroscopy and Torsional Structure of the CSH-
Bending and CH$_3$-Rocking Bands of Methyl Mercaptan

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Fourier transform spectra of the lower infrared vibrational bands of CH$_3$SH have been investigated from 650 to 1200 cm$^{-1}$ at 0.001 cm$^{-1}$ resolution employing synchrotron radiation at the Canadian Light Source in Saskatoon. The relative band strengths and structures are remarkably different from those for the analogous CH$_3$OH methanol relative, with the CSH bend being very weak and both the in-plane and out-of-plane CH$_3$ rocks being strong with intensities comparable to the C-S stretch. The CSH bend has parallel $a$-type character with no detectable $b$-type component. The out-of-plane CH$_3$ rock is a purely $c$-type perpendicular band, whereas the in-plane rock is of mixed $alb$ character. The $K$-reduced $v_i = 0$ sub-state origins for the CSH bend follow the normal oscillatory torsional pattern as a function of $K$ with an amplitude of 0.362 cm$^{-1}$, as compared to 0.653 cm$^{-1}$ for the ground state and 0.801 cm$^{-1}$ for the C-S stretching mode. The torsional energy curves for the out-of-plane rock are also well-behaved but are inverted, with an amplitude of 1.33 cm$^{-1}$. In contrast, the sub-state origins for the in-plane rock do not display a clear oscillatory structure but are scattered over a range of about 2 cm$^{-1}$, with indications of some significant perturbations. Our sub-band assignments extend up to about $K = 10$ for all the modes and are well-determined from GSCD relations, particularly for the $alb$ in-plane rock for which $\Delta K = 0, +1$ and $-1$ transitions are all observed.
On the Ro -Vibrational Study of “Hot” Transitions in C$_2$D$_4$: 
The $v_7 + v_{10} - v_{10}$ and $v_{10} + v_{12} - v_{10}$ bands

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The main goal of the present study is the analysis of the rotational structure of two 
excited vibrational states, ($v_7 = v_{10} = 1$, $B_{3g}$) and ($v_{10} = v_{12} = 1$, $B_{1g}$). The bands $v_7 + v_{10}$ and $v_{10} + v_{12}$ are forbidden by symmetry of the molecule and cannot be 
seen in absorption spectra, in principle. The only way for study of the rotational structure of the 
states ($v_7 = v_{10} = 1$, $B_{3g}$) and ($v_{10} = v_{12} = 1$, $B_{1g}$) by the methods of infrared spectroscopy is 
the analysis of “hot” bands, such, e.g., as $v_7 + v_{10} - v_{10}$ and $v_{10} + v_{12} - v_{10}$.

In the present investigation, the experimental spectrum of C$_2$D$_4$ was recorded with the 
Bruker IFS-120 HR Fourier transform infrared spectrometer in Braunschweig University of 
Technology (Germany). Both of these bands are located in the region of the considerably stronger bands, $v_7$ and $v_{12}$.$^1$ On this reason, as the first step of analysis, we "cleaned" the experimental spectrum from transitions belonging to strong bands $v_7$ and $v_{12}$. Assignment of remaining weak transitions was made on the basis of the calculation scheme from Ref. [2]. As the result, about 550 transitions with $J_{\text{max}}=25$ and $K_{\text{a max}}=17$ were assigned to the band $v_7 + v_{10} - v_{10}$, and about 230 transitions with $J_{\text{max}}=17$ and $K_{\text{a max}}=11$ were assigned to the band $v_{10} + v_{12} - v_{10}$. On that basis, the rotational energies of the vibrational states ($v_7 = v_{10} = 1$) and ($v_{10} = v_{12} = 1$) were 
determined and used as input data in the weighted fit procedure.

The set of parameters obtained from the fit reproduced the experimental data with an 
accuracy close to experimental uncertainties.

References
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High Resolution Analysis of the $v_4$, $v_6$, $v_7$, $v_8$ and $v_{10}$ Vibrational Bands of C$_2$H$_2$D$_2$-cis

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In the present study we present the results of the high resolution analysis of the $v_4$, $v_6$, $v_7$, $v_8$ and $v_{10}$ bands of the C$_2$H$_2$D$_2$-cis molecule. C$_2$H$_2$D$_2$-cis is an asymmetric top molecule with twelve different vibrational modes. Because of its symmetry (C$_{2v}$), all vibrational states of the C$_2$H$_2$D$_2$-cis molecule are divided into 4 groups of states of different symmetry.

