

DFT and TD DFT modeling of vibrational structures in high resolution MATI and REMPI spectra of chromium bisarene complexes

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Together with metallocenes, metal bisarene derivatives play key roles in both fundamental and applied organometallic chemistry because of their relevance for theoretical and experimental studies of metal–ligand bonding, organic synthesis, catalysis, metal-containing polymers, biomedicine and nanoelectronics. New insights into their electronic structures are provided by the high-resolution laser spectroscopic techniques exploring resonance enhanced and threshold ionization processes. The mass-analyzed threshold ionization (MATI) spectra of chromium bisarene complexes (C₆H₆–nRn)(C₆H₆–mRm)Cr (R = Me, Ph; n, m = 0–3) show complicated vibrational structures arising mainly from skeletal and CH modes. The DFT calculations of the Franck–Condon intensities at the B3P–W91/6–311++G(d,p) level of theory appear to reproduce very well the experimental high-resolution MATI spectra of the complexes with benzene, toluene, xylenes and biphenyl. The DFT modeling makes it possible to interpret the dependence of the MATI vibrational structures on the nature, number and location of the substituents in the rings. This is especially important for the sandwich systems bearing substituents in both ligands since these molecules form several rotational isomers [1, 2]. The new assignments of the MATI peaks to individual conformers are presented.

Another type of DFT modeling concerns vibronic structures of the REMPI spectra of bis(benzene)chromium and its deuterated derivatives. These structures correspond to the lowest Rydberg px,y transition. The R4px,y state is degenerate and the REMPI spectra reveal components arising from the Jahn–Teller active e2g vibrations [3]. To model the vibronic structures one needs to optimize the excited-state molecules and calculate the Rydberg vibrational frequencies. The latter task is extremely computationally expensive when using the TD DFT approach though the B3LYP/6–311++G(d,p) and BPW91/6–311++G(d,p) levels of theory provide a good agreement with the experiment. The much simpler variants of the REMPI simulations with use of the TD DFT Rydberg–state geometries and the Hessian obtained by stationary DFT with the ground-state neutral or cation wavefunction appear to give similar pictures. This can be explained by similarities in the bis(benzene)chromium Rydberg vibrational frequencies and those of ground-state (C₆H₆)₂Cr⁰ and (C₆H₆)₂Cr⁺ (both Rydberg transition and ionization involve the chromium non-bonding 3d_{z²} electron). The approaches developed in the present work will be employed for further prediction of the vibronic structures in high-resolution electronic spectra of other sandwich compounds.

Acknowledgements

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Vibronic emission spectroscopy of *o*-Ethynylbenzyl radical generated from corona discharge of *o*-Ethynyltoluene

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Whereas benzyl radical, a prototype of aromatic free radicals, had attracted much attention from spectroscopists for the subject of large molecular radicals,¹ alkyl-substituted benzyl radicals have been less studied, presumably due to the difficulties associated with production in corona discharge from precursors. Nevertheless, several alkyl-substituted benzyl radicals^{2,3} have been identified through the analysis of the vibronic emission spectra observed from the corona discharge of precursor molecules.

The *o*-ethynylbenzyl radical was generated from the corona discharge of precursor *o*-ethynyltoluene seeded in a large amount of carrier gas helium using a technique of corona excited supersonic expansion (CESE) coupled with a pinhole-type glass nozzle which has been well developed in this laboratory. The emission from the jet-cooled but vibronically excited radicals was recorded with a long-path monochromator in the visible region.

The vibronic spectrum observed was analyzed to determine the position of the origin band of the $D_1 \rightarrow D_0$ transition and identify the species generated in corona discharge by assigning the vibronic bands to the vibrational modes in the ground state.

The electronic transition of the *o*-ethynylbenzyl radical exhibits a large red-shift of the origin band with respect to the parental benzyl radical at $22,002\text{cm}^{-1}$, rationalizing the extension of π electron delocalization to ethynyl group which is conjugated to the benzene ring. The vibronic assignments of the bands clearly confirm the observation of the *o*-ethynylbenzyl radical in this experiment.

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High resolution study of CH₂=CD₂ molecule: line intensities and half-widths

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Present work is the next step in our study of high resolution spectra of the CH₂=CD₂ molecule [1–2]. Here we introduce the results of the line intensities and half-widths analysis in the region of 1400–1650 cm⁻¹.

The absorption spectra of CH₂=CD₂ in the region of 1400–1650 cm⁻¹ were recorded with a Bruker IFS 120HR FTIR spectrometer at the Technische Universität Braunschweig (Germany) under various conditions. Spectra assignment as well as the results of the ro-vibrational analysis were presented at HRMS–2017 [3].

Individual line strengths were determined from the fit of the line shapes using Hartmann–Tran profile. As to the line half-widths, a multi-spectrum fitting procedure with the Hartmann–Tran profile of lines was used, so self-broadening coefficients were obtained by fitting the measured line shapes recorded at various pressures.

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The classification of lung cancers and their degree of malignancy by FTIR, PCA–LDA analysis, and a physics–based computational model

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Lung cancer has the highest mortality rate of all malignant tumours. The current effects of cancer treatment, as well as its diagnostics, are unsatisfactory. Therefore it is very important to introduce modern diagnostic tools, which will allow for rapid classification of lung cancers and their degree of malignancy. For this purpose, the authors propose the use of Fourier Transform InfraRed (FTIR) spectroscopy combined with Principal Component Analysis–Linear Discriminant Analysis (PCA–LDA) and a physics–based computational model. The results obtained for lung cancer tissues, adenocarcinoma and squamous cell carcinoma FTIR spectra, show a shift in wavenumbers compared to control tissue FTIR spectra. Furthermore, in the FTIR spectra of adenocarcinoma there are no peaks corresponding to glutamate or phospholipid functional groups. Moreover, in the case of G2 and G3 malignancy of adenocarcinoma lung cancer, the absence of an OH groups peak was noticed. The PCA–LDA analysis of differences in chemical compositions derived from selected FTIR spectral regions corresponding to protein and lipid vibrations. These IR ranges were used for all spectra obtained (control and cancers). The significantly distinct morphological areas were spectroscopically discriminated using unsupervised exploratory PCA. Therefore these areas can be analysed separately to determine the biochemical markers that differentiate control tissues, as well as cancerous lung tissues. Moreover, sensitivity and specificity were calculated not only for PCA–LDA results for healthy tissues and each type of cancer but also for every sample of each. These results produced information where, by using sensitivity and specificity, it is possible to distinguish not only between cancerous and non-cancerous tissues but also to identify different stages of the same cancerous tissues. Our results showed that the sensitivity of our model is between 78% and 99%, and the specificity between 65% and 99%. Summarizing, it seems that FTIR spectroscopy is a valuable tool to classify lung cancer and to determine the degree of its malignancy.

Spectroscopy Group at the University of the Basque Country

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The structural elucidation of molecular systems is a vastly explored aspect of science, as evidenced by the wide variety of techniques devoted to the task. In particular, high-resolution gas phase spectroscopy is able to unveil subtle structural and dynamical effects directly related to the chemical physical properties exhibited by a system, by isolating it from interactions with solvent or crystal packing. Moreover, by coupling these techniques with supersonic expansions, we can access the native conformational and aggregation preferences of molecules and intermolecular complexes.

The Spectroscopy Group at the University of the Basque Country (UPV/EHU) and the Biofísica Institute (CSIC-UPV/EHU) has built several microwave spectrometers. In our group, we have a chirped-pulsed FT-microwave spectrometer (CP-FTMW) equipped with a customized multi-valves system,[1] and a cavity based FT-MW spectrometer coupled with an UV ultrafast laser vaporization system.[2,3] Both set-ups are cutting-edge in the field of microwave spectroscopy. In addition, the Spectroscopy Group has strong collaborations with Prof. Corzana (Universidad de la Rioja), Dr. Çarçabal (Institut des Sciences Moléculaires d'Orsay) and Dr. Fernández (Universidad del País Vasco). These interdisciplinary collaborations allow us to investigate different biological and astrophysical topics since they grant us access to custom-made samples and various instrumentations and methodologies.

In order to illustrate our strategy, we present recent results focused on solving various structural problems of Chemistry at the molecular level. In particular, the conformational landscape of large clusters and biomolecules, including sugars, glycopeptides and drugs have been studied by our group recently.[3-6]



Figure. Microwave facilities available in Dr. Cocinero's Group at the University of the Basque Country (UPV/EHU).

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Spectroscopic characterization of the unsaturated Hydrocabons C_3H and C_5H using highly correlated ab initio methods

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Unsaturated carbon chains and hydrocarbons can play important roles in the chemical evolution of the interstellar sources. They can be considered as building blocks of large carbon species. Charged chains are reactive species that can participate in many chemical processes at low temperatures.

We present state-of-the-art ab initio calculations focused to the determination of equilibrium structures and spectroscopic parameters corresponding to various electronic states of the C_3H and C_5H chains containing an odd number of carbon atoms. Both species C_3H and C_5H present various isomers that can be linear or cyclic forms. All of them show non-zero dipole moments that can help their identification. Some of them are relatively stable structures.

Because, astronomers have dedicated special attention to the charged species during the last years, calculations of cations and anions are also provided. For all the cases, neutral, negative and positive charged species, excitations to the low electronic states are determined. We provide electron affinities and ionization potentials. Spin-orbit effects are predicted. The employed methodology was first used to describe other carbon chains containing even number of atoms [1-3]

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Broadening and shifting coefficients of rovibrational lines of HCl perturbed by He in the fundamental and the first overtone regions

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We present new data obtained using a modern high-resolution FTIR technique on He-broadening and shifting coefficients for the spectral lines for the fundamental and the first overtone vibration-rotation absorption bands of the HCl molecule. [1]

The both bands were recorded simultaneously by using a 20 cm stainless cell with sapphire windows and a Bruker IFS 125HR Fourier spectrometer with a resolution of 0.007 cm⁻¹. The pressure of He was kept in the range of 1–5 atm. Resulting 47 spectra allowed us to evaluate the line parameters in a large interval of J : $J_{\max} = 15$ for the fundamental band and $J_{\max} = 11$ for the overtone band. Most of the values, especially for the overtone transition, are novel.

All observed rovibrational lines have hypsochromic (blue) shift, which is a typical behavior upon collisions with helium. We did not register any statistically significant difference between the broadening and shift coefficients for H³⁵Cl and H³⁷Cl within our experimental uncertainty. The results are compared with existing literature values, the data for other hydrogen halides perturbed by helium [2] and HCl in mixture with other collision partners [3–6].

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Predissociation of the B state of S₂: measurements and modeling

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Photoabsorption cross sections for the strong, predissociating vibrational bands, $v > 10$, in the S₂ B ${}^3\Sigma^-_u - X {}^3\Sigma^-_g (v,0)$ system were measured in a radio-frequency discharge through H₂S seeded in helium and in a two-temperature sulfur furnace, at temperatures of 370 K and 823 K, respectively. S₂ column densities were determined in each source by combining experimental line strengths in low- v non-predissociating B – X bands ($v < 7$) with calculated line f -values based on measured radiative lifetimes and calculated branching ratios. The broad-band capabilities of two vacuum-ultraviolet Fourier-transform spectrometers allowed for simultaneous recordings of both non-predissociating and predissociating bands, thus placing the predissociating-band cross sections on a common absolute scale. The bands studied ($11 \leq B(v) \leq 27$) exhibit varying degrees of diffuseness, with corresponding predissociation line widths ranging from 4 cm⁻¹ to 60 cm⁻¹. The experimental cross sections and measured line width patterns are used to inform a coupled-channel Schrödinger-equation model of predissociation in the B ${}^3\Sigma^-_u$ state of S₂. Just as in the analogous case of O₂, the B(v)-state predissociation in S₂ is caused principally by spin-orbit interactions with ${}^3\Pi_u$, ${}^1\Pi_u$, ${}^5\Pi_u$, and ${}^3\Sigma^+_u$ states. An inner limb crossing with B'' ${}^3\Pi_u$ is responsible for the predissociation of B($v = 11$) and provides a significant, slowly-varying contribution for B($v > 11$). Outer crossings with the ${}^1\Pi_u$, ${}^5\Pi_u$, and ${}^3\Sigma^+_u$ states are responsible for oscillatory contributions to the predissociation widths, with first peaks at $v = 13, 20$, and 24 , respectively, with the ${}^5\Pi_u$ contribution dominant.

