The spectral broadening of the alkali D\textsubscript{1}(np^2P\textsuperscript{1/2} - ns^2S\textsuperscript{1/2}) and D\textsubscript{2}(np^2P\textsuperscript{3/2} - ns^2S\textsuperscript{1/2}) lines, induced by atom-atom interactions, is of interest to the astrophysical community as a possible diagnostic of brown dwarf atmospheres and extrasolar giant planets, which exhibit strong alkali absorption features that are broadened by collisions with helium and hydrogen molecules. The spectra have appreciable values as they are very powerful tools to scan the environments of the brown dwarfs and extrasolar planets. They are even capable to identify their different chemical components and specify their physical properties [1]. Similarly, the spectral broadening of the D\textsubscript{1} and D\textsubscript{2} lines of alkali atoms induced by collisions has aroused a great interest among laser specialists. They have particularly paid attention to optically pumped alkali laser (OPAL) systems by providing a mechanism with which the D\textsubscript{2} alkali line can be broadened to more closely match the optical pump bandwidth [2]. Instead of pumping the D\textsubscript{2} line of the alkali atom, exciplex-pumped alkali laser (XPAL) systems pump a collisionally induced blue satellite [3]. The importance of the alkali-rare gas molecules, selected from the field of pumped molecular exciplex lasers, is robustly linked to their molecular structure that has bound and unbound excited states. Accordingly, the comprehension of the mechanisms of exciplex formation is mostly based on accurate potential-energy curves associated with ground and first excited states [4]. We are concerned by the quantal determination of the far-wing pressure broadening profiles generated by D\textsubscript{1} and D\textsubscript{2} atomic lines when perturbed by the presence of He atoms in both absorption and emission. In this framework the low-density limit will be taken into account for consider only the binary collisions between Rb and He pair of atoms. For this purpose, we have chosen to use the potential-energy curves (PECs) and transition dipole moments (TDMs) of the RbHe molecule which we have generated by ab initio calculations, where we adopted the state-averaged complete active space self consistent field (SA-CASSCF) with the multireference configuration interaction (MRCI) methods including the spin-orbit coupling effects (SO), as it is more significant than the lighter alkali-rare gas systems. Subsequently, we will characterize the potential-energy curves of the X ²Σ\textsuperscript{1/2}, A ²Π\textsuperscript{1/2}, A ²Π\textsuperscript{3/2}, and B ²Σ\textsuperscript{1/2}\textsuperscript{*} molecular states by determining their spectroscopic parameters like the equilibrium distance R\textsubscript{e}, and the well depth D\textsubscript{e}. We will then analyze the behavior of absorption and emission profiles versus temperatures, and determine the position of the eventual satellites in the wings and specify the type and the origin of the radiative transitions from which the satellites may arise. Finally, we compare the calculated pressure broadening profiles with other theoretical studies and also with measured experimental data.

HIGH SENSITIVITY CAVITY RING DOWN SPECTROSCOPY OF CARBON DIOXIDE IN THE 1.19-1.26 µm REGION

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The absorption spectrum of natural carbon dioxide has been recorded between 7909 and 8370 cm$^{-1}$ (1.19-1.26 µm) by very high sensitivity Cavity Ring Down Spectroscopy with a fiber-connected External Cavity Diode Laser (ECDL) [1]. The recordings were performed at room temperature for pressure values of 0.1, 5 and 10 Torr. The achieved sensitivity (noise equivalent absorption $\alpha_{\text{min}} \approx 10^{-10}$-10$^{-11}$ cm$^{-1}$) has allowed the detection of 3425 transitions of 61 bands belonging to 37, 9, 8, 4, 2 and 1 bands of $^{12}$C$^{16}$O$_2$, $^{13}$C$^{16}$O$_2$, $^{16}$O$^{13}$C$^{18}$O, $^{16}$O$^{12}$C$^{17}$O, $^{16}$O$^{15}$C$^{18}$O and $^{16}$O$^{13}$C$^{17}$O, respectively. For comparison, only fourteen $^{12}$C$^{16}$O$_2$ absorption bands were previously known in the region (mostly from Venus spectra).

All identified bands corresponding to $\Delta P=11$ series of transitions, where $P=2V_1+V_2+3V_3$ is the polyad number ($V_i$ are vibrational quantum numbers). The assignments were carried out on the basis of the predictions of the global effective Hamiltonian model [2, 3]. Line intensities were predicted using the set of $\Delta P=11$ effective dipole moment parameters of the principal isotopologue [4].

The band-by-band analysis has allowed deriving accurate spectroscopic constants of 57 bands from a fit of the measured line positions.

The global fits of the obtained intensities of the $\Delta P=11$ series of transitions were used to refine the corresponding set of effective dipole moment parameters of the six studied isotopologues.

The obtained results will help to improve the spectral line parameters in the most currently used spectroscopic databases of carbon dioxide.