The spectra were recorded with a Brucker IFS 120HR Fourier transform infrared spectrometer in Technische Universität Braunschweig (Germany). The measurements were carried out in the 600 - 1200 cm$^{-1}$ region at room temperature with sample gas pressure of 1.5 and 2 mbar and an absorption path length of 4 m and 24 m, respectively.

For all studied bands, transitions have been assigned with higher values of quantum numbers $J_{\text{max}}$ and $K_{a\text{max}}$ than it was made before$^{1,2}$. Transitions belonging to the $v_4$, $v_8$ and $v_{10}$ bands were assigned for the first time. The assigned transitions were used then in the weighted fit of the effective Hamiltonian parameters. Resonance interactions between all analyzed bands were taken into account. The set of obtained parameters reproduces the experimental line positions with an accuracy close to experimental uncertainties.

References
High Resolution Study of $^{13}$C$_2$H$_4$ in the Region of 1700 – 2150 cm$^{-1}$:
The $v_8 + v_{10}$, $v_7 + v_8$, $v_4 + v_8$, $v_6 + v_{10}$, and $v_3 + v_{10}$ Bands

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The main goal of the present study is to analyze rotational structure of five excited vibrational states: $(v_8 = v_{10} = 1, A_u)$, $(v_7 = v_8 = 1, B_{3u})$, $(v_4 = v_8 = 1, B_{2u})$, $(v_6 = v_{10} = 1, B_{3u})$, and $(v_3 = v_{10} = 1, B_{2u})$. The $v_8 + v_{10}$ band is forbidden by symmetry of the molecule and can appear in absorption spectra only because of resonance interactions with allowed bands.

In the present study the experimental high resolution spectrum of $^{13}$C$_2$H$_4$ in the region of 1700 – 2150 cm$^{-1}$ was recorded for the first time with the Bruker IFS-120 HR Fourier spectrometer in Braunschweig University of Technology (Germany). As the result of assignment, about 1200 experimental transitions with the maximum values of quantum numbers $J_{\text{max}} = 34$ and $K_{a,\text{max}} = 17$ were assigned to the band $v_8 + v_{10}$; about 2500, 1750, 2300, and 1500 transitions with $J_{\text{max}}/K_{a,\text{max}} = 44/15$, 28/12, 40/15, and 30/11 were assigned to the bands $v_7 + v_8$, $v_4 + v_8$, $v_6 + v_{10}$, and $v_3 + v_{10}$, respectively. On that basis, the rotational energies of the upper vibrational states were determined, and then they were used as an input data in the weighted fit.
Sulfur Dioxide Application of Operator Perturbation and Isotopic Substitution Theories to the Dipole Moment Analysis

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The method of effective operators, symmetry properties and operator perturbation theory are used to give the most general form for the effective dipole moment parameters of the XY₂ (C₂ᵥ) molecule. On this basis, the isotopic relations between different effective dipole moment parameters are derived between the “mother” molecule, ³²S¹⁶O₂ and the isotopic modifications, ³²S¹⁸O₂ and ³⁴S¹⁶O₂.
High Resolution Study of the $^{15}$NH$_2$D and $^{15}$NHD$_2$ in the Region 1000-1800cm$^{-1}$: the $v_4$ Bands

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High resolution spectra of the $^{15}$NH$_2$D and $^{15}$NHD$_2$ species were recorded in the region of 1000-1800 cm$^{-1}$ with the Brucker 120HR in LISA Research Laboratory of Université Paris Diderot at room temperature and different pressures (0.521 and 2.375 mbar) with resolution 0.004cm$^{-1}$.

Assignment of transitions belonging to the $v_{4a}/v_{4b}$ ro-vibrational bands was made on the basis of the ground state combinational differences method. Necessary for the assignment rotational energy values of the ground vibrational states ($a$ and $s$) have been refined in the Watson’s Hamiltonian model in $A$-reduction and $I^r$ representation on the basis of experimental microwave and FIR rotational transitions. Obtained upper energy values were used as initial data in the weighted fit of parameters of the effective Hamiltonian, which takes into account resonance interactions between studied bands.