Resonant two-photon ionization and mass-analyzed threshold ionization spectroscopy of 2,4-Difluoroanisole

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We report the vibronic and cation spectra of 2,4-difluoroanisole (24DFAN), recorded by using the resonant two-photon ionization and mass-analyzed threshold ionization spectroscopic techniques. The band origin of the $S_1 \leftarrow S_0$ electronic transition of 24DFAN appears at $35556 \pm 2 \text{ cm}^{-1}$; and the adiabatic ionization energy is determined to be $67568 \pm 5 \text{ cm}^{-1}$. The cation spectra were recorded by ionizing via the 0^0 , X^1 , τCH_3 , 15^1 , $9a^1$, and $6a^1$ levels in the electronically excited S_1 state. This allowed us to investigate the change in molecular geometry upon ionization and to detect more active vibrations of the cation.

The spectral assignment was made by comparing the present experimental data of 2,4-difluoroanisole with those of anisole, 2-fluoroanisole, and 4-fluoroanisole, 3,4-difluoroanisole, 2,4-difluorophenol and 2,4-difluoroaniline and the predicted values from the B3PW91/6-311++G(d,p) calculations. The observed active vibrations of 24DFAN in the S_1 and cationic ground D_0 states include methyl torsion, substituent-sensitive out-of-plane and in-plane ring bending and deformation modes. Comparison of the present data with those of fluorine substituted anisole, phenol, and aniline reveals the effect of fluorine substitution and additivity rule on electronic transition and molecular vibration. This enables us to have insights into ring-substituent and through-space substituent-substituent interactions.

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High precision spectrum of the second overtone of $^{12}\text{C}^{16}\text{O}$

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CO is the second most abundant molecule in the universe. Precise spectrum of the carbon monoxide molecule is great importance in astrophysical observation and in the test of the quantum chemistry model. Thirty-nine ro-vibrational transitions of $^{12}\text{C}^{16}\text{O}$ in the second overtone band were measured by a comb-locked cavity ring-down spectrometer [1]. The line positions were determined with sub-kHz accuracy, or relatively 10^{-12} level. Improved molecular constants were obtained for the ground and second-overtone vibrational states. The calculated pure rotational line positions agree with the experimental values recorded by lamb-dip spectrometer within the experimental uncertainties. By comparing the calculated and experimental results, we present perspectives of the precision spectroscopy of the carbon monoxide molecule in the determination of the atom mass of ^{17}O by the Dunham-Watson model with first-order Born-Oppenheimer breakdown parameters.

CO₂-broadening and shift coefficients in the ν_3 and $\nu_2+(\nu_4+\nu_5)^0$ bands of acetylene

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The absorption spectra of the mixture of C₂H₂ and CO₂ at different partial pressures of both gases have been recorded at room temperature in the 3 μm region using the Bruker IFS 125 HR FTIR spectrometer. The multispectrum fitting procedure has been applied to these spectra to recover the broadening and shift parameters of the acetylene spectral lines. The CO₂ broadening and pressure induced shift coefficients for 119 lines of the ν_3 and $\nu_2+(\nu_4+\nu_5)^0$ bands of acetylene have been derived. The rotational dependence of the values of these coefficients is discussed. The comparison of the obtained coefficients to those published by other authors for the ν_3 and $\nu_2+(\nu_4+\nu_5)^0$ bands is performed.

The *ab initio* line–shape calculations for purely rotational transitions in the CO–N₂ system

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Collisional line–shape effects play an important role in optical spectroscopy. Molecular collisions manifest as a perturbation of the optical line shapes. Proper treatment of these effects is important to reach high accuracy in spectroscopy–based optical metrology [1,2]. The CO–N₂ system is of particular importance for terrestrial atmospheric measurements. Here we report the first line–shape parameters for this system based on quantum scattering calculations performed on an accurate *ab initio* potential energy surface (PES) [3].

The four–dimensional PES [3], with the interatomic distances in N₂ and CO set to the experimental values (1.09768 and 1.128323 Å, respectively [4]) is used. The interaction energies are calculated with the coupled–cluster CCSD(T) method and Dunning’s aug–cc–pVQZ basis set extended further with midbond functions for more than 10 100 *ab initio* points, corresponding to 12 values of θ_{N_2} , 13 values of θ_{CO} in a range of 0–180°, 5 values of φ in a range of 0–90° and 14 values of R in a range of 4–40 a₀. The calculated PES is expanded over bispherical harmonics [5] leading to 205 radial coupling terms. The close–coupling equations are solved for a wide range of kinetic energies using the MOLSCAT code [6]. The calculations of generalized spectroscopic cross sections are performed for several purely rotational lines from the R branch. Finally, the standard pressure broadening and shifting coefficients are obtained. The data provided through this investigation can be used for upgrading the HITRAN database [7] and the HITRAN Application Programming Interface (HAPI) [8].

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Spectroscopic study of the $7^1\Pi_u$ and $7^1\Sigma_u^+$ states of Rb_2 molecule

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Rubidium dimers are relatively easy to produce and observe experimentally but difficult for theoretical description, with a total of 74 electrons making in particular all–electron ab–initio treatment ineffective. Yet surprisingly, the theoretical knowledge of excited electronic states of this molecule is to date considerably larger than information provided by experiments [1]. To fill the gap between theory and experiment and to test the quality of theoretical description in the range of excitation energies close to the limits of calculations, we investigated two highly excited electronic states of Rb_2 , $7^1\Pi_u$ and $7^1\Sigma_u^+$.

Both states were observed in excitation spectra through transitions from the ground $X^1\Sigma_g^-$ state of rubidium dimer, using two–laser polarisation labelling spectroscopy technique [1]. Vapour containing Rb_2 molecules was produced by heating metallic rubidium (natural isotopic composition) to about 500 K in a heat–pipe oven in a presence of a few Torr of argon buffer gas. The spectra were recorded in the region 27000 – 29400 cm^{-1} with both resolution and accuracy slightly better than 0.1 cm^{-1} . In this region we identified more than 800 transitions to the $7^1\Pi_u$ state and 400 transitions to the $7^1\Sigma_u^+$ state, the frequencies of which were converted to energies of rovibrational levels in both states using the precisely known molecular constants of the ground state [2]. Observation cover the lowest 47 and 21 vibrational levels in the $7^1\Pi_u$ and $7^1\Sigma_u^+$ states, respectively. The spectroscopic parameters and potential energy curves for both states will be presented and compared with the state–of–the–art theoretical predictions.

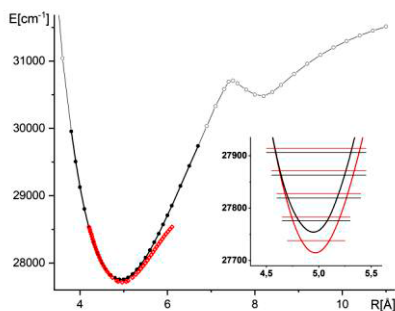


Figure caption: The experimental potential curves of the electronic states of Rb_2 investigated in this work: the RKR curve for the $7^1\Sigma_u^+$ state (red diamonds) and the pointwise IPA curve for the $7^1\Pi_u$ state (black circles connected with solid line). Open circles denote points of the potential virtually unaffected by the experimental data. The inset displays relative position of the lowest vibrational levels of both states (for $J=0$), illustrating why no strong interaction between both states have been observed despite the apparent similarity of their potential curves.

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The $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ absorption spectra at 296 K and 200 K in the range between 6600 and 12000 cm^{-1}

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The $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ absorption spectra in the range between 6600 and 12000 cm^{-1} have been recorded at 296 K and 200 K by the Fourier spectrometer IFS – 125M at pressures from 11 to 300 mbar, and spectral resolution 0.03 cm^{-1} . Multi-pass cell with a length of 60 cm and 44 passes was used, which provided the pathlength of 2640 cm and threshold sensitivity to absorption of the order of 10^{-8} cm^{-1} . Empirical values of the lower state energy level were derived from the intensity ratios of the lines measured at 200 K and 296 K. Line assignment of the $\nu_2+2\nu_3$ band of the $^{13}\text{CH}_4$ molecule and the $3\nu_3$ band of the $^{12}\text{CH}_4$ molecule was performed. The parameters of Voigt contour (the line center, intensity, self-broadening coefficient and self-shift coefficient) were determined using multi-fitting procedure at 296K.

The work partly was supported by the Russian Scientific Foundation (Grants N^o 17-17-01170).

Study of hydrates of verbenone by microwave Fourier transform spectroscopy and computational chemistry

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The first studies of hydrates of aldehydes and ketones were performed by Lovas and Lugez on the formaldehyde - water system in 1996 [1] and by Melandri et al. in the cyclobutanone - water system in 2005 [2]. More recently, Pérez et al. investigated the interaction of water with camphor [3]. They were able to characterize a trihydrate constituted by a chain of three water molecules around the camphor molecule. We present here our results on the verbenone - water system. Verbenone is a bicyclic ketone, with an intracyclic carbon - carbon double bond conjugated with the carbonyl moiety. It could be interesting to investigate if the delocalization of p -electrons within verbenone influences or not the formation of hydrates.

The rotational spectrum of verbenone being already known [4], we started with the study of the hydrates. The structures of two monohydrates, two dihydrates and four trihydrates of verbenone were optimized at the DFT B3LYP-D3BJ / def2-TZVP and *ab initio* MP2 / 6-311++G(d,p) levels. Experimentally, a gas mixture of verbenone - water - neon was expanded into the cavity of a Balle-Flygare type Fourier transform microwave spectrometer operating in the 2 - 20 GHz frequency range. Scanning around the predicted frequencies of each hydrate, we were able to find the spectral signatures of the two mono- and two dihydrates, and of the lowest energy conformer of the trihydrate. A similar study replacing normal water by ¹⁸O labeled water allowed the identification of the spectra of all possible isotopomers, leading to the calculation of the substitution coordinates of water oxygen atoms, and of the effective structure of the water molecules arrangements around verbenone. A comparison of our results with those obtained by Pérez et al. on camphor is presented.

The present work was funded by the French ANR Labex CaPPA through the PIA under contract ANR-11-LABX-0005-01, by the Regional Council Hauts de France, by the European Funds for Regional Economic Development (FEDER), and by the French Ministry of Higher Education and Research. It is a contribution to the CPER research Project CLIMBIO.

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Study of the H₂O–N₂ line broadening and shifting in the region of 16500–17000 cm⁻¹

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The broadening of the spectral lines of water vapor by air and nitrogen pressure is of great interest for various atmospheric problems. The spectra have been recorded with a spectral resolution of 0.05 cm⁻¹ by a Fourier transform spectrometer using high luminance LED light source. A high signal-to-noise ratio ($S/N \approx 10\,000$) permitted to analyze the lines with intensities of 1.54×10^{-23} to 2.0×10^{-26} cm/molecule. The N₂-broadening and shifting coefficients of the water vapor lines in the region of 16600–17000 cm⁻¹ were obtained using multi-spectrum fitting. The results of the measurements are compared with calculations using the semi-empiric method, which is based on the impact theory of broadening, and includes the correction factors whose parameters are determined by fitting the broadening coefficients to the experimental data. The method is further developed by using anharmonic wavefunctions in the estimates of line profiles. This approach explicitly takes into account all scattering channels induced by collisions. In principle, the use of the accurate wave functions, obtained from global variational calculations, extends the applicability of the method up to dissociation energy of molecule.