The absorption spectrum of highly $^{18}$O enriched carbon dioxide has been recorded between 5851 and 6990 cm$^{-1}$ (1.71-1.43 µm) by very high sensitivity Cavity Ring Down Spectroscopy [1-3]. The achieved sensitivity (noise equivalent absorption $\alpha_{\text{min}} \sim 1 \times 10^{-10}$, 4$\times$$10^{-11}$ cm$^{-1}$) has allowed the detection of 19526 transitions of 301 bands belonging to 11 isotopologues of carbon dioxide. The analysis and modeling of the $^{16}$O$^{12}$C$^{18}$O, $^{12}$C$^{18}$O$_2$, $^{13}$C$^{18}$O$_2$ and $^{18}$O$^2$C$^{18}$O line positions and intensities were previously published [1, 2]. In this report, we present the analysis of the bands of five $^{17}$O containing isotopologues present at very low concentration in the $^{18}$O enriched sample. The rovibrational assignments were carried out on the basis of the predictions of the effective operators approach [4, 5]. A total of 1759, 1786, 335, 273 and 551 transitions belonging to 24, 24, 5, 4 and 7 bands were rovibrationally assigned for the $^{16}$O$^{12}$C$^{17}$O, $^{17}$O$^{12}$C$^{18}$O, $^{16}$O$^{13}$C$^{17}$O, $^{17}$O$^{13}$C$^{18}$O and $^{12}$C$^{17}$O$_2$ isotopologues, respectively. For comparison, only five bands were previously measured in the region for the $^{17}$O$^{12}$C$^{18}$O species. The band-by-band analysis has allowed deriving accurate spectroscopic constants of 61 bands from a fit of the measured line positions. The studied spectral region is formed by $\Delta P= 8$ and 9 series of transitions, where $P= 2V_1+V_2+3V_3$ is the polyad number ($V_i$ are vibrational quantum numbers). Two interpolyad resonance perturbations have been evidenced in the spectrum. The global modeling of the line positions within the framework of the effective Hamiltonian approach was performed and new sets of Hamiltonian parameters were obtained for the $^{17}$O$^{12}$C$^{18}$O, $^{16}$O$^{13}$C$^{17}$O and $^{17}$O$^{13}$C$^{18}$O isotopologues. For the five studied isotopologues, the effective dipole moment parameters of the $\Delta P= 8$ and 9 series of transitions were derived from a global fit of the measured line intensities. The obtained results will help to improve the quality of the line positions and intensities in the most currently used spectroscopic databases of carbon dioxide.

Nitric oxide (NO) molecules play a key role in atmospheric phenomena, interstellar space and combustion. In biological systems, NO plays a significant beneficial role in a variety of processes including vascular relaxation, anti-tumour and anti-pathogen response, mitochondrial respiration, and it is a ubiquitous signalling molecule in the cardiovascular system. However, detailed studies of NO complexes are required for a quantitative modelling of these media.

The aim of the present work is to study the lower bound states of Rg-NO open-shell van der Waals complexes using Fourier Transform Microwave Spectroscopy (FTMS). The experiments employ a pulsed supersonic expansion of gas mixture (Ar/NO) into a Fabry-Perot cavity. The frequency range covered the region between 6 and 18 GHz. Three pairs of mutually perpendicular Helmholtz coils were used to generate a near-null field in the centre of spectrometer. In this way, magnetic-field-free spectra were recorded, and we report here some new transitions. Our results are analysed using a rigid model, and a dynamical one, which takes into account the large amplitude vibrational motion.

In addition to this, we present the first systematic study of magnetic effects on this complex. In this case, the Helmholtz coils were used to augment the Earth’s magnetic field and spectra up to 3.6 Gauss were recorded. The effect of weak magnetic fields was examined using two geometries: a) the magnetic field being parallel to the electric field (thus allowing $\Delta M_z=0$ transitions), b) the magnetic field being perpendicular to the electric field (thus allowing $\Delta M_z=\pm 1$ transitions). There are no previous studies on magnetic properties of complexes of open shell molecules that need multiple potential energy surfaces (PESs) to be described, and especially with hyperfine resolution. The only exception is a previous study on NeNO complex. Such measurements could provide additional information on the nature of the intermolecular potential surface, and especially on the difference potential. The absolute values for the $g$-factors for many rotational levels have been obtained and their rotational dependence is discussed. A comparison between the magnetic properties of ArNO and NeNO is also presented.

We hope that our work will inspire further quantitative work in weak magnetic effects of free radicals complexes.

FIRST-PRINCIPLE CALCULATION OF CH$_3$D AND PH$_3$ SPECTRA IN THE INFRARED

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Fig 1. Example of comparison of our *ab initio* predictions (lower panel) with HITRAN for PH$_3$

Global calculations of rovibrational spectra and dipole transition intensities of CH$_3$D and PH$_3$ using our recent *ab initio* dipole moment and potential surfaces [1-3] will be reported. For a full account of symmetry properties, a recently published variational tensor formalism in normal modes is applied, the convergence of high-J calculations being improved using vibrational eigenfunctions with a compressed basis set for solving the rovibrational problem [4]. Line positions and line intensities are in a very good agreement with experimental data [5-7].

METASTABLE VIBRATIONAL STATES OF OZONE ABOVE THE DISSOCIATION THRESHOLD: LIFETIME CALCULATIONS, IMPACT ON THE DYNAMICS

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The new potential energy surface (PES) of ozone recently developed \cite{1} is used to determine energies of vibrational bound and predissociated resonances of \( \text{O}_3 \). For the vibrational state calculations, the hyperspherical coordinates and the methods of slow-variable discretization with a complex absorbing potential are used \cite{2}. The bound vibrational states obtained in this study perfectly agree with the previous calculations \cite{1} and reproduce the experimental energies up to the region 8000 cm\(^{-1}\) above the minimum of the potential. The method takes into account the coupling between the three potential wells of the ozone molecule. The correct representation of the coupling between the three wells is important for the correct treatment of excited vibrational levels and resonances. The method can treat symmetric and asymmetric isotopologues. For symmetric isotopologues, states of all possible irreducible representations are calculated.