References

High Resolution Rovibrational Analysis of the CH$_2$=CD$_2$ Molecule: $v_7 + v_{10} - v_{10}$ and $v_8 + v_{10} - v_{10}$ Hot Bands

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In this contribution we present results of our study of the CH$_2$=CD$_2$ isotopologue of ethylene, and our main goal is to investigate the combination bands $v_7 + v_{10}$ and $v_8 + v_{10}$. Due to the symmetry properties, the direct observation of these bands is impossible in absorption, and the only way to study them is to analyze related hot bands, e.g., $v_7 + v_{10} - v_{10}$ and $v_8 + v_{10} - v_{10}$.

The absorption spectrum of CH$_2$=CD$_2$ in the region of 600-1100 cm$^{-1}$ was recorded with a Bruker IFS-120 HR FTIR spectrometer at the Technische Universität Braunschweig (Germany). There are several strong fundamental bands ($v_{10}$, $v_7$, $v_8$, $v_3$) in that region, so the first step was to "clean" the experimental spectrum from the spectral lines of these strong bands.

The assignment of hot bands transitions was performed on the basis of the combination differences method. In this case, the rotational energies of the lower vibrational state, ($v_{10} = 1$), were used from our recent paper$^1$. As the result of spectrum assignment, the rotational energies of the vibrational states ($v_7 = v_{10} = 1$) and ($v_8 = v_{10} = 1$) were determined and then used as input data in the weighted fit. A set of obtained parameters reproduces the initial experimental data with an accuracy close to experimental uncertainties.

References
Ethylene C$_2$H$_3$D Isotopologue:  
High Resolution Study of $v_6$, $v_4$, $v_8$, $v_7$, and $v_{10}$ Fundamentals

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High Resolution Fourier transform infrared spectra of the C$_2$H$_3$D molecule were recorded with Doppler limited resolution in the region of 600 - 1250 cm$^{-1}$ at room temperature. The measurements were carried out under several different absorption conditions using the Bruker 120 HR spectrometer in Braunschweig Technical University. Five fundamentals $v_6$, $v_4$, $v_8$, $v_7$, and $v_{10}$ were observed and found to be perturbed by different resonance interactions.

About 6000 lines were assigned in the recorded spectrum. They were used then in the weighted fit procedure with the effective Hamiltonian taking into account five strongly interacting states.
On the Study of Fundamental Properties of Ethylene: Analytical Form for Ambiguity Parameters and Isotopic Relations for Spectroscopic Constants

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Fundamental characters of a molecule, such as structural parameters and intramolecular force field constants are the clue point in understanding of its physical and chemical properties. Study of ethylene is important for numerous both fundamental and applied problems of biophysics, astrochemistry, astrophysics, etc. Ethylene is one of the climate-relevant trace gas and plays an important role in green-house effect. At the same time, as the literature analysis shows, fundamental properties of ethylene are not well studied until now. There are only few studies concerning to the ethylene potential energy surface determination.

The ultimate goal of current work is to obtain fundamental characters of ethylene molecule in the most general analytical form. As it is well known from ro-vibrational theory, the clue role in ro-vibrational spectroscopy is belong to, so-called, $\ell$-transformation coefficients\textsuperscript{1}. Transformation coefficients are of fundamental significance because any spectroscopic parameters, such as interaction parameters, harmonic frequencies, anharmonic coefficients, centrifugal distortion coefficients, etc. are functions on $\ell$-transformation coefficients.

Expanded Local Mode (ELM) approach was earlier derived for $XY_2$ ($C_{2v}$)$^2$, $XY_3$ ($C_{3v}$)$^3$, and $XY_4$ ($T_d$)$^4$-type molecules. In application to ethylene molecule $C_2H_4$ ($D_{2h}$), number of independent $\ell$-parameters (so called ambiguity parameters) were obtained in the framework of ELM as a simple analytical formulas. It gives us possibility, on the one hand, to derive simple formulas for different spectroscopic parameters of the $C_2H_4$ molecule, and, on the other hand, to obtain very simple values of transformation $\ell'_{\text{iso}}$ coefficients for the $C_2H_4D/C_2HD_3$ species of the ethylene molecule on the basis of the general isotopic substitution theory. On this basis, isotopic relations between different spectroscopic constants of mother, $C_2H_4$, molecule and deuterated, $C_2H_4D/C_2HD_3$, species are derived. Comparison of the theoretically and experimentally obtained values of spectroscopic parameters shows more than satisfactory correlation between the results.