The work was supported by the Russian Foundation for Basic Research (Grants No. 16–43–700492, 17–52–16022_a).

Rotational–predissociation double resonance spectroscopy of the He–HCO⁺ complex

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Cation–Helium complexes are interesting spectroscopic systems due to the floppy bond of the helium atom. He–HCO⁺ is a particularly prominent test system, as it is linear and has a ¹Σ ground state.

So far experimental data have been limited to infrared studies on the ν₁ C–H stretching mode of He–HCO⁺ [1].

In this work, we present for the first time high–resolution rotational data for this complex, applying a novel rotational–predissociation double resonance method.

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Combined PGOPHER analysis of bands in the 1st positive system of N₂, 4500 – 15500 cm⁻¹

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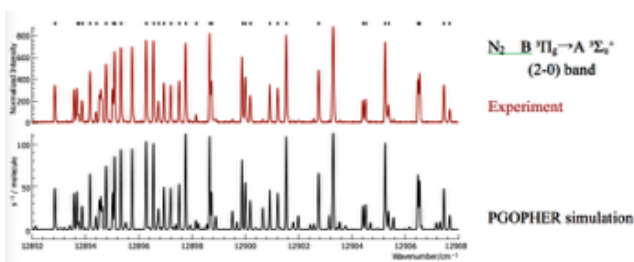
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Boesch and Reiners recently pointed out [1] that spectral line lists for nitrogen gas could provide useful wavelength calibration for high-resolution astrophysical spectrographs. Boesch and Reiners recently pointed out [1] that spectral line lists for nitrogen gas could provide useful wavelength calibration for high-resolution astrophysical spectrographs. They recorded and reported extensive spectra in the infrared 4500–11000 cm⁻¹, revisiting notably the first positive system of N₂ (A³Σ_u⁺ – B³Π_g, B¹Σ_u⁻ – B³Π_g and W³Δ_u – B³Π_g), and the Meinel bands of N₂⁺, since there is no electronic record of spectra recorded in the late 1970's [2,3]. Working at slightly shorter wavelengths with an intracavity experiment designed to study discharge-formed species, we saw lines of the first positive bands of N₂ in absorption as impurity contributions, and realized that N₂ can provide spectral calibration for the Ti:sapphire based Vernier frequency-comb spectrometer [4]. We therefore recorded a new FT 'reference' N₂ emission spectrum. This spectrum (nominal resolution 0.023 cm⁻¹) was corrected for instrumental intensity response, and is available in ascii format.

The N₂ bands recorded in [1] have been analysed together with this spectrum using the PGOPHER program [5], providing constants for the A³Σ_u⁺, B³Π_g, B¹Σ_u⁻ and W³Δ_u states, automatically rejecting blends to optimize parameter reliability. Final parameters are consistent with those reported in refs [2,3], but better defined, and from a more standard Hamiltonian. They allow a reference spectrum to be constructed for different conditions (temperature, lineshape, resolution), if the raw, Doppler-limited measurements are unsuitable for comparison. The figure below shows part of the N₂ emission spectrum, compared with PGOPHER simulation. The tick marks at the top of the plot indicate transitions retained (by automatic selection) in the fit. Note that the excluded transitions – including some strong features – are also well modeled.



Keywords: Astrophysics/Atmospheric VIS/UV Gas Phase/jets Small molecules

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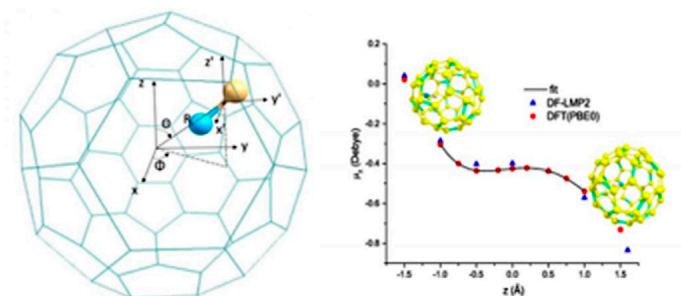
Properties of HF@C₆₀ endofullerene from first principles

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Endofullerenes, fullerenes with an atom or molecule inside, have attracted significant attention during the past decade [1, 2]. Of particular interest is small dipolar molecules inside the buckyballs. The materials composed of such systems could have ferroelectric properties. We have chosen to study HF@C₆₀ system (Fig. 1), first synthesized in 2016 using “molecular surgery” [3] technique. The potential energy (PES) and dipole moment (DMS) surfaces for the case of I_h symmetry of C₆₀ (rigid cage) were obtained based on *ab initio* and DFT computed data (see Fig. 2 for example computation of dipole moment). The cc-pVTZ basis set was employed throughout the work. Using these PES and DMS of HF@C₆₀ we were able to compute translation-rotation energy levels and molecular polarizability (temperature-dependent). Also, a model potential was suggested that takes into account the splitting of j=1 rotational level of HF. This splitting was observed in experiment [3].



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High sensitivity Cavity Ring Down Spectroscopy of the $\nu_1+4\nu_3$ band of NO_2 near $1.34\ \mu\text{m}$

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The very weak $\nu_1+4\nu_3$ B-type absorption band of nitrogen dioxide ($^{14}\text{N}^{16}\text{O}_2$) is newly detected by high sensitivity continuous wave-cavity ring down spectroscopy between 7376 and $7550\ \text{cm}^{-1}$. The noise equivalent absorption of the recordings is $\alpha_{\text{min}} \gg 1 \times 10^{-10}\ \text{cm}^{-1}$. The $\nu_1+4\nu_3$ band is the highest energy B-type absorption band of NO_2 detected so far by absorption within the ground electronic state. More than 500 lines are assigned with rotational quantum numbers N and K_a up to 50 and 7, respectively, what corresponds to 1117 spin-rotation-vibration transitions. No resonance perturbation of the spectrum was evidenced. The fitted set of the effective Hamiltonian parameters reproduces the observed line positions with an *rms* of $3.7 \times 10^{-3}\ \text{cm}^{-1}$. A selected set of the measured line intensities are used to determine the effective dipole moment parameters including the Herman-Wallis type parameters describing the line intensities of this band. The *rms* deviation of the fit is 15.24%.

Laser absorption spectroscopy of methane at 1000 K between 1.75 and 1.3 μm

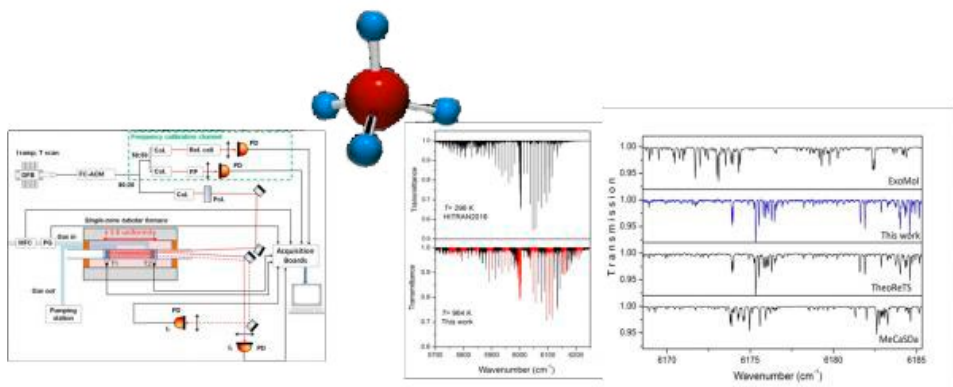
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A tubular furnace is combined with a diode laser spectrometer to record the high temperature near infrared absorption spectrum of methane at a pressure of 80 Torr. The investigated spectral range covers the 5693–6257 cm^{-1} range of the tetradecad dominated by the $2\nu_3$ band near 6000 cm^{-1} [1] and the icosad between 6800 and 7700 cm^{-1} . The spectra were recorded at 523 K and 773 K in both regions and additionally at 964 K in the tetradecad region. At 964 K, lines with intensity larger than 5×10^{-24} $\text{cm}^2/\text{molecule}$ were measured.

As a result of the high temperature, high- J rovibrational transitions up to $J \approx 20$ and hot bands are identified in the spectrum. The recorded spectra provide tests of various methane line lists recently released in the literature: HITRAN2016, experimental list derived from emission spectra, the MeCaSDa empirical line list and the TheoReTs and ExoMol theoretical line lists. Overall, the agreement with the TheoReTs line list is found to be very good, in particular in the tetradecad region.



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Double resonance rotational spectroscopy of $\text{CH}_3^+ - \text{He}$

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A new double resonance method combined with cryogenic trapping is applied to the $\text{CH}_3^+ - \text{He}$ system. For this purpose, the ions are trapped in a 22-pole ion trap, cooled down to 4 K and are exposed to two radiation sources. On double resonance, a mm-wave leads to excitation into a rotationally excited state followed by IR vibrational excitation into a dissociative state. The vibrational spectra of the C-H stretching motions ν_1 and ν_3 have been recorded and used for predissociation. In total, 24 *P* and *R* branch transitions are resolved for the antisymmetric band (ν_3) and ten partly resolved features are measured for the symmetric band (ν_1). Both spectra show perturbations which seem to be characteristic for these complexes. The pure rotational ground state transitions are highly resolved ($\sigma \sim 3$ kHz), revealing unexpected splittings for the $K = 1$ transitions. This splitting is most probably given by the large amplitude motion of the Helium atom.

The absorption band of nitrogen dioxide ($^{14}\text{N}^{16}\text{O}_2$) by CRDS near 6000 cm^{-1}

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The high resolution absorption spectrum of the NO_2 molecule is recorded between 5800 and 6000 cm^{-1} by high sensitivity cavity ring down spectroscopy (CRDS). Positions and intensities in the range from 2×10^{-28} to $4 \times 10^{-23}\text{ cm/molecule}$ are derived from the line profile fitting for more than 7500 lines. The spectrum is dominated by the transitions of the $103\text{-}000$ vibrational band centered at 5984.704 cm^{-1} . The spectrum is assigned and modeled using an effective Hamiltonian which explicitly takes into account a spin-rotational interaction and interaction of the (103) bright state with three "dark" states: (122) , (080) and (410) . The n_1+3n_3 band was already analyzed by Fourier transform spectroscopy in Ref. [1], where resonance interactions between the (103) state and the (122) , and (080) "dark" states at 5898.940 and 5965.610 cm^{-1} , respectively – were taken into account. More than 3000 lines are presently assigned with rotational quantum numbers N and K_a up to 57 and 13 , respectively (In Ref. [1], 1147 transitions were identified with maximum N and K_a values of 47 and 8 , respectively). The measured line positions are reproduced with an *rms* of 0.0024 cm^{-1} by variation of 39 parameters of the effective Hamiltonian. About 80 transitions reaching the highly excited (080) bending upper state and borrowing their intensity from the resonance coupling with the $103\text{-}000$ band were assigned for the first time. The main parameters in the transition moment series are determined for the (103) vibrational state from the fitting of the measured intensities and the detailed synthetic spectrum is generated.

P1.23.

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Isolated small-amplitude fundamental embedded in a pure torsional bath: assignment and fit of the FIR and microwave spectra of the ν_{10} vibrational state of acetaldehyde.