The widths of the resonances in the region 0-3000 cm\(^{-1}\) above the dissociation have been determined. The most of the obtained resonances have widths between 0.1 cm\(^{-1}\) and 10 cm\(^{-1}\). The widths depend on the nature of the short-range part of resonance wave functions: The resonances differ from each other by a degree of excitation of different vibrational modes and also by the relative angular momentum of the dissociating O-O\(_2\) system, which can also be viewed as motion between the three potential wells. Wave functions of the predissociated resonances obtained for asymmetric molecules provides information about the exchange reaction \( \text{O}^+\text{O}^+\text{O} \rightarrow \text{O}^+\text{O}^+\text{O} \) or \( \text{O}^+\text{O}^+\text{O} \rightarrow \text{O}^+\text{O}^+\text{O} \). A possible impact on the dynamics will be discussed.

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TP07

IR SPECTRA OF 1-CHLORO-1-FLUOROETHENE INVESTIGATED BY A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY

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Over the last decade, different chlorinated ethenes have been the subjects of many spectroscopic investigations on the basis of their role in atmospheric chemistry as trace gas pollutants and potential sources of chlorine atoms. In the present contribution we report on the detailed vibrational analysis of 1-chloro-1-fluoroethene (CClF=CH₂), carried out in the range 400-6500 cm⁻¹, and we discuss the corresponding high-level quantum chemical computations which thoroughly supported the band assignment.

The gas-phase infrared spectra of CClF=CH₂ were recorded at medium resolution (up to 0.2 cm⁻¹) by employing a FTIR spectrometer (Bruker Vertex 70) and the corresponding vibrational analysis was performed by assignments carried out in terms of fundamentals, overtones, combination and hot bands up to three quanta of vibrational excitation. The analysis of absorption cross section spectra, obtained at 298(1) K, by means of a multi-spectrum least square procedure carried out on spectra acquired at 0.5 cm⁻¹ resolution and with sample pressures varying in the range 0.187-70.0 hPa, led to the determination of accurate values of integrated band intensities for the most relevant spectral features in the range 400-4500 cm⁻¹.

High-level quantum chemical calculations were carried out to support the vibrational analysis: equilibrium geometry, harmonic and anharmonic force fields (cubic and quartic semi-diagonal terms) were computed at CCSD(T) level of theory employing different correlation consistent basis sets. Within the framework of VPT2 theory, reliable results for anharmonic frequencies, anharmonic interaction parameters and spectroscopic constants were obtained. Resonance denominators in matrix elements, anharmonic constants and the effect of resonances have been taken into account in the interacting vibrational levels polyad. A general good agreement between computed and observed transitions validates the ab initio force field.

Details of the spectroscopic analysis and of the ab initio calculations will be presented and discussed.
A JOINT EXPERIMENTAL AND COMPUTATIONAL STUDY ON THE VIBRATIONAL SPECTRA OF R1122

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The well known adverse environmental effects due to halocarbons have motivated many experimental and theoretical investigations on their spectroscopic properties. Here we present the main results obtained by means of a combined experimental study and ab initio investigation on the vibrational spectra of \( \text{CF}_2=\text{CClH} \) (2-chloro-1,1-difluoroethene, R1122).

The gas-phase infrared spectra were recorded at medium resolution (up to 0.2 \( \text{cm}^{-1} \)) in the range 400-6500 \( \text{cm}^{-1} \) by employing a Bruker Vertex 70 FTIR interferometer. The vibrational analysis was performed in terms of fundamentals, overtones, combination and hot bands. Besides, by means of a multiple spectrum least square procedure, accurate and reliable values for integrated band intensities were retrieved by the analysis of absorption cross section spectra recorded in the range 400-4500 \( \text{cm}^{-1} \) at a temperature of 298(1) K and at resolution of 0.2 \( \text{cm}^{-1} \).

The vibrational assignment was supported by high-level ab initio calculations; equilibrium geometries, harmonic force fields and the corresponding spectroscopic parameters were obtained at the CCSD(T) level of theory and by employing different correlation consistent basis sets. Anharmonic corrections were included by employing the cubic and quartic semi-diagonal force constants obtained by computations carried out at MP2 and B2PLYP levels of theory. In the framework of vibrational perturbation theory to the second order (VPT2), both GVPT2 and HDCPT2 approaches were employed to derive the anharmonic corrections to harmonic results.

Details of the experimental work and of the ab initio calculations will be presented together with the preliminary results.
HIGH RESOLUTION ANALYSIS OF THE $\nu_3$ BAND OF $^{36}$SF$_6$ AND NEW GLOBAL FIT OF $^{32}$SF$_6$ PARAMETERS INCLUDING NEW $3\nu_3$ BAND DATA

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Aiming at a better modeling of the atmospheric absorption of sulfur hexafluoride (SF$_6$), we recently performed new measurements at the AILES Beamline of the Synchrotron SOLEIL facility in Paris. Using the IFS125HR interferometer coupled with a cryogenic multipass cell [1] containing the SF$_6$ gas, new spectra have been recorded in the 800 - 3200 cm$^{-1}$ range, using the internal IR source. The cryogenic cell was set with a 93 m optical path length and regulated at 150 ± 2 K temperature along the entire optical path. A spectrum with a gas pressure of 1.25 mbar was recorded at 0.0025 cm$^{-1}$ resolution in the 800−3200 cm$^{-1}$ region, leading to the observation of 17 rovibrational bands of SF$_6$.