References
Newly observed g-, h- and i-levels of atomic sulphur.

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The time resolved Fourier-transform infrared spectroscopy measurements have been carried out to observe the new highly-excited Rydberg states of atomic sulphur. In spite of the fact that sulphur is one of significant atoms, very few studies of S I spectra in infrared region have been reported. Emission spectra have been studied in the 800–8000 cm⁻¹ spectral region. To obtain better resolution and better signal-to-noise ratio for weak lines the time-resolved synchronous continuous scanning method have been used.

We report 55 lines not previously observed and revise energy values for 8 newly observed energy levels. The line classification is performed using relative line strengths expressed in terms of transition dipole matrix elements calculated with the help of quantum defect theory (QDT)1. The measured S I lines are in agreement with the solar spectra recorded in Atmospheric Chemistry Experiment (ACE).

We also present the QDT calculations of the matrix elements for all dipole transitions of S I in the 800-8000 cm⁻¹ range.

V.Ch. acknowledges the support from RF Ministry of Education & Science (State order No.1122). E.M.Z. and D.Yu.T. appreciate a financial support from RFBR according to the research project No. 16-32-00034.

References

Acknowledgement: This work is a part of research series funded by the Grant Agency of the Czech Republic (grant no. 14-12010S) and the Technological Agency of the Czech Republic (grant no. TA04010135).
Time-resolved FTIR study of Rydberg states of atomic selenium: fine structure of 5g levels.

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Laser Induced Plasma Spectroscopy in connection with synchronous continuous scanning FTIR spectroscopy was used for observation of time-resolved infrared spectra of atomic selenium in the region 2000–3500 cm⁻¹. The most prominent Se lines in the region under study were identified as the 4f–5g multiplet fine-structure components which have not been previously observed.

Our study gives the first laboratory observation evidence for 14 levels of Se I. The most intensive emission lines in the 2000–3500 cm⁻¹ region correspond to the 4f–5g transitions. Fine structure of this multiplet was identified with help of relative line strengths expressed in terms of transition dipole matrix elements calculated using quantum defect theory (QDT)¹.

V.Ch. acknowledges the support from RF Ministry of Education & Science (State order No.1122).

References

Acknowledgement: This work is a part of research series funded by the Grant Agency of the Czech Republic (grant no. 14-12010S) and the Technological Agency of the Czech Republic (grant no. TA04010135).
Analysis of Meteor Emission Spectra using Comparative Laboratory Experiments and Calibration Free Method

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In order to understand better the chemistry and spectroscopy of meteor plasma, we implemented Calibration Free data processing in emission data evaluation. Moreover, the spectra are compared with references acquired in laboratory experiments involving Laser Induced Breakdown Spectroscopy of Meteorite samples, Laser Induced Sparks in atmospheric gases and electric discharges and in situ simultaneous measurement by meteor spectrograph.

The most remarkable advantage of comparative measurements using LIBS lies in applicability of this method for real time in situ analysis of any sample of real meteorite without any preceding treatment, preparation or isolation. The meteorite plasma is generated in the laboratory under strictly defined conditions and the elements are evaporated together with the whole matrix as well as during the meteoroid descend. These attributes position LIBS for qualitative analysis, but the situation is different if quantitative elemental determination is required. In a series of previous studies dealing with LIBS method, the authors demonstrated that emission intensity of particular spectral line of studied analyte depends not only on physical parameters of the line and quantity of emitting element, but also on the matrix where it is embedded. This matrix dependence leads to the necessity of calibration curves or matrix matched standards which in some practical situations including sample of meteorite are simply unavailable.

Ciucci et al. proposed a novel Calibration Free Laser Induced Breakdown Spectroscopy (CF-LIBS) procedure in order to overcome the mentioned matrix effect. The CF-LIBS method is based on direct analysis of emission lines of an analyte together with matrix instead of looking the matrix as an independent problem. In the current study, we analyzed by this method a wide range of chondrite meteorites, we developed all the subsequent steps of data processing using Calibration Free method suitable for meteor analysis and we used this method to our knowledge for the first time for interpretation of real meteor spectra.