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We present results of our analysis of the FIR spectrum of the ν_{10} vibrational state of acetaldehyde near 509 cm^{-1} . The analysis of the 509 cm^{-1} band involves energy levels that belong to the $\nu_t = 0, 1$ torsional states of the ν_{10} vibrational state and is accompanied by the assignment of microwave spectra of the $(\nu_{10}, \nu_{15}) = (1,0), (1,1), (0,3), (0,4)$ states of acetaldehyde, where the ν_{15} state corresponds to large amplitude torsional vibration in the molecule. The analysis employs a new program which was recently developed for fitting several isolated small-amplitude fundamentals embedded in a pure torsional bath in molecules like acetaldehyde, in which the frame has C_s symmetry and the methyl top has C_{3v} symmetry. In the fit the new assignments of the transitions with J up to 50 are combined with data available in the literature for the $\nu_t = 0, 1, 2, 3, 4$ torsional states of the molecule [1,2]. Our results provide significant progress in comparison with previous fitting attempts [1] for the ν_{10} band of acetaldehyde near 509 cm^{-1} .

Acknowledgements: This work was done under support of the Volkswagen foundation. The assistance of Science and Technology Center in Ukraine is acknowledged (STCU partner project #P686).

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The high resolution spectrum of $^{14}\text{ND}_3$ in the far-infrared

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Triply deuterated ammonia is the prototype molecule of the multiply deuterated species containing nitrogen. Due to its astrophysical role, the spectroscopic characterization of its ground state (GS) and of the vibration energy patterns should be extended. The analysis of the vibration-rotation-inversion transitions from high resolution IR spectra of the $\nu_2/\nu_4/2\nu_2$ and $\nu_1/\nu_3/2\nu_4$ band systems has been reported in [1]. Recently, the pure inversion and rotation-inversion transitions in the GS [2] have been re-analyzed together with ground state combination differences from allowed and perturbation allowed ro-vibration transitions [3]. Accurate values of C , D_K and H_K constants in the s and a GS levels could be derived from the first time.

New spectra of the $^{14}\text{ND}_3$ have been recorded in the 65–1200 cm^{-1} range at an unapodized resolution of 0.00096 cm^{-1} , using the Bruker IFS 125 Fourier transform spectrometer located at the far-infrared beam line, Canadian Light Source, Saskatoon, Canada. All the spectra were recorded at 298 K using a 2 m base multi pass absorption cell, set for 8 m, with 7 Pa of sample pressure, and 72 m, with 1.3, 13 and 133 Pa of sample pressures. The high sensitivity, resolution and enhanced signal to noise ratio of the new spectra will allow the detection of weak rotation-inversion transitions of $^{14}\text{ND}_3$ in the GS and in the low lying bending excited states, $\nu_2 = 1, 2$ and $\nu_4 = 1$. Eventually, the identification of very weak $\Delta J = 1$, $\Delta K = \pm 3$ $s \leftarrow s$ and $a \leftarrow a$ forbidden transitions will improve the accuracy of the K -dependent parameters. The preliminary results of this analysis will be presented.

P1.25.

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Line positions and intensities for the ν_3 band of 5 isotopologues of germane for planetary applications

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Germane (GeH_4) is present in the atmospheres of the giant planets Jupiter and Saturn. The ongoing NASA mission Juno has renewed interest in its spectroscopy. The accurate modeling of which is essential for the retrieval of other tropospheric species. We present here the first complete analysis and modeling of line positions and intensities in the strongly absorbing ν_1/ν_3 stretching dyad region near 2100 cm^{-1} , for all five germane isotopologues in natural abundance. New infrared spectra were recorded, absolute intensities were extracted through a careful procedure and modeled thanks to the formalism and programs developed in Dijon. A database of calculated germane lines, GeCaSDa, is available online through the Virtual Atomic and Molecular Data Centre (VAMDC) portal (<http://portal.vamdc.org>) and at <http://vamdc.icb.cnrs.fr/PHP/gecasda.php>. GeH4 will integrate the HITRAN database as molecule number 52.

The third and fourth torsional states of acetic acid

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Acetic acid is of intrinsic spectroscopic interest since several of its hindered internal rotation characteristics make it a well-suited molecule to test the performances of the methods applied to the analysis of internal rotation phenomena. Previous experimental investigations resulted in a thorough analysis of the $v_t = 0, 1, 2$ torsion–rotation transitions with J up to 79 and K_a up to 44[1]. In this study we present the results of investigation of the millimeter wave spectrum of the $v_t = 3$ and 4 excited torsional states of acetic acid. The data set found in the literature has been augmented by about 1900 new $v_t = 3$ and 4 transition frequencies in the 49 – 149 GHz range obtained in Kharkiv. The new measurements as well as the previous ones published earlier[1] were included in a global fit involving $v_t = 0, 1, 2, 3$, and 4 states of acetic acid. The RAM approach, successfully used in the past for this molecule, provided a weighted standard deviation of 1.2 for 17241 line frequencies using 107 parameters. In the presentation the details of this new study will be discussed.

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First detection of H_2^{36}S in the infrared region

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High-Resolution spectra of hydrogen sulfide have been measured with the Bruker IFS125HR Fourier transform Zürich prototype infrared spectrometer ZP2001, [1] which was modified to increase the optical resolution up to 0.00096 cm^{-1} . The recorded spectral region $600\text{--}5000\text{ cm}^{-1}$ have been analyzed with the GSCD method. For this purpose, rotational energy levels were obtained on the basis of microwave transitions from [2–3].

Parameters of the effective operators of the ground vibrational state were determined from the inverse problem solution.

Sample of hydrogen sulfide of 99.5% stated purity (Merck/Sigma-Aldrich AG) was taken in natural composition. For the spectra analysis of the least abundant, H_2^{36}S , isotopologue parameters of the effective Hamiltonian of ro-vibrational states, as well as, effective dipole moment parameters for corresponding bands, were predicted on the basis of isotopic substitution theory [4] and approved by extrapolation from H_2^{32}S , H_2^{33}S , H_2^{34}S isotopologues. As a result, 3 ro-vibrational bands of H_2^{36}S were analyzed for the first time.

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New electronic states in the spectra of TaH and TaD

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We have recorded electronic spectra of tantalum hydride (TaH) and deuteride (TaD) over the region 605–665 nm. The molecules were produced by sputtering tantalum in a hollow cathode source with a dilute mixture of hydrogen or deuterium in argon. The spectra were recorded by laser excitation spectroscopy at Doppler-limited resolution using a continuous-wave ring dye laser. We have identified a total of 10 different bands in TaH and 4 in TaD, all of which involve distinct excited electronic states. The various transitions originate from one of two low-lying electronic states, with $\Omega = 2$ or 0^+ .

Calculations by the Gordon group [1] and previous experimental work on the molecule in our group [2] agree that the $\Omega = 2$ state is largely derived from a $\delta^1\pi^1$, $^3\Phi_2$ state. The $\Omega = 0^+$ state, which is largely a mixture of $^3\Sigma^-$ and $^3\Pi$, is calculated to lie within 600 cm^{-1} of the $\Omega = 2$ state [1]. We are conducting dispersed fluorescence experiments with the aim of determining which of these two low-lying states is the true ground state. Preliminary results indicate the presence of a third state about 1400 cm^{-1} above the $\Omega = 2$ state, which may be the $\Omega = 1$ component of the mixed $^3\Sigma^- / ^3\Pi$ state. The various electronic states have been fitted by least-squares using a Hund's case (c) Hamiltonian. We will report term energies, rotational and centrifugal distortion constants, bond lengths and vibrational intervals for all of these states.

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Accurate first principles global calculations and isotopic effects on infrared spectra for phosphine PH₃ and hydrocarbons (CH₄, C₂H₄)

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Isotopic substitutions as H → D or even ¹²C → ¹³C have substantial consequences on molecular spectra. To interpret correctly the experimentally observed spectra of molecules in their natural abundances, it is essential to have realistic and reliable theoretical models.

There is much less information on assigned experimental spectra of rare isotopologues, particularly for the intensities. The corresponding line lists at medium spectral resolution could be provided by the *ab initio* theory and global nuclear motion variational calculations.

The aim of this work will be to study the effects of isotopic substitutions in PH₃, CH₄, and C₂H₄, on both line positions and line intensities, from nonlinear transformations and symmetry considerations. In case of phosphine we consider PH₂D, PHD₂ isotopologues [5], and ¹²C → ¹³C substituted species for the methane and the ethylene. All calculations are based on our recent *ab initio* potential and dipole moment surfaces [1, 2, 3] using variational normal mode calculations [4]. The corresponding line lists will be made available via the TheoReTS information system [6] (<http://theorets.univ-reims.fr>, <http://theorets.tsu.ru>).

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Vibrational dependence and prediction of line shape parameters for the H₂O–H₂ collisional system

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The Modified Complex Robert–Bonamy (MCRB) formalism was used to calculate the half-width, γ , and line shift, δ , for the H₂O–H₂ collision system at 14 temperatures between 200 and 3000 K for over 7 thousand rotational transitions for the rotation band, the (301)–(000) band and bands for ν_1 , ν_2 , and ν_3 with 1–4 vibrational quanta exchanged. The calculations include all complex terms, explicit velocity integration, and a potential composed of electrostatic, induction, London dispersion, and atom–atom (expanded to 20th order and rank 4) terms using the parameters of Renaud *et al.* [1], and ground state reduced matrix elements. These data were used to study the vibrational dependence of the half-width and line shift. It is shown that the H₂O–H₂ collision system is strongly off-resonance. The results demonstrate strong and unusual vibrational dependence.

The half-width and line shift data for different vibrational bands were used to develop a prediction routine for γ and δ . Following the work of Jacquemart *et al.* [2] and Gamache and Lamouroux [3], the expressions

$$\gamma[(\nu_1 \setminus \nu_2 \setminus \nu_3) \leftarrow (\nu_1'', \nu_2'', \nu_3'')]_i = I_{f \leftarrow i}^{\gamma} + A_{f \leftarrow i} (C_1 |\Delta \nu_1| + C_2 |\Delta \nu_2| + C_3 |\Delta \nu_3|)^{p_{\gamma}}$$

and

$$\delta[(\nu_1 \setminus \nu_2 \setminus \nu_3) \leftarrow (\nu_1'', \nu_2'', \nu_3'')]_i = I_{f \leftarrow i}^{\delta} + B_{f \leftarrow i} (C_1 |\Delta \nu_1| + C_2 |\Delta \nu_2| + C_3 |\Delta \nu_3|)^{p_{\delta}}$$

were used to predict the half-width and line shift where the powers p_{γ} , p_{δ} , and coefficients $I_{f \leftarrow i}^{\gamma}$, $A_{f \leftarrow i}$, $I_{f \leftarrow i}^{\delta}$, and $B_{f \leftarrow i}$ were determined by non-linear least-squares techniques. It is shown that the fits need to be made separately for bands with stretch–quanta exchanges and bend–quanta exchanges. From these fits, a prediction routine was developed that gives very reasonable results.

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Ab initio reduced matrix elements for H₂¹⁶O: application to H₂O–H₂ line shape calculations via the modified complex Robert–Bonamy method

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The determination of the reduced matrix elements (RMEs) is an important part of the Modified Complex Robert–Bonamy (MCRB) calculations. Lamouroux *et al.* [1] used the *ab initio* wavefunction of Partridge and Schwenke [2] to determine these RMEs. In the same work, they also derived sums rules, which allow one to check the calculated RMEs. They show that for a state i , the sum of the square of the RME over all collisionally connected states equals one.

In this work, the sums rules have been applied to rotational states of a number of vibrational states. For a number rotational states the sum rules are obeyed, however for many others they do not give the correct sum. It is shown that the use of incorrect RMEs is a source of inaccuracy in the MCRB calculations, which significantly affects the determination the collisional half-width and the line-shift. Calculations, using the ground state and the vibrational dependent RMEs, were performed to show the influence of this spectroscopic effect.