These results allowed us to perform the detailed analysis of several bands. Thereby, for the first time, the weak $\nu_3$ band of the $^{36}$SF$_6$ isotopologue (with 0.02% of natural abundance) has been assigned and fitted. We also analyzed in detail the $3\nu_3$ third stretching overtone of the $^{32}$SF$_6$ main isotopologue. Including these new parameters of $3\nu_3$ in the XTDS model [2], we substantially improved the previous global fit [3] of SF$_6$ parameters. The analysis of other bands is in progress.

[3] M. Faye, A. Le Ven, V. Boudon, L. Manceron, P. Asselin, P. Soulard, F. K. Tchana and P. Roy, “High-resolution spectroscopy of difference and combination bands of SF$_6$ to elucidate the $\nu_3 + \nu_1 - \nu_1$ and $\nu_3 + \nu_2 - \nu_2$ hot band structures in the $\nu_3$ region”, Molecular Physics, in press (2014).
AB INITIO STRUCTURAL AND SPECTROSCOPIC STUDY OF HPS\textsuperscript{x} AND HSP\textsuperscript{x} (x = 0, +1, -1) IN THE GAS PHASE

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Accurate \textit{ab initio} computations of structural and spectroscopic parameters for the HPS/HSP molecules and corresponding cations and anions have been performed. For the electronic structure computations, standard and explicitly correlated coupled cluster techniques in conjunction with large basis sets have been adopted. In particular, we present equilibrium geometries, rotational constants, harmonic vibrational frequencies, adiabatic ionization energies, electron affinities and, for the neutral species, singlet-triplet relative energies. Besides, the full-dimensional potential energy surfaces (PESs) for HPS\textsuperscript{x} and HSP\textsuperscript{x} (x=-1,0,1) systems have been generated at the standard coupled cluster level with a basis set of augmented quintuple-zeta quality. By applying perturbation theory to the calculated PESs an extended set of spectroscopic constants, including τ, first-order centrifugal distortion and anharmonic vibrational constants has been obtained. In addition, the potentials have been used in a variational approach to deduce the whole pattern of vibrational levels up to 4000 cm\textsuperscript{-1} above the minima of the corresponding PESs.
Interactions between energy levels in excited states of polyatomic molecules are of great interest not only in fundamental science but in various applications. Since the interactions appear as minute effects in spectra, high resolution spectroscopy have been required to reveal the effects. Recently, we studied high resolution spectroscopy of molecular iodine assisted by an optical frequency comb [1]. Optical frequency combs have been applied not only to metrology, but also to molecular spectroscopy. In the present study, we developed a high resolution spectroscopic system with an optical frequency comb for precise measurement of rovibronic spectra of naphthalene. This is the first application of an optical frequency comb to high resolution spectroscopy of rovibronic transition of polyatomic molecules.

Our system has a frequency calibration scheme with an optical frequency comb and an acousto-optic modulator (AOM) to realize precise frequency measurement of a scanning dye laser. The uncertainty of the frequency measurement in the system is determined by fluctuations of comb modes which are stabilized to a GPS-disciplined clock resulting in an uncertainty of $10^{-11}$ in 1 s gate time. The calibrated dye laser is used as a light source of Doppler-free two-photon absorption (DFTPA) spectroscopy of naphthalene. The resolution is limited only by a linewidth of the scanning dye laser, and the linewidth is less than 150 kHz.

We measured DFTPA spectra of $S_1^1B_{1u} (v_4 = 1) \leftrightarrow S_0^1A_g (v = 0)$ transition at around 298 nm. A part of obtained spectra is shown on the bottom in the figure. The top and second plots are modulation frequency of the AOM and measured beat frequency between comb modes and the scanning dye laser, respectively. The horizontal axis is calibrated by the developed frequency calibration system, and the uncertainty is about 5 kHz. The spectral lines are rotationally resolved and have near natural width which is calculated from the life time of the excited state. We determined absolute frequencies of the spectra and calculated rotational constants of the electric excited states. We can obtain information about detailed structures of excited states and perturbations from other excited states.

**Figure** A part of Doppler-free two photon absorption spectrum of $S_1^1B_{1u} (v_4 = 1) \leftrightarrow S_0^1A_g (v = 0)$ transition of naphthalene (33577.86 – 33578.06 cm$^{-1}$).