Acknowledgement: This work is a part of research series funded by the Program for Regional Cooperation, Czech Academy of Sciences (grant no. R200401521), by the Internal Grant of the J. Heyrovsky Institute of Physical Chemistry (reg no. 994316) and the Grant Agency of the Czech Republic (grant no. 14-12010S).
High-resolution overtone spectroscopy of methylamine

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Methylamine (CH₃NH₂) is a simplest primary amine important in organic chemistry biological processes and were also detected in interstellar space [1]. The molecule is well known as an example of non-rigid molecule exhibiting two strongly coupled large-amplitude motion of methyl group (torsion) and the amine group (inversion). Due to this phenomena, the molecule became the focus of a number theoretical and experimental studies. Despite the fact that infrared spectrum of CH₃NH₂ was measured for the first time in 1939 [2], the high resolution analysis of rovibrational spectra in a fundamental region is quite limited and no high resolution spectra in NH overtone region are available. This region was studied till now only by low resolution techniques [3, 4].

In this contribution, we present first high-resolution overtone spectra of methylamine (CH₃NH₂) recorded in the region of symmetric and antisymmetric NH-stretch combination band v₁+ν₁₀. To aid high-resolution measurement, the spectrum was recorded by OPO/OPA-photoacoustic detection technique at room temperature with 1.5 cm⁻¹ instrumental resolution and a reduced pressure of 5 Tor. The spectrum was measured in the range of 6300-6900 cm⁻¹ (see Fig 1) and exhibit quite a strong absorption in NH-stretch overtone region comprised of several absorption bands. The next step was the measurement of the spectra at low temperature Dopler limited resolution by tunable diode laser spectrometer in combination with supersonic jet expansion. The spectra were measured in He and Ne expansion in the range from 6600 to 6625cm⁻¹. Surprisingly the spectra show weaker absorption than estimated from the OPO/OPA-photoacoustic measurement. This could be due to the clustering in the supersonic expansion.

Fig. 1: OPO/OPA-photoacoustic spectrum of methylamine

References

A simple photoacoustic detector for highly corrosive gases

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Photoacoustic detection is a useful technique used in a wide range of spectroscopic applications. In general it is credited for high sensitivity and ease of application. Small and affordable electret microphones are often used for the acoustic detector. We have however found, that they are quickly destroyed by corrosive gasses, notably HBr and HCl. In this contribution we describe a new design of the cantilever-type¹,² photoacoustic (PA) detector and its application for such highly corrosive gaseous samples. In the presented detector a thin cantilever vibration is excited via the photoacoustic effect and its deflection is measured. The cantilever is the only part which comes into contact with the sample as its deflection is sensed by a probe laser from the outside of the gas cell. A thin slice of mica has been used for the cantilever material as it is resistive to the acids, and can be easily fabricated to desired size and thickness. The detector is simple, compact, and can be manufactured without any special materials or fabrication procedures in standard mechanical and electronic workshop. We have tested the detector in the noisy environment of the laboratory by measuring of PA spectra of HCl and HBr gases. The PA pressure is initiated by a commercially available pulsed IR tunable optical parametric oscillator and amplifier delivering millijoules of energy per pulse. A ro-vibration PA spectrum of the first overtone ($\nu = 0 \rightarrow \nu = 2$) of HCl molecules in range from 5315 to 5855 cm$^{-1}$ and fundamental ($\nu = 0 \rightarrow \nu = 1$) of HBr in range from 2280 to 2760 cm$^{-1}$ is presented.

Fig. 1: Left: Setup for the PA spectra measurement with the presented detector, right: PA responses for two different pressures of sample gas.

References
Infrared absorption due to H$_2$ and H$_2$O isolated in a CH$_4$ matrix

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The molecular complex of H$_2$O and H$_2$ (H$_2$O-H$_2$) has attracted an interest in astrophysics. It has been theoretically predicted that the most stable structure of the complex depends on the combination of the rotational states of H$_2$O and H$_2$.\(^1\) The stretching vibration of H$_2$ becomes infrared active owing to the dipole induced by H$_2$O. In fact, infrared spectra of H$_2$-H$_2$O \(^2\) in a Ne matrix showed both H$_2$- and H$_2$O-related absorption peaks. As was found in a previous study, methane is the effective matrix species\(^4\) because the infrared active vibrational modes of CH$_4$ enable one to investigate the structure of the matrix itself. In the present study, we measured infrared spectra of H$_2$ in solid CH$_4$ containing dilute H$_2$O to explore the interaction of H$_2$ with H$_2$O and CH$_4$.