It is shown that the best calculations of the line shape parameters are those using RMEs that obey the sum rules.

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Classical trajectory simulation of collision-induced absorption spectra

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Various theoretical approaches (see e.g. [1–4]) are used in order to simulate collision-induced absorption (CIA) spectra, reliable knowledge of which is required nowadays for planetary climate modeling. Among these approaches the use of classical trajectory simulation is particularly promising since it makes possible relatively cheap evaluation of the spectral profiles using presently available ab initio calculated potential energy (PES) and induced dipole (IDS) surfaces.

The goal of the current paper consists of development and numerical realization of the procedure that enables simulation of the rototranslational CIA band profile for interacting monomers of arbitrary symmetry. We start by constructing a classical intermolecular Hamiltonian in a chosen body-fixed frame. Then the equations of motion are derived along with the trajectory density function. Methods of computer algebra are used to ensure correct results. Finally extensive classical trajectory calculations are carried out to compute the resulting CIA spectrum. Markov chain technique is applied to generate a set of initial points properly distributed in the phase space.

Simple anisotropic CO₂-Ar prototype system was first taken as an example. The spectra for this system were considered recently in Ref. [4] using classical trajectory analysis, though the formalism in Ref. [4] is significantly at variance from our approach.

Our trajectory simulation for concrete molecular pairs is supported by extensive ab initio PES and IDS calculations on a grid of angles and intermolecular separations followed by their analytical fit.

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Atlas of experimental and theoretical high-temperature methane cross-sections from T=296 K to 1000 K in the mid-infrared range

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Spectra of hot methane were recorded at Old Dominion Norfolk University using a tube furnace, a quartz cell (optical path length of 50 cm) and a Bruker 120/125HR spectrometer. For each temperature, a total of 600 interferograms were recorded for both the sample and corresponding background at a resolution of 0.02 cm⁻¹. The experimental setup is similar to that of ref [1]. In this work, we obtained experimental absorption spectra at eight temperatures T= 296 K, 400 K, 500 K, 600 K, 700 K, 800 K, 900 K and 1000 K. These experimental records cover the mid infrared range from 5400 to 9000 cm⁻¹. We have converted this to the atlas of T-by-T absorption cross-sections for the methane polyad corresponding to the Tetradecad, Icosad and Triadecad excluding some particular intervals strongly contaminated by water. On the theoretical side the spectra were simulated from ab initio based Reims-Tomsk line list for the same experimental conditions. It has been constructed by global variational calculations from potential energy and dipole moment surfaces followed by empirical line position corrections deduced from previously published cold T analyses as described in [2-4] (and references therein). The comparisons showed very good overall agreement between observations and the theory at least at the medium spectral resolution. Preliminary assignments resulted to identifications of more than 10000 lines in each T spectrum. A full set of the theoretical absorption cross-sections is also included in the Atlas. The data could be of major interest for interpretation of current and future astronomical observations [5].

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High-resolution laser spectroscopy of nitrogen dioxide in the region of 14500–16800 cm⁻¹

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The nitrogen dioxide (NO₂) is one of the important stable free radicals to investigate the intra-molecular interactions of polyatomic molecules. The visible absorption spectrum shows complexity which comes from the fine structure due to the spin $S=1/2$ of the unpaired electron and the hyperfine structure due to the nuclear spin $I=1$ of the ¹⁴N atom. Several previous studies examined the hyperfine structures of $N=1$ levels of the excited electronic states, and reported that the hyperfine interaction constants correlated with the state mixing of the X and A states. In this study, we observed hyperfine-resolved high-resolution fluorescence excitation spectra of the $A\ ^2B_2 \leftarrow X\ ^2A_1$ electronic transition of ¹⁴NO₂ radical in 14500–16800 cm⁻¹ energy region by crossing a single-mode laser beam perpendicular to a collimated molecular beam [1]. In the observed region, the ⁹R₀(0) lines ($k = 0, N = 1 \leftarrow 0$ transition) were observed for more than 80 vibronic bands, and their hyperfine interaction constants; the Fermi contact interaction constants and the dipole-dipole interaction constants were determined. The determined Fermi contact interaction constants in the 14500–16100 cm⁻¹ region were found to be intermediate in magnitude between those in lower and higher energy region reported by other groups. On the other hand, a sharp decreasing of the Fermi contact interaction constant was found in 16 200 – 16 600 cm⁻¹ region, and it may be caused by the interaction with the dark C ²A₂ state.

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Modified complex Robert–Bonamy calculations including line coupling on the H₂O–N₂ and CO₂–N₂ molecular systems

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The Modified Complex Robert–Bonamy formalism [1,2] has been recently refined by Ma *et al.* [3] to go beyond the isolated line approximation by introducing the effect of the line coupling. The modification leads to off-diagonal terms in the $S_{2,middle}$ operator. This coupling effect has been successfully implemented in our line shape code and applied to the H₂O–N₂ and CO₂–N₂ collisional systems. The half widths and the line shifts calculations, considering the coupling effect, include all complex terms, explicit velocity integration and an extract trajectory model. The intermolecular potential is comprised of electrostatic, atom–atom (expanded to 20th order and 4th rank), induction and London dispersion terms.

Depending on the transition and collisional system, the effects of line coupling effect go from being negligible to large. The addition of line coupling to the calculation reduced the value of the half-width, sometimes substantially. More importantly, the reduction is in the direction of the measured values. For example, in early MCRB calculation, Gamache *et al.* [4] had to set the CO₂ quadrupole moment “at the lower error estimate” in order to reproduce measurements. This reduction is no longer needed when line coupling is included. The CO₂–X intermolecular potential adjustments (X = N₂, O₂, air, CO₂) will be reinvestigated with calculations employing line coupling.

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Temperature dependence of line broadening coefficient of chloromethane diluted in carbon dioxide

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The chloromethane is one of the primary chlorine ion source in the upper atmosphere, and is on the watch list of the World Meteorological Organization regarding climate change monitoring [1]. It originates both from natural sources, such as biomass burnings or tropical forests, and from human industrialization [2,3].

In this work, we studied line broadenings of chloromethane diluted in carbon dioxide in the $^{\circ}P$ branch of the ν_1 band at low temperature (200K to room temperature). The spectra were recorded with a high resolution diode laser spectrometer.

To retrieve the broadening coefficients, we fitted theoretical line shape models on the experimental profiles. We used the common Voigt profile, as well as the Rautian and Sobel'man and the Galatry profiles. We then computed the temperature dependence coefficients.

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A room-temperature HCN line list with a new dipole moment surface

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A new *ab initio* high accuracy dipole moment surface is constructed for the HCN system. The IC-MRCI all-electrons method was used to compute dipole moments. 902 dipole points were computed using external field method and fitted using a polynomial functional form with a standard deviation less than 10^{-5} Debye. The refined potential energy surface (PES) from our previous study [1] was also improved and giving energy levels accurate to better than about 0.03 cm^{-1} .

We report improved calculated intensities for all the fundamental bands of HCN. The standard deviation of calculated intensities for transitions within the ν_1 and ν_2^0 bands from the experimental values is reduced to about 1%. Our key improvement is for ν_3 stretching transitions. The P-branch intensities in our last calculated line-list [2] differed from the experimental ones by 36%; our new calculations have a corresponding difference of about 21%. The location of the second R-branch intensity minimum is also improved.

Our ultimate goal is to calculate a high-level global high-temperature line-list for HCN/HNC system. Our new DMS and the previously reported PES [1,3] represent an important step on towards this goal. Our room-temperature HCN line list will both improve the accuracy with which transition intensities are predicted and cover a wider wavenumber range than the previous line list [2], which was based on combination of experimental and recent *ab initio* calculated data [4].

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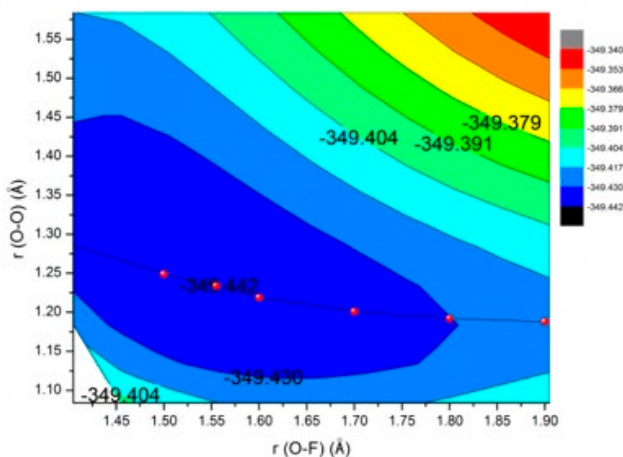
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Quantum chemical characterisation of difluorine peroxide FOOF

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Dioxygen difluoride has been known for a long time to possess very unusual equilibrium geometry, whose theoretical characterization was considered a "nightmare for theoreticians". In the present work we have identified the reason for this resistance: the flatness of the OO, and more important OF, stretching potential energy curves, which make it difficult to localise the global minimum. It is not related to the weak multi-reference character. Using high-level CCSD(T)-F12/VTZ-F12 ab initio theory, the global minimum has been properly located and vibrationally averaged bond lengths obtained. These vibrationally averaged parameters agree with experimental data to within 0.01 Å. We have then simulated the IR and UV spectra, which compare well with experimental data and permit identification of the observed transitions. The problem that has persisted for more than forty years, highlighted in a recent review article by Oberhammer titled "Gas phase structures of peroxides: experiments and computational problems", has been resolved.



P1.39.

On the consistency of absolute ozone intensities in MW, 10 and 5 micron ranges from ab initio predictions and laboratory observations

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The problems of the consistency of the ozone intensity data of the ozone molecule in various spectral infrared regions including 10 mm, 5 mm and the UV cross-sections has been subject of many discussion in the past decades but is not yet completely solved [1–6]. We present *ab initio* calculations for absolute line intensities in the most important absorption regions: in the microwave (rotational transitions), in the 10 micron range (stretching fundamentals) and in the 5 micron range (first triad of stretching overtone and combination bands) using our potential energy [6] and dipole moment [7] surfaces. The estimated intensity accuracy of our theoretical list is expected to be about 1% or even better. Our *ab initio* predictions will be compared to the recent yet unpublished FTS measurements of GSMA Reims group covering the ranges 800 – 2300 cm⁻¹ as well as to existing databases (S&MPO [8], HITRAN [9], GEISA [10], JPL [11]). Origins of various error sources and data inconsistencies will be discussed. We acknowledge the support from LEFE CHAT CNRS French program and from Mendeleev funding TSU grant.

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Rotational and vibrational dependences of line half-widths for CO confined in silica aerogel

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Molecules in nanopores are detected both in gas phase and adsorbed on the inner surface [1]. Contrary to adsorbed molecules, gas-phase ones freely move inside nanopores and collide with their walls, and the absorption spectra of these molecules have a fine rotational structure. Inside nanopores, spectral line parameters of molecules are induced predominantly by collisions with their walls. In papers [2, 3] different rotational dependences for CO confined in nanoporous materials with different structures were obtained.

In this report we present study of absorption spectra of carbon monoxide confined in silica aerogel with the density of 0.058 g/cm³. The measurements were performed within 2000 – 2300 and 4100 – 4400 cm⁻¹ spectral regions at room temperature using Bruker IFS 125HR Fourier spectrometer. Dependences of the HWHM values on rotational and vibrational quantum numbers were studied and compared with data available in literature [2–4].