The high-resolution absorption spectrum of trifluoromethyliodide (CF$_3$I), an alternative gas to chlorofluorocarbon but with potential greenhouse effects, has been recorded at 0.001 cm$^{-1}$ resolution in the 200-350 cm$^{-1}$ region with the Bruker IFS125HR Fourier transform spectrometer at the AILES Beamline at SOLEIL[1]. Due to the spectral congestion and the presence of numerous hot bands, the spectra have been recorded either at room temperature using a 150 m optical path length cell or at 163 K using the new LISA-SOLEIL cryogenic cell [2]. This enables a detailed analysis of the $v_3$ band at 286.29712(3) cm$^{-1}$ of CF$_3$I. The results of previous microwave analyses [3,4] were combined with those of the present infrared analysis of the $v_3$ band to get an improved set of parameters band for the $v_3=1$ (C-I stretching) and $v_6=1$ (I-C-F bending) interacting vibrational states. Indeed this new calculation accounts for the Coriolis resonance coupling the $v_3=1$ energy levels with those from the dark $v_6=1$ state (located at ~ 261.5 or at 267.6 cm$^{-1}$).

Finally, the $2v_3-v_3$ hot band was also investigated. The outcome of this work can contribute to a better modelling of the infrared signature of this molecule, considered as a replacement for some chlorine- or bromine-containing gases in industrial applications.

DETECTION OF ATMOSPHERIC $^{15}$NO$_2$ ENABLED BY NEW $\nu_3$ LINELIST

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Starting from the results of a previous analysis [1], an improved linelist of the $\nu_3$ band of $^{15}$NO$_2$ has been generated. This linelist was used to detect this isotopologue in the atmosphere for the first time, using balloon-borne solar occultation spectra measured by the JPL MkIV Fourier Transform spectrometer. It is shown that over the 15-35 km altitude range where $^{15}$NO$_2$ can be detected, the retrieved 15/14 NO$_2$ ratio is within 5% of the expected value (0.00364), implying that the absolute line intensities in the new linelist are accurate. Over the same altitude range the RMS spectral fitting residuals reduce significantly as a result of including the new $^{15}$NO$_2$ linelist, improving the accuracy of retrievals of all gases that absorb in the 1550-1650 cm$^{-1}$ region (e.g., $^{14}$NO$_2$, H$_2$O, HDO, O$_2$).

ROVIBRATIONAL SPECTRUM OF DEUTERATED FLUOROFORM IN THE 1900 cm\(^{-1}\) REGION: HIGH-RESOLUTION STUDY OF THE \(v_3+2v_6\) FERMI-INTERACTING BANDS

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The perpendicular combination bands \(v_3+v_4\) (1900.21 cm\(^{-1}\)) and \(2v_3+v_6\) (1889.30 cm\(^{-1}\)) of DCF\(_3\) were investigated for the first time with high-resolution, using a Fourier-transform infrared spectrum recorded in the 1600-2000 cm\(^{-1}\) region, at a resolution of 0.0024 cm\(^{-1}\).

Like the \(v_3=v_4=1\) and \(v_3=v_6=1\) degenerate combination levels (Fig. 1) strongly interact through a Fermi-type anharmonic coupling. Besides the Fermi-interaction, other important Coriolis (\(\Delta k=\pm 1, \Delta l=\mp 2\)) and higher-order (\(\Delta k=\pm 2, \Delta l=\pm 2\)) inter-vibrational interactions were also considered, in a similar manner as in the lower \(v_4/v_3+v_6\) dyad [1].

The theoretical model proposed by Sarka and Stříteská [2] and already employed for the \(v_4/v_3+v_6\) dyad [1], could be successfully extrapolated to the present case. The reproduction of all experimental data is quantitative and results in very accurate molecular parameters for both the studied levels [3].

Fig. 1. Diagram of vibrational levels of DCF\(_3\) between 1000 and 2000 cm\(^{-1}\), separated to non-degenerate (\(A_1, A_2\)) and degenerate (\(E\)) levels. Those levels which have to be treated as polyads are enclosed in rectangles.

ROVIBRATIONAL SPECTRA OF DCF$_3$ IN THE 2000 cm$^{-1}$ REGION: HIGH-RESOLUTION STUDY OF THE $v_5=2$ AND $v_2=v_5=1$ LEVELS

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The $2v_5$ overtone and $v_2+v_5$ combination bands of DCF$_3$ were investigated for the first time with high-resolution, using Fourier-transform infrared spectra recorded in the 1850-2500 cm$^{-1}$ region, at a resolution of 0.002 cm$^{-1}$. This analysis may be thought as a necessary step towards the reinvestigation of the complicated vibrational pattern in the CD stretching fundamental region, near 2200 cm$^{-1}$.

The $v_5=2$ ($A_1+E$) and $v_2=v_5=1$ (E) levels, at 1950 and 2085 cm$^{-1}$ respectively, were found to have a sufficient separation to justify their distinct treatment. The Fermi and Coriolis interactions, either between the $v_5=2$ and $v_5=1$, $v_6=2$ levels, or between the $v_2=v_5=1$ and $v_2=1$, $v_6=2$ levels, were however taken into account.

The $v_5=2$ overtone levels were treated by considering their important anharmonic and Coriolis interactions with the neighboring ($v_5=1$, $v_6=2$) ‘dark’ levels. The reproduction of the experimental data is quantitative and results in very accurate molecular parameters.

For the $v_2=v_5=1/v_6=2$ interacting states, we have used a model extrapolated from the $v_2=1/v_5=2$ lower dyad [1]. We have shown that the effects of neglected interactions with the complex vibrational polyad near 2200 cm$^{-1}$ can be absorbed into effective values of the centrifugal distortion constants of the $v_2=v_5=1$ level.