The experimental apparatus consists of a vacuum chamber equipped with a liquid-helium cryostat, a Fourier transform infrared spectrometer, and a HgCdTe detector. Gas mixtures were prepared at the ratios of CH$_4$ : H$_2$ = 22 : 1 and CH$_4$ : H$_2$O : H$_2$ = 61 : 1 : 100 and were condensed on a gold substrate at 6.9 K. Infrared absorption spectra were measured in the reflection geometry with the incident angle of 80 degrees.

An infrared spectrum of H$_2$ in solid CH$_4$ indicated an absorption peak at 4133 cm$^{-1}$ with a low-frequency tail. The peak decreased in intensity with time, whereas the tail grew to a peak at 4112 cm$^{-1}$. In a spectrum of H$_2$O and H$_2$ in solid CH$_4$, a broad absorption band around 4140 cm$^{-1}$ was detected along with a tail in the low frequency side. The band was decomposed into two Gaussian peaks at 4131 and 4143 cm$^{-1}$. With increasing time, the component at 4143 cm$^{-1}$ was drastically reduced in contrast to the invariance of the one at 4131 cm$^{-1}$. Comparing the spectra with and without H$_2$O, we concluded that the 4143 cm$^{-1}$ component is due to H$_2$ interacting with H$_2$O. We will discuss the origins of the detected peaks in detail.

References

Terahertz-spectroscopic study of H$_2$O ice and solid CH$_4$

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To reveal the role of the hydrogen-bond interaction is important in understanding the thermodynamical properties of water and ice. Since the H$_2$O cluster is a familiar example of the hydrogen-bond system, it has been the subject of many experimental and theoretical efforts.$^{1,2}$ Infrared reflection-absorption spectroscopy (IRAS) combined with the matrix isolation technique has been used to clarify the intra-molecular vibrational states of H$_2$O clusters. In a previous study, we measured infrared spectra of the clusters in a CH$_4$ matrix, which has the advantages of the chemical inertness and infrared-active property.$^3$ On the other hand, terahertz spectroscopy is required for the observation of the inter-molecular vibrations of the clusters. In the present study, we constructed an apparatus for spectroscopy in the range from 100 to 600 cm$^{-1}$ under ultrahigh vacuum to investigate H$_2$O ice and solid CH$_4$ as a preliminary step of obtaining terahertz spectra of H$_2$O clusters isolated in a CH$_4$ matrix.

The apparatus for terahertz spectroscopy is composed of a Fourier transform infrared (FTIR) spectrometer, a liquid-helium-cooled silicon bolometer detector, and a stainless steel sample chamber equipped with a continuous-flow helium cryostat. The chamber was evacuated to ultra-high vacuum condition by two turbo molecular pumps and a diaphragm pump connected in series. The whole optical path was pumped out to high vacuum condition. Samples were prepared on a gold plate mounted on the bottom of the cryostat. Terahertz spectroscopy was performed in the reflection configuration with the incident angle of 80°. The far infrared light emerging from the FTIR spectrometer entered and exited the chamber through diamond windows sealed by Viton O-rings.

We observed terahertz spectra of polycrystalline H$_2$O ice at 150 K and amorphous CH$_4$ at 10 K. The former spectrum showed one broad band located near 300 cm$^{-1}$ whose linewidth was about 30 cm$^{-1}$. This band is likely to be attributed to the purely translational modes of H$_2$O.$^4$ In the latter spectrum, we found a broad band extending from 140 to 320 cm$^{-1}$. Similar bands have been reported in a study of phase II solid CH$_4$ at 12 K.$^5$ We will discuss the origins of these bands in detail.