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Measurements and calculations of H₂- broadening and shift parameters of water vapor transitions in 6700–9000 cm⁻¹ spectral region

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Hydrogen pressure induced broadening and shift coefficients for water vapor absorption lines in the 6700–9000 cm⁻¹ region have been measured and calculated. The spectra were recorded using Bruker IFS 125 HR spectrometer at room temperature, at the spectral resolution of 0.01 cm⁻¹ and in a wide pressure range of H₂. The multispectrum fittings with the quadratic speed dependent Voigt profile were performed to retrieve the broadening parameters for H₂O spectral lines of 11 vibrational bands (2ν₁, 2ν₃, ν₁+ν₃, 2ν₂+ν₃, ν₁+2ν₂, ν₂+2ν₃, 2ν₁+ν₂, 3ν₂+ν₃, ν₁+3ν₂, ν₁+ν₂+ν₃ and 6ν₂).

The calculations of the broadening coefficients were performed in the framework of the semi-classical method with use of an effective vibrationally depended interaction potential [1]. The obtained broadening coefficients and literature data [2, 3] were used to determine the analytical dependence of some potential parameters on vibrational quantum numbers. The analytical expressions that reproduce the broadening coefficients for different vibrational bands are proposed.

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The use of spectral moments to simulate rototranslational collision-induced bandshapes

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Reliable knowledge of collision-induced absorption (CIA) is presently in demand for climate modeling. Traditional theories of CIA bandshapes [1] are inadequate to fully take into account intermolecular anisotropy, though this is indispensable provided polyatomic monomers are considered. Recent advances in quantum and classical theory (see e.g. refs. [2–4]) are impressive though extremely expensive as both human and computer resources are concerned. Irrespective to theoretical formalism chosen to simulate the spectrum the use of spectral moments is important to quantify dipole-forbidden absorbance. On the one hand, spectral moments are defined as integrals of the properly weighted binary absorption coefficient. On the other hand, the zeroth and second moments can be calculated directly via statistical average of either squared induced dipole or Poisson bracket composed of the dipole and Hamiltonian derivatives, respectively.

Current paper aims at rigorous derivation of classical expression for the second spectral moment followed by its use in the spectral absorption bandshape simulation. Several pair systems are considered as examples, such as CO₂-Ar, CH₄-Ar, N₂-H₂, CO₂-H₂. For each of these systems rigorous classical Hamiltonians are first derived assuming rigid monomers. Explicit *ab initio* potential energy and induced dipole surfaces for the above mentioned pairs are either newly calculated or borrowed from the literature. Then the zeroth and second moments of rototranslational CIA bands are calculated as functions of temperature. These theoretically found values are then compared with the experimental ones, which are available for a limited number of molecular pairs at some selected temperatures only. For heteromolecular systems the CIA profiles are simulated assuming that the CIA band can be represented as a sum of properly weighted CIA profiles for pure gases as was previously attempted in ref. [5]. The importance of spectrum desymmetrization procedure is demonstrated in order to take into account quantum effects when light hydrogen molecule is part of a pair under consideration. Special attention is paid to analysis of the CO₂-H₂ rototranslational band, for which first experimental data were recently obtained [6].

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The high resolution far infrared spectrum of ^{18}O enriched water vapor at the SOLEIL synchrotron

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The absorption spectrum of an highly ^{18}O enriched sample of water vapor is recorded by Fourier transform spectroscopy between 40 and 700 cm^{-1} at the AILES beam line using a standard radiation mode of the SOLEIL synchrotron. The ^{18}O enrichment of the sample was about 97% while pressure and pathlength values were 0.97 mbar and 151.75 m, respectively.

More than 5200 absorption lines were measured between 44 and 678 cm^{-1} . Among them, about 4500 water lines were assigned to more than 4800 transitions of seven isotopologues: H_2^{18}O , H_2^{17}O , H_2^{16}O , HD^{18}O , HD^{17}O , HD^{16}O , and D_2^{18}O . Numerous significant differences of line positions compared to those of the HITRAN2016 database [1] were found for the H_2^{17}O , H_2^{18}O , HD^{17}O , and HD^{18}O species. The maximum position deviation exceeds 0.15 cm^{-1} . The incomplete HITRAN's assignments of more than 90 transitions of H_2^{18}O and H_2^{17}O were finalized.

The lines of more than 2550 transitions of seven most abundant isotopologues were observed for the first time ($\text{H}_2^{16}\text{O} - 30$, $\text{H}_2^{17}\text{O} - 322$, $\text{H}_2^{18}\text{O} - 772$, $\text{HD}^{16}\text{O} - 130$, $\text{HD}^{17}\text{O} - 331$, $\text{HD}^{18}\text{O} - 931$, $\text{D}_2^{18}\text{O} - 28$). In particular, 28 new lines of D_2^{18}O were found in addition to the only study in this region [2]. The measured line positions will allow to refine and complete sets of the ground and first vibrational levels of H_2^{18}O and H_2^{17}O [3], HD^{18}O and HD^{17}O [4] and D_2^{18}O [5].

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Global deperturbation treatment of $5^1\Sigma_u^+$ and $5^1\Pi_u$ states in Rb_2

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New experimental data in the region 27 000 – 29 000 cm^{-1} enforced us to revisit the recently published analysis of the $5^1\Sigma_u^+$ and $5^1\Pi_u$ states in Rb_2 (Halalyova et. al JQSRT **202**, 328–334 2017). The new measurements, performed by polarization labeling spectroscopy not only significantly extended the range of experimental data to much higher vibrational levels of the $5^1\Pi_u$ state but also allowed us to identify transitions to two previously unobserved electronic states. The presence of both e and f parity levels and the analysis of the recent theoretical calculations (Allouche RA, private communication, 2017, Tomza M, private communication, 2017) suggested that these might be the $5^3\Pi_u$, $3^3\Delta_u$ or other triplet states, which become accessible from the singlet ground state through spin-orbit interactions.

Revealing the multiple structures of Glutamine

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Glutamine is α -amino acid that is used in the biosynthesis of proteins. The large flexibility of the molecule has several potential conformational candidates. Among them, the three most stable isomers have been characterized both using a laser ablation chirped pulse Fourier-transform microwave spectrometer (LA-CP-FTMW) and a laser ablation molecular-beam Fourier-transform microwave spectrometer (LA-MB-FTMW). Two of the conformers can be determined using the spectroscopic constants provided by the theoretical methods. On the other hand, the third conformer is not reproduced by conventional theoretical methods, and one should use some tricks to characterize the conformer's structure. Also, even the slightest different prediction in the site position of the nitrogen atoms makes the conformer's spectroscopic characterization very challenging because the nuclear quadrupole coupling interactions depend critically on the electronic environment, position and orientation of the ^{14}N nuclei. In this work, we highlight that more accurate theoretical methods are needed, and that glutamine can be used as a test to benchmark the calculations. We propose one trick to help the scientific community when the calculations are not sufficient to predict the structure and how to deal with the complex ^{14}N nuclear quadrupole hyperfine structure with no starting grounds.

Linear Rayleigh and Raman scattering to second order

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Both Rayleigh and Raman scattering are frequently used in spectroscopic measurements. The scattering can be described in terms of molecular polarisability tensors – with the resulting terms, arising from multipolar expansions of the scatterer's charge distribution, normally retained up to products of the electric-dipole electric-dipole polarisability with the electric-dipole magnetic-dipole/electric-dipole electric-quadrupole polarisabilities. In this work, we extend this usual multipolar theory of linear Rayleigh and Raman scattering to include the next-order correction.

The new terms promise a wealth of information about the shape of a scatterer, and yet are insensitive to the scatterer's chirality. Our extended theory might therefore prove especially useful for analysing samples in which the scatterers have non-trivial shapes but no chiral preference overall, as the zeroth-order theory offers little information about shape and the first-order correction is often quenched for such samples. A basic estimate suggests that our extended theory can be applied when the characteristic size of the scatterer is no more than approximately 1/50 of the incident wavelength. In this regime, the error resulting from neglect of the third- and higher-order corrections will be smaller than 0.1%.

Our results are entirely analytical, and apply to elastic light scattering in rarefied samples, and inelastic light scattering at essentially all sample densities – in both cases provided that the individual scatterers are independent, and multiple scattering is not important.

It remains to incorporate our results into more realistic, sample-specific theories, where the motions of the scatterers, local field corrections and other subtleties are taken into account. This is especially important for small scatterers and / or long wavelengths, as the second-order correction will be especially small in such cases.

The CRDS spectrum of natural and ^{13}C enriched carbon dioxide in the $1.73\ \mu\text{m}$ window

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The CRDS spectra of natural and ^{13}C enriched carbon dioxide have been recorded by high sensitivity cavity ring down spectroscopy (CRDS) at room temperature in the $1.73\ \mu\text{m}$ window ($5694 - 5879\ \text{cm}^{-1}$) [1]. The investigated region corresponds to a transparency window of very weak opacity which is of particular interest for Venus.

A total of more than 1100 and 980 line positions and intensities were rovibrationally assigned to 26 and 22 bands in the natural and ^{13}C enriched carbon dioxide spectra, respectively, by the comparison with the accurate predictions provided by a global effective Hamiltonian and effective dipole moment operators. All identified bands belong to $\Delta P=8$ and 9 series of transitions, where $P=2V_1+V_2+3V_3$ is the polyad number (V_i being the vibrational quantum numbers). The weakest assigned lines have intensities on the order of $1 \times 10^{-30}\ \text{cm}^2/\text{molecule}$. Spectroscopic parameters were derived for the upper vibrational levels from a band-by-band fit of the line positions (typical *rms* values are on the order of $8 \times 10^{-4}\ \text{cm}^{-1}$).

Newly observed bands in the CRDS spectra of natural carbon dioxide include perturbed bands, weak hot bands and bands of minor isotopologues and provide critical validation tests for the most recent spectroscopic databases. The comparison to the Carbon Dioxide Spectroscopic Databank (CDS), HITRAN2016 database and recent *ab initio* line lists is presented. Deficiencies are evidenced for some weak perpendicular bands of the HITRAN2016 list and identified as due to inaccurate CDS intensities which were preferred to *ab initio* intensities. While Ames and UCL *ab initio* intensities are believed to be accurate within a few % for the strong unperturbed bands, the reported measurements allow evidencing important (>50%) differences between *ab initio* values of some weak perturbed bands.

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Rotational spectroscopy of organophosphorus chemical agents: Cresyl and Phenyl Saligenin Phosphate

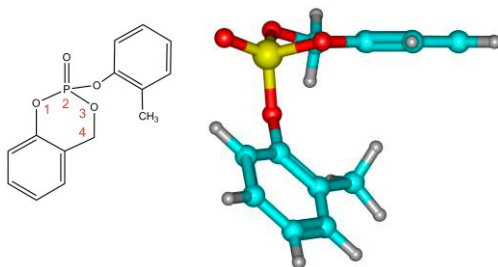
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Synthetic organophosphorous compounds (OPs) are used as pesticides, pharmaceuticals, additives or warfare agents, like the G- or V-series phosphonates. Microwave (MW) spectroscopy can be used for detection of these compounds based on its extreme frequency resolution and specificity, especially since the introduction of chirped-pulse excitation techniques allows for fast broadband operation. We have synthesized the neurotoxic organophosphates cresyl (CBDP) and phenyl (PSP) saligenin phosphate and characterized the molecules using cm-wave (2–8 GHz) chirped-pulse Fourier-transform microwave spectroscopy in a jet expansion. The molecules adopt a single conformation, with the six-membered dioxaphosphorinane ring adopting a P-O(3) half-chair configuration due to the introduction of a condensed benzene ring. In the two molecules, the oxygen double bond is equatorial, while the phenoxy group is axial to the dioxaphosphorinane ring. The introduction of a methyl group in the phenoxy group of CBDP (figure below) does not significantly change the orientation of the aromatic ring with respect to PSP. Rotational parameters and supporting ab initio/DFT calculations will be reported at the Conference.