ON THE "EXPANDED LOCAL MODE" APPROACH APPLIED TO THE ETHYLENE MOLECULE

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Earlier derived, [1] - [2], for the XY₂ (C₂v) and XY₃ (C₃v) molecules, the “expanded local mode model” (see also [3]) is applied to the ethylene-type, X₂H₄, molecule. On the basis of specially obtained values of the ambiguity parameters, sin γᵢ (i=1...6), simple approximate values of transformation coefficients, lₙα, are obtained for the C₂H₄ molecule. It gives us possibility to derive simple relations between different spectroscopic parameters (harmonic frequencies, anharmonic parameters, etc.) of the C₂H₄ molecule.

One can expect that the obtained simple relations may give a correct qualitative picture of the peculiarities in the complicated spectra of the ethylene molecule.

We present the results of the analysis of three vibrational bands of $^{16}$O$_3$ and four bands of $^{18}$O$_3$ recorded by high sensitivity CW-CRDS (Cavity Ring Down Spectroscopy) technique. These extremely weak bands are located between 7300 and 7900 cm$^{-1}$ i.e. only a few % below the dissociation limit, $D_0$, at about 8480 cm$^{-1}$ [1]. This work completes our previous analysis of the near infrared CRDS spectra of $^{16}$O$_3$ and $^{18}$O$_3$ above 5850 cm$^{-1}$ [1-3].

The effective Hamiltonian approach was adopted to model the positions and intensities. The derived band centres and rotational constants show a very good agreement with recent theoretical predictions based on a new ab initio potential energy surface [4]. It has been recently shown that the vibrational energy levels deduced from our CRDS spectra analyses are quite sensitive to the shape of the ozone potential energy surface at large internuclear distances and allow thus new insight on the properties of the ozone transition state towards the dissociation [5].

The CW-Cavity Ring Down Spectra of $^{18}\text{O}$ enriched ozone isotopologues have been recorded in the 5850-6920 cm$^{-1}$ spectral range with a noise equivalent absorption $\alpha_{\text{min}} \approx 1 \times 10^{-10}$ cm$^{-1}$). Our recent works [1-3] were devoted to the analysis of the 5930–6340 cm$^{-1}$ region, where eight bands of the M50 isotopologues (668 and 686) and five bands of the M52 isotopologues (688 and 868) have been detected and modelled within the effective Hamiltonian approach. Here, we extend the study to the 6340-6800 cm$^{-1}$ spectral domain where three new bands of $^{18}\text{O}^{16}\text{O}^{18}\text{O}$ and one band of $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ are newly detected. Thanks to accurate theoretical predictions based on a new ozone potential energy surface (PES) [4,5], using the Contact Transformations method, they were assigned as $2\nu_1+5\nu_3$, $\nu_1+4\nu_2+3\nu_3$, $3\nu_2+5\nu_3$ and $2\nu_1+5\nu_3$, respectively. These bands are the highest vibrational bands analysed so far for these isotopologues. Overall, more than 1550 rovibrational transitions are rovibrationally assigned and 933 energy levels are derived from the assigned spectra. We present in addition to the effective spectroscopic parameters the comparisons between observed and synthetic spectra which illustrate the quality of the final line-lists derived from our analyses. We also present the comparison of the experimental values of the band centres with their predicted values for all bands of M52 isotopologues, analysed by CRDS.

Let us consider the set of stretching coordinates \( \{q_1, q_2, \ldots, q_n\} \) and assume that all other coordinates are frozen. If we have restricted ourselves consideration of the configuration where only one atom (\( M_{ij} \)) connected with few other atoms than the common form of the representation of the exact vibrational kinetic energy operator (VKEO) in this case is:

\[
K = \sum_i \left( \frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial q_i^2} + G_i \right) + \sum_{i,j,i,j} 2G_{ij} \frac{\partial^2}{\partial q_i \partial q_j} - H_u = -\frac{\hbar^2}{2\mu_{M,M_i}} q_{\mu} + q_i
\]

If we now want to use symmetry coordinate of form \( q' = \frac{1}{\sqrt{n}} \sum_i q_i \) for symmetric flat molecules like \( AB_n \) (now \( M_i \rightarrow M_B ; M_y \rightarrow M_A \)) we will have the troubles with \( H_u \) as VKEO will still depend on the mass of \( M_{ij} \) atom. To avoid this problem we have to use more common form of VKEO. Considering only first derivatives in (1) we can get:

\[
\sum_i H_u \frac{\partial}{\partial q_i} = -\frac{\hbar^2}{2} \sum_i \left( \frac{1}{M_A} \text{div}_i \xi_{\alpha}^a + M_A \text{div}_i \xi_{\alpha}^s \right) \frac{\partial}{\partial q_i}
\]

where \( \xi_{\alpha}^a, \xi_{\alpha}^s \) - Wilsons vectors for stretching coordinates. Using \( q' \) we can transform (2):

\[
-\frac{\hbar^2}{2} \sum_i \left( \frac{1}{M_A} \text{div}_i \xi_{\alpha}^a + M_A \text{div}_i \xi_{\alpha}^s \right) \frac{\partial}{\partial q_i} = -\frac{\hbar^2}{2\sqrt{n}} \sum_i \left( \frac{1}{M_A} \text{div}_i \xi_{\alpha}^a + M_A \text{div}_i \sum_i \xi_{\alpha}^s \right) \frac{\partial}{\partial q'}
\]