References

FTIR spectroscopy of CH₄-D₂O complex trapped in Ar matrices

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Understanding of the interaction between methane and water molecules is important to elucidate various chemical reactions in the atmosphere and interstellar environment. The complexes of CH₄ and H₂O have been investigated mainly in gaseous phase using far-infrared spectroscopy¹ and microwave one². On the other hand, there have been no spectroscopic investigation in mid-infrared region. In the present study, we measured mid-infrared absorption spectra of solid Ar doped with CH₄ and D₂O, and investigated the concentration- and temperature-dependence of the spectrum.

The measurements were carried out in an ultrahigh vacuum (UHV) chamber equipped with a gas handling system, a Fourier-transform infrared spectrometer, and an external HgCdTe detector. The base pressure of the UHV chamber was 1 × 10⁻⁸ Pa. The gas mixture of CH₄, D₂O, and Ar was prepared in the gas handling system and was dosed onto a gold substrate at 5.6 K. The infrared absorption spectra were recorded at a resolution of 1 cm⁻¹ in reflection configuration with the incident angle of 80°.

Figure 1(a) shows the infrared spectrum of D₂O in an Ar matrix at 5.6 K. The peak at 2770 cm⁻¹ is due to the asymmetric stretch (ν₃) of non-rotating (nr) D₂O monomer. The peaks at 2759, 2782, and 2793 cm⁻¹ are attributed to the ν₃ rovibrational transitions of D₂O with the changes of the rotational quantum number, 1₀₁→0₀₀, 0₀₀→1₀₁, and 1₀₁→2₀₂, respectively. As shown in Fig. 1(b), a new band appeared at 2776 cm⁻¹ when CH₄ was added. The intensity of this band varied reversibly with the temperature, just like the ν₃ rovibrational bands of D₂O. We tentatively assigned this new peak to the ν₃ rovibrational transition of D₂O complexed with CH₄.

In the presentation, we will discuss the reliability of this assignment and the intermolecular interaction between D₂O and CH₄ taking into account the temperature dependence of the spectrum and the comparison with the vibrational frequencies of the CH₄-D₂O complex isomers obtained by ab initio calculation.

![Infrared spectra of D₂O and CH₄ in Ar matrices at 5.6 K, with the different CH₄/D₂O/Ar concentration ratios. (a) 0/10/3000, (b) 15/1/3000. The solid arrow indicates the peak at 2776 cm⁻¹.](image)

Analysis of near-IR laser-induced fluorescence spectra of NiD

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We have recorded NiD fluorescence following excitation of $B^2\Delta_{5/2}$ or $F^2\Phi_{7/2}$ states by a cw dye laser operating around 17100 or 18100 cm$^{-1}$. NiD is formed in a sputter source1 with a flow of 5% $D_2$ in Ar (commercial mix) operating at ~ 1 Torr. Collisional energy transfer (much less efficient than in NiH$^+$) populates many of the $\Omega'$=3/2 states reported by Kadavathu et al. Emission from these locates low-lying vibrational levels of the $X_1^2\Delta_{5/2}$, $X_2^2\Delta_{5/2}$ and $W_1^2\Pi_{3/2}$ states. The $\Omega''$=3/2 states have irregular vibrational separations. They have been labeled according to energy level predictions from an isotopically scaled 'supermultiplet' model4 for NiH, whose output is in good agreement with ab initio predictions from Marian5. The e/f splittings in the lower $^2\Delta_{5/2}$ state are in large excess of 'normal' $\Lambda$-doubling, and are proving difficult to model without direct observation of the $^2\Sigma^+$ component of the NiD(3d$^9$)D$^+$ supermultiplet. We will report on this analysis, which is still in progress.

Fig. 1: Transitions seen in dispersed fluorescence in NiD. Laser excited Q(2.5) 1-0 B-X.

References

**Ab Initio and Relativistic DFT Calculations of Spin-rotation and NMR Shielding Constants in CH$_3$Br and CH$_3$I**

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The relativistic effects on the spin-rotation constants $C_x$ and NMR shielding constants $\sigma$ have been investigating by *ab initio* coupled cluster (CCSD(T)) method and four-component relativistic density functional theory (DFT). To determine the precise relativistic effects of $C_x$ and $\sigma$ several different basis sets, number of electrons and different functionals have been taken into account. Due to the absence of a microwave experimental data for equilibrium geometry of CH$_3$Br, the calculations have been based both on high accurate *ab initio* and available experimental data.