FTIR laboratory measurement of O I spectra in the 0.77–12.5 μm spectral range: Rydberg states and oscillator strengths

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The normal system of O I terms available in the NIST Atomic Spectra Database was established more than a half-century ago and, in fact, reproduce the measurements performed by a Lund University group [1]. Although the accuracy of their wavenumbers was quite high, the accuracy of their level energies is critically dependent on the accuracy of the triplet 3s level. Moreover, for a better internal consistency of the system of transitions, it would be desirable to include the transitions between n l levels with different $n = 3-8$, not only 3s, 3p and 3d. Some of these transitions lay in the wavelength range longer than 2 μm , which has never been measured in a laboratory with high resolution (except for two narrow bands studied in Ref.[2]).

The present work attempts to address the above issues. We exploit the great advantages of IR Fourier transform spectroscopy (FTS), such as its constant high resolution and energy throughput, to record high-resolution O I spectra in a wide range of 800–13000 cm^{-1} (0.77–12.5 μm). With the help of recent high-accuracy (0.004 cm^{-1}) direct measurements of the 3p level in the UV [3], we perform a reoptimization of O I level energies. Together with these UV lines and old line lists [1], we included high-resolution diode-laser measurements [2] and high precision fine structure splittings [3–4] into our reoptimization. This reoptimization also uses our own 135 O I lines in the infrared (including 51 lines not measured previously in the laboratory) to yield a consistent (within not worse than 0.01 cm^{-1}) system of O I levels with $n = 4-7$, $l \leq 6$. For some of these levels, we experimentally find fine structure splitting for the first time.

We also provide a long list of E1 line strengths, transition probabilities and oscillator strengths for O I IR transitions between high- l states ($3 \leq l \leq 6$). These values are calculated with the help of quantum defect theory and show good agreement with the NIST values available for the transitions involving low- l states ($l \leq 3$).

This work is funded by Czech Science Foundation (contract 13-07724S and grant 17-05076S), Russian Ministry of Education and Science (grants 3.4826.2017/8.9 and 3.1761.2017/4.6) and Russian Basic Research Foundation (project 16-32-0003)

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Structural determination of aroma molecules in the gas-phase

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High-resolution gas-phase studies allow for a fundamental understanding of molecular properties without any influences from the environment such as crystal fields or solvent effects. Therefore, understanding the molecular physics and intra-molecular properties of molecules can be extremely useful to fully elucidate changes during solvation (full- as well as stepwise micro-solvation) and molecular detection within complex environments such as the biological media. Here, we report and compare the structure and dynamic of several volatile molecules in the gas-phase [1]. Using a combination of molecular beam Fourier-transform microwave (MB-FTMW) spectroscopy and quantum chemical calculations we obtain highly accurate information of the conformational flexibility of our systems, which is used directly to validate quantum chemical calculations. Finally, we compare the energy differences of the most abundant conformers observed in the gas-phase in different implicit solvent models to compare their stability in various environments. The overall comparison of such aroma chemicals in different environments will help to push-forward the fields of molecular recognition, where until now, the prediction of molecular properties and biological activities remain underdeveloped and provide a great challenge.

High resolution study of the strongly interacting $\nu_3(F_2)/\nu_1(A_1)$ bands of $^{28}\text{SiD}_4$

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The high resolution infrared spectra of $^{28}\text{SiD}_4$ were measured in the 1500 – 1700 cm^{-1} region with a Bruker IFS 120HR Fourier transform spectrometer. The 1073 transitions with $J^{\text{max}} = 42$ were assigned to the ν_3 band of $^{28}\text{SiD}_4$. Rotational, centrifugal distortion, tetrahedral splitting, and resonance interaction parameters for the (0010) and (1000) vibrational states were determined from the weighted fit of experimental line positions. The obtained set of parameters reproduces the initial experimental data with an accuracy close to experimental uncertainties. A further analysis of 150 experimental ro-vibrational lines was performed using the Hartmann-Tran profile to simulate the measured line shape and to determine experimental line intensities. The 3 effective dipole moment parameters were obtained on that basis from the weighted fit, which reproduce the initial experimental intensities of the 150 initial lines (both strong and weak) with the $d_{\text{rms}} = 7.5\%$. The half-widths of 50 ro-vibrational lines are analyzed from the multi-spectrum fit, and self-pressure broadening coefficients are determined.

Molecular spectroscopy using radio-acoustic detection and high power radiation in THz region

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Method of opto-acoustic (also called radio- or photo-acoustic) molecular spectroscopy is a powerful tool for both fundamental studies and applications. In this method the result of the interaction of the radiation with matter is detected by the change of the parameters of the matter and not of the radiation. It is likely the only method allowing reaching high sensitivity by increasing radiation power. This was particularly demonstrated in terahertz (THz) region in our recent work [1] using spectrometer with radio-acoustic detection of absorption (RAD spectrometer) [2] and radiation of a free-running gyrotron operating in continuous wave regime with up to 1 kW power [3].

In the reported study the gyrotron facilities were significantly improved for spectroscopic needs. In particular, the radiation frequency was stabilized against a reference oscillator using phase-lock loop (PLL) system in the anode voltage control [4]. The system provides high stability, narrow bandwidth (relative width about 10^{-12}) and accurate frequency control. Sample spectrum recording was possible at first (263 GHz), second (526 GHz) and third (789 GHz) harmonic of radiation frequency with modulation of both power and frequency. Typical spectra of different molecules obtained using the gyrotron and RAD method in different regimes of registration will be presented. Routine sensitivity of the spectrometer was demonstrated to be about $8 \times 10^{-10} \text{ cm}^{-1}$. Results were confirmed by high resolution spectra obtained using a BWO-based video spectrometer. Further perspectives of employing gyrotron for spectroscopy will be discussed.

The study was supported by Russian Science Foundation (project 17-19-01602).

Temperature dependence of collisional parameters of water 183-GHz line

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Water vapor line near 183 GHz is an important object for atmosphere remote sensing. This requires accurate spectroscopic information about line parameters, in particular, line intensity, pressure broadening and shifting, speed dependence coefficients and their temperature dependences.

Present study is devoted to measurement of temperature behavior of collisional parameters of the line. A BWO-based spectrometer with radio-acoustic detection of absorption [1] was employed. Main atmospheric species such as water and air (initially prepared as 78% of nitrogen, 21% of oxygen and 1% of argon) were chosen as buffer gases. Spectra were obtained at pressures from 0.01 Torr to 2 Torr in a wide temperature range from -25 to 85 C. Both Voigt and the quadratic Speed Dependent Voigt profiles were used for spectra analysis. Pressure broadening, shifting and their speed dependence were retrieved from the fit in wide temperature range. Temperature behavior of the measured parameters will be discussed. For the first time change of sign of self-shifting coefficient with increasing temperature was detected for this line. Obtained results may be useful for developing theory of molecular interactions, updating spectroscopic databases and for improving accuracy of radiation propagation models used for atmosphere remote sensing data analysis.

The study was partially supported by RFBR (grants No 18-02-00705, 18-05-00698).

Production of theoretical line lists for polyatomic molecules: SiH₄, C₂H₄, CH₃Cl, CH₃F, C₂H₂, NH₃, OH₃⁺, P₂H₂

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The ExoMol project aims to provide molecular line lists for exoplanets and other atmospheres with a particular emphasis on those atmospheres which are significantly hotter than the Earth's [1]. ExoMol has now computed line lists for about 50 molecules, many of which are polyatomics. The last ExoMol update included line list for following polyatomic molecules: SiH₄ [2], C₂H₄ [3], CH₃Cl [4] and CH₃F [5]. The line lists for C₂H₂, NH₃, OH₃⁺, P₂H₂ are close to be completed. The lists are produced using high level ab initio potential energy (PE) and dipole moment (DM) surfaces. For the variational calculations our programs DVR3D [6] and TROVE [7] are employed. The PE surfaces have to be refined by fitting to experimental data to reach the required quality. This contribution will discuss different important aspects of the production and storage of the hot molecular line lists. The high quality of our most recent line lists will be illustrated by comparing to the experimental data, including high temperature spectra.

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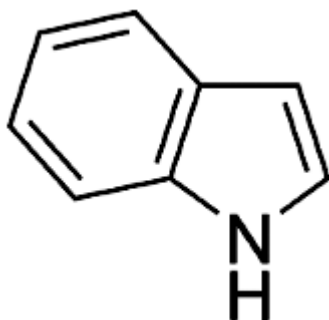
Indole rotational spectra

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Indole is a prototypical aromatic heterocycle molecule included in the human scent[1]. The rotational spectra of indole were investigated in 1988 in the frequency ranges of 9–12 GHz and 26.5–60 GHz[2]. In 1990, they were further studied in the frequency range of 18–40 GHz[3] and last year using FTMW spectroscopy in the frequency range of 7–19.5 GHz[4]. In these studies, the rotational and quartic centrifugal distortion constants of the ground and first vibrational states were obtained.

The present indole study was performed using the Prague millimeterwave spectrometer[5] in the frequency ranges of 140–160 GHz and 390–410 GHz. Hundreds of new rotational transitions were measured and assigned. A global fit of all the new and previously assigned transitions was performed by Pickett's SPFIT program[6]. The refined rotational and quartic distortion constants are presented and discussed.



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The visible spectrum of AID⁺: the experimental and theoretical treatment

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The emission spectrum of the AID⁺ ion has been studied by Fourier transform spectroscopy technique, as a further step of our investigation of the AID neutral molecule [1]. The 0-0 and 1-1 bands of the A²Π - X²Σ⁺ system have been recorded in the 27.000-29.000 cm⁻¹ region with an instrumental resolution of 0.03 cm⁻¹. In total, almost 500 rotational frequencies were measured with an absolute accuracy of about 0.005 cm⁻¹. It improved the experimental accuracy of the determined frequencies by the factor 10 compared to the previous work [2]. The rotational analysis has shown irregularities in the Λ-doubling splitting of the A²Π, v = 0, 1. Consequently, the A²Π state has been represented by the rotational term values, while the regular X²Σ⁺ state by the molecular constants. The causes of the irregularities were identified in the interaction between the A²Π state the lying higher the B²Σ⁺ state.

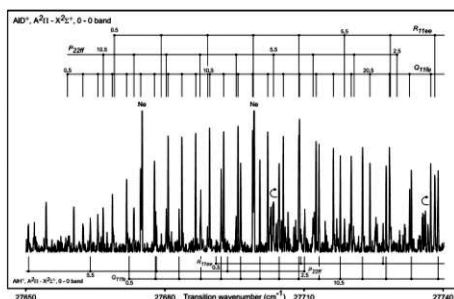


Fig.1. The VIS-FT emission spectrum of the AID⁺ A²Π - X²Σ⁺ (0-0) band.

Ab initio calculations on the ion were performed using a parallel version of the MOLPRO [3] (version 2010.1) suite of quantum chemistry codes. The static electron correlation was calculated using SA-CASSCF method [4]. The active space consisted of all the occupied valence orbitals of the aluminum atom plus the 1s orbital from the deuterium atom. The 1s orbital of the Al⁺ atom is kept frozen while the 2s2p orbitals are closed (kept doubly occupied in all configurations). In addition, SA-CASSCF can be used to calculate the excited electronic states corresponding to the Al⁺(³P)+D(²S) asymptote so a total of five states are included (2 × ²Σ⁺, ²Π, ⁴Σ⁺, ⁴Π). The accuracy of the potentials can be improved by including dynamic electron correlation, that was handled here by using MRCI method [5].