As well-known \( \xi_{\alpha}^a = \xi_{\alpha}^s \) and hence \( \sum_i \xi_{\alpha}^a = \sum_i \xi_{\alpha}^s = 0 \) for any symmetric flat (\( D_{nh} \)) molecules like \( AB_n \). So in this case VKEO will not depends on the \( M_A \) mass. We can expand this approach to the molecules with low symmetry. For example for bent \( AB_2 \) like molecule we can get using (3) and \( q' = \frac{1}{\sqrt{2}} \sum_i q_i \):

\[
-\frac{\hbar^2}{2\sqrt{2}} \left( \sum_i \frac{1}{M_A} \text{div}_i \xi_{\alpha}^a + \frac{1}{M_A} \text{div}_i \sum_i \xi_{\alpha}^s \right) \frac{\partial}{\partial q'} = \left( \sum_i \xi_{\alpha}^a = \sum_i \xi_{\alpha}^s = 2 \cos \frac{\theta_{\alpha}}{2} \right) = \frac{\hbar^2}{2\sqrt{2}} \left( \sum_i \frac{1}{M_A} \text{div}_i \xi_{\alpha}^a + \frac{1}{M_A} \text{div}_i \left( 2 \cos \frac{\theta_{\alpha}}{2} \right) \right) \frac{\partial}{\partial q'}
\]

One can see from (4) that \( H_u \) in this case related with molecular geometry. Of course this approach can be expand to bend or other type of valence coordinates. It is seems that relation of \( H_u \) elements with molecular geometric parameters must exist in (1) for no symmetric molecules too.
MODELING THE 10 μm REGION OF THE ETHYLENE SPECTRUM USING THE D_{2h} TOP DATA SYSTEM: FREQUENCY AND INTENSITY ANALYSIS

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A tensorial formalism adapted to X_2Y_4 planar asymmetric tops with D_{2h} symmetry has been developed in Dijon [1] and a program suite called D_{2h}TDS was proposed to calculate their high-resolution spectra [2]. As the Hamiltonian and transition moment operators can be systematically expanded up to a given order and for any group of vibrational levels, the theory makes global analyses of many rovibrational bands easier to perform. With such theoretical and computational means, we aim to describe globally the low energy (0 to 3500 cm⁻¹) spectrum of ethylene (C_2H_4) and similar molecules, and compare the performances of such a modeling with approaches based on a Watson-type Hamiltonian [3, 4]. Prior to carrying out the global analysis, we re-investigate some infrared and Raman bands to determine initial sets of tensorial parameters. The first step into this effort was a frequency and intensity analysis of the v_{12} band near 1442 cm⁻¹ [5]. The present contribution extends that work to the whole infrared tetrad at 10 μm (620-1520 cm⁻¹), involving the v_{10}/v_{7}/v_{4}/v_{12} bands near 826, 949 and 1026 cm⁻¹ in addition to v_{12}.

Our frequency and intensity analysis currently combines previously reported measurements [5,6,7] with line positions and intensities measured in high-resolution spectra of the v_{10}/v_{7}/v_{4}/v_{12} tetrad region of ethylene, specifically recorded using a Bruker IFS 120 to 125HR upgraded Fourier transform spectrometer. Including the Coriolis interactions affecting the upper vibrational levels 10, 7, 4, and 12, a total of 11667 line positions and 648 line intensities have been assigned and fitted with global root mean square deviations of 3.3 × 10⁻⁴ cm⁻¹ and 2.5 %, respectively. The results of the frequency analysis are in good agreement with previous work [4], and this is the first time that a global intensity analysis is performed in this region of the ethylene spectrum. Results of this work will be presented.

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Carbon monoxide is one of the simplest and most studied infrared active molecules. The first low-temperature measurements on CO were performed many decades ago. Nevertheless, recently two papers on determination of temperature dependence of CO broadening coefficients were published [1, 2]. Although the spectroscopic data becomes better and better, there is still missing a metrological approach.

In the framework of the European project EUMETRISPEC [3], much effort is made to determine the spectroscopic line parameters as accurate as possible. One step in this direction is to measure environment parameters such as temperature and pressure traceably.

To achieve this goal, a FTIR measurement infrastructure was built, which includes apart from high-resolution FTIR spectrometer IFS-125HR, a new custom temperature controlled and stabilized measurement cell, with attached traceably calibrated precision PT100 resistance thermometers and baratron pressure sensors.

We present our recent temperature-dependent measurements on pure CO in the temperature range from 213 to 296 K, and derive new self-broadening coefficients and their temperature dependence for the lines R16 to R23 in the ν2 band (4313 – 4332 cm⁻¹). A detailed discussion of the resulting uncertainties and a comparison with literature values will also be presented.

This work describes the determination of sulfur in some nuts and dried fruits using a High Resolution Continuum Source Electrothermal Atomic Absorption Spectrometer (HR-CS ET AAS) and evaluating the two rotational molecular of carbon monosulfide (CS) at 257.959 nm and 258.056 nm simultaneously. Sulfur was determined in a tungsten coated graphite tube/platform at 257.959 nm and 258.056 nm simultaneously, using thiourea as a calibrant, Pd/citric acid as a modifier and applying a pyrolysis temperature of 800 °C and a molecule forming (vaporization) temperature of 2200 °C. The calibration curve prepared from thiourea was linear up to 2500 ng of S. The limit of detection and characteristic mass of the method were 21.6 ng and 7.4 ng of S, respectively. The accuracy of the method was tested by analyzing certified reference spinach, milk powder, tea samples applying linear calibration technique prepared from thiourea aqueous standard. The results were in good agreement with the certified values.
Mass resolved REMPI spectra for HI, showing resonance excitation to Rydberg states and ion-pair vibrational states in the two-photon resonance excitation region 69.600 – 72.400 cm\(^{-1}\), were recorded and analyzed. A few systems of perturbing states were addressed independently in terms of state interactions by interpreting observed line-shifts, line-intensity alterations and line-width effects. In cases when the different observations depend on the same dynamical properties, the results of the analysis were found to be supportive in nature. Quantitative analysis revealed interaction strengths and spectroscopic parameters for deperturbed states derived from analysis of the line-shifts and parameters relevant to photodissociation processes derived from the line-intensity alterations. Small but significant changes are derived for the spectroscopic parameters, since observed line-shifts are near-resonance in nature, showing as localized shifts of lines and energy levels but limited alterations in overall trends.

Methyl chloride is well known as the most abundant halocarbon in the Earth’s atmosphere and the main source of stratospheric chlorine atoms involved in the chemical reactions of ozone layer depletion. Its spectroscopic parameters for perturbation by main terrestrial-atmosphere gases have been very intensively studied over last years (updated line positions and intensities [1] as well as N₂-, O₂-, air-, H₂-, CO₂- and self-broadening coefficients [2-6]). In the present work we extend these measurements to the case of some atomic perturbers: He, Ar and Kr.

Experiments were performed with a frequency-modulated spectrometer operating in the 180-950 GHz range. It consists of a 10-18.5 GHz frequency synthesizer followed by a frequency multiplier chain based on solid-state devices, a 1.1 meter long absorption cell and a bolometric detection.

Rotational lines R(6), R(10), R(17), R(22), R(31) and R(33), ranging from 186 up to 901 GHz, have been studied in details. Their line-shapes were analyzed with various models (Voigt, Galatry, Speed-Dependent Voigt) in order to probe velocity-dependence and diffusion effects. The hyperfine structure related to the 35Cl atom was included and the full implementation of the Beer-Lambert law was considered in order to take account of the large absorbance of CH₃Cl lines [4].

Because of complications resulting from the hyperfine structure related to the 35Cl atom, higher frequency lines were analyzed first. For the He-induced relaxation case, the observed line shapes have been rather well explained by using Voigt profile model. By contrast, in the case of heavier buffer atoms, Ar and most of all Kr, strong departures from the Voigt profile have been stated and attributed partly to the molecular diffusion but mainly to the speed-dependence of relaxation rates.

With the support of this preliminary study, all recorded lines have been analyzed using the meaningful Speed-Dependent Voigt profile. For completeness, the Voigt profile has been also employed since it still continues to be used in applications. The presented results concern the dependence of relaxation rates on the quantum numbers J and K as well as on the R(6)-line hyperfine components.

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SPECTROSCOPIC INVESTIGATION OF THE $V_1 + V_2$ VIBRATIONAL BAND OF THE TRANS-FORMIC ACID AT ROOM TEMPERATURE AND IN A FREE JET EXPANSION

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Room temperature cavity enhanced absorption spectroscopy [1, 2] and jet-cooled CW-cavity ringdown spectroscopy [3] were used to record high-resolution absorption spectra of trans-formic acid in the range of the OH+CH ($v_1 + v_2$) vibrational band centered at 6507.1 cm$^{-1}$, using the Femto-FT-CEAS set-ups and the Fantasio+ set-ups, respectively. The rotational temperature of formic acid is estimated to be 10 K in the free jet expansion. Two series of lines were identified involving b-type and a-type transitions. A line-by-line analysis was attempted to produce vibration-rotation constants. The latest results of the analysis will be presented.

With the help of a semi-analytical procedure the oscillator strengths for Rydberg electronic transitions in the ArH molecule are calculated by accounting for the effects of $l$-coupling (due to dipole potential of the core) and $l$-uncoupling (due to rotation of the core) [1]. Such effects result in non-zero oscillator strength values for some transitions which are forbidden in the widely used atom-like model of molecular Rydberg states. For the allowed transitions we also report the difference between the atom-like calculations and the calculations which take into account the dipole moment of the molecular core in the frame of both one-channel and multi-channel quantum defect theories.

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SELF BROADENING COEFFICIENTS AND IMPROVED LINE INTENSITIES FOR THE $\nu_7$ BAND OF C$_2$H$_4$ NEAR 10.5 $\mu$m, AND IMPACT ON ETHYLENE RETRIEVALS FROM JUNGFRAUJOCH SOLAR SPECTRA

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Ethylene is a tropospheric pollutant on the Earth, also present as a by-product of methane photochemistry in the atmosphere of outer solar system bodies. Remote sensing of ethylene in the infrared range relies on the 10 $\mu$m region. This spectral range corresponds to the excitation of 7 modes of vibration of $^{12}$C$_2$H$_4$, 4 of which being infrared active (see Fig. 1 of [1]). The corresponding $\nu_{10}$, $\nu_7$, $\nu_4$ and $\nu_{12}$ bands are located near 826, 949, 1026 and 1442 cm$^{-1}$, respectively [1]. Among these