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High-resolution Fourier-transform spectroscopy of the comet-tail system in the $^{12}\text{C}^{17}\text{O}^+$ ion

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In the emission spectrum of $^{12}\text{C}^{17}\text{O}^+$ molecule new observations and analyses were performed. The (1,0) and (1,1) bands of the comet-tail ($A^2\Pi_1 - X^2\Sigma^+$) system in the 18,900 to 22,100 cm^{-1} region were recorded with the Fourier-transform spectrometer (BRUKER IFS 125-HR). The absolute accuracy of wavenumbers was about 0.005 cm^{-1} . The measurement cycle included 128 scans within 1.5 h. As a source of the studied spectrum an air-cooled, carbon hollow-cathode (HC) lamp operated at 780 V, 54 mA dc was used. The lamp was filled with a static mixture of $^{17}\text{O}_2$ (70 %) and $^{16}\text{O}_2$ (30 %) at a pressure of about 1 Torr. During the discharge process, the O_2 molecules react with the ^{12}C atoms ejected from the carbon filler placed inside the cathode, thus forming $^{12}\text{C}^{17}\text{O}$ and $^{12}\text{C}^{17}\text{O}^+$ molecules in the gas phase, in amounts sufficient to finally achieve a signal-to-noise ratio (SNR) of 100:1 for the $^{12}\text{C}^{17}\text{O}^+$ ion. As a result of a detailed spectral analysis the individual molecular constants of both $A^2\Pi_1$ and $X^2\Sigma^+$ states were obtained. For the upper $A^2\Pi_1$ state all these constants were delivered for the first time. The parameters for the lower $X^2\Sigma^+$ state were also calculated and can be compared with these determined previously [1].

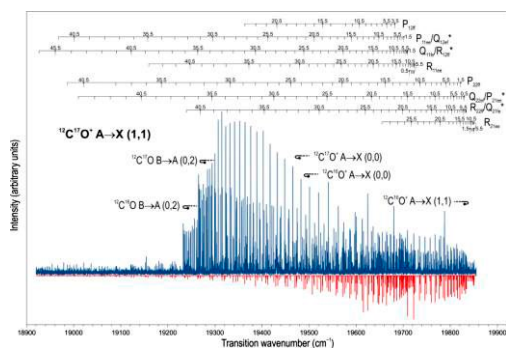


Fig. 1. High-resolution emission spectrum (upper trace) of the (1,1) band of the comet-tail ($A^2\Pi_1 - X^2\Sigma^+$) system in the rare $^{12}\text{C}^{17}\text{O}^+$ isotopologue together with simulated spectrum [2] (lower trace) of this band. During analyses the influence of the other bands was taken into consideration: $^{12}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ B-A system (0,2) bands [3,4] as well as $^{12}\text{C}^{16}\text{O}^+$ and $^{12}\text{C}^{17}\text{O}^+$ A-X system (0,0) bands and $^{12}\text{C}^{16}\text{O}^+$ A-X system (1,1) band, simulated on the basis of constants from Ref. [5]. In case of P_{11}/Q_{12} , Q_{11}/R_{12} , Q_{22}/P_{21} and R_{22}/Q_{21} main/satellite branches (denoted by an asterisk) the values of the rotational quantum number J are provided just for the main branches.

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Self-broadening coefficients of rotational transitions of H₂S measured by submillimeter-wave spectroscopy

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Hydrogen sulfide (H₂S) is an asymmetric top molecules present in the atmosphere and that has been intensively studied by rotational and rovibrational spectroscopies [1]. It is a minor atmospheric pollutant produced by natural sources (volcanoes) and industrial processing of sulfur containing fossil fuels. Furthermore it is a byproduct of human activity such as water treatment processes. H₂S has also been observed in interstellar clouds in our galaxy (starburst galaxies) [2, 3].

However, as well as accurately measured and assigned line positions, pressure broadening coefficients are required for precise atmospheric monitoring and atmospheric column density determination. Rotational spectroscopy in the submillimeter domain has been chosen to determine self-broadening coefficients of H₂S from pure rotational transitions.

Using a frequency modulated computer-controlled spectrometer located at LPCA in Dunkerque [4], several ground-state rotational transitions of H₂S have been measured at room temperature in the region 168–865 GHz for pressures between 0.08 and 1 mbar. A non-linear least squares fitting of second harmonic spectra using the Voigt and speed-dependent Voigt profiles [5, 6] has been used to obtain the self-broadening coefficients of 32 lines ($0 \leq J'' \leq 11, 0 \leq K_a'' \leq 7$). The observed J and K_a rotational dependences have been compared with values obtained by infrared and microwave measurements. No vibrational dependence of the self-broadening coefficients has been observed.

P1.59.

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Photodissociation dynamics of CF_2I_2 in solution

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Although chemical reaction dynamics of isolated molecules has been extensively explored and understood, that in liquid phase is much less comprehended due to the complication of solvent-solute interaction. One strategy to study reaction dynamics in solution is comparing solution-phase reactions with their gas-phase counterparts. The comparison helps us to explore which ideas from the study of gas phase reaction can be applied to that in solution [1]. Recent advances in ultrafast spectroscopic techniques make it possible to obtain a detailed information on the reaction dynamics in liquids. In particular, time-resolved infrared (IR) spectroscopy can probe transient molecular structures involved in chemical reaction pathways, providing critical information needed in solving the mechanisms of chemical reactions [2]. Here, photodissociation dynamics of CF_2I_2 in CCl_4 and $\text{c-C}_6\text{H}_{12}$ were probed by time-resolved IR spectroscopy in the time range from subpicosecond to microsecond. We were able to compose a complete photolysis dynamics of CF_2I_2 in solution including the fate of all the produced intermediates.

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Influence of the epigenetics marks in the non-covalent interactions between amino acids and DNA

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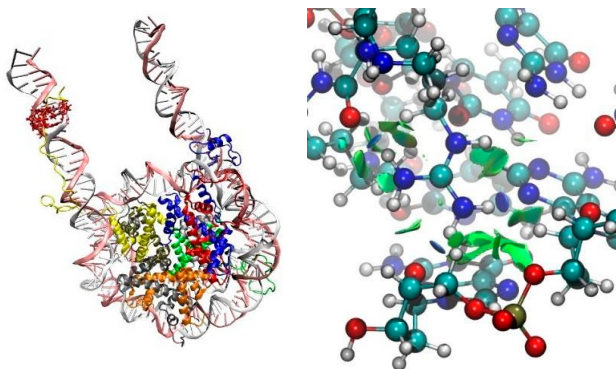
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The chromatin is a complex made by the DNA chain and proteins that, after an extremely efficient folding and packaging process, forms the chromosome in the nucleus of eukaryotic cells. Actually, the total length of all of the DNA in a human is around 300 times the Sun–Earth distance [1]. The basic repeating structural, and functional, unit of chromatin is the nucleosome. It has a disk shape that is stacked up in the packaging process to form the chromosome. This characteristic form is due to the quaternary structure of the proteins of the chromatin complex: the histones. Two of each of the H2A, H2B, H3, and H4 histones form an octamer, and about 146 base pairs bind and warp around the octamer in a 1.7 turns of DNA. The whole process is driven by non-covalent interactions, which enable easy unpacking whenever the DNA needs to be accessible for protein expression.

The DNA–histone interactions can be easily modulated, by placing methyl groups in the adequate sites of either the protein or the DNA strand. With this simple mechanism, it is possible to “silence” a gene and prevent it for being expressed into proteins. This modulation of the genomic machinery is known as Epigenetics and the methylation may even persist during reproduction, passing to the next generation.

In this work we built a realistic model [2], where the tripeptide H3A7–H3R8–H3K9 (Ala–Arg–Lys of the histone H3) interacts with a sequence of 3 DNA pair bases to see how the mono, di, and trimethylation of K9 affect the interaction of R8 with the minor groove of DNA, since these processes have been identified as transcriptional activation or repression depending on the number of the methyl fragments inserted. The structures of 4 models (252–261 atoms depending on the methylation state) have been optimized at PBE0–D3(BJ)/def2–TZVP level, using the COSMO approximation as implicit water solvent. The three dimensional NCI plots have been represented and analyzed to highlight the differences among the models and try to understand how the Lysine methylation process can facilitate or complicate DNA availability.



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Investigation on the degree of dissociation of Hydrogen plasma in PIG ion source via optical emission spectroscopy

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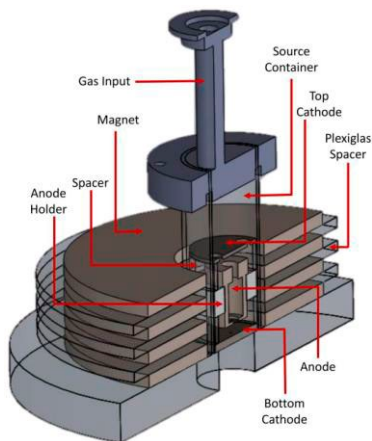
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2) Institute for Research in Fundamental Sciences

Penning-type discharge plasma ion source is a powerful discharge device applied extensively in many fields [1]. Penning-type discharge ion source can work at the pressures below 1.33mbar and creates plasma with the electron temperature, higher than 5eV [2]. Our study perform at pressure and during the experiment it is constant.

Optical emission spectroscopy is easy and inexpensive methods for obtain important plasma parameters from spectral. We evaluated the electron temperature of the produced hydrogen plasma with Saha equation and the spectra lines emitted by neutral atomic hydrogen [3].

Main propose for this work is applying the spectroscopic method (OES[1]) for determination of the degree of dissociation of the hydrogen. For this aim we made PIG[II] with OES facility, Figure1.



[I] Optical Emission Spectroscopy

[II] Penning Ion Source

The method is based on the measurements of the relative intensities of two atomic lines of the Balmer series, H_{α} and H_{β} , and molecular line, (2-2) Q1 line of the Fulcher- α bands system and the method for determining the gas temperature is based on measured rotational distribution of intensity of Fulcher- α (2-2) Q bands of hydrogen, discuss in [4]. Finally, we extracted the degree of dissociation quantity from the electron temperature, gas temperature, Balmer and Fulcher intensities of plasma.

Key words: Electron temperature, Gas temperature, Penning ion source, Dissociation degree.

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The optimal origin for computation of wave functions of polar molecules

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It is commonly stated that the origin for the multipole expansion should be chosen in a way to minimize the magnitude of multipole term with the minimal l from the truncated ones [1,2]. This principle can allow to choose the optimal origin for computation of energy, but it can be shown that this origin is not universally optimal for computation of wave functions and related objects, like the probability density, dipole transition elements and oscillator strengths.

It can be shown, that the optimal location of the origin should be chosen in a way to minimize the distance to the most remote charge.

Fig. 1 shows that multipole computation gives quite high precision with the minimal number of multipole terms if the origin is optimally chosen (in the geometrical center of the system). The dipole-spherical function can be rather good approximation of the solution of Schrodinger equation if the origin is properly chosen.

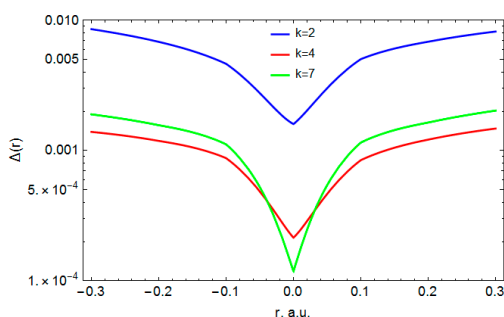


Fig. 1. The discrepancy between accurate solution of Schrodinger equation for three-center Coulomb potential and the solution for multipole expansion of the same potential as a function of origin location. k is the number of multipole terms used in expansion.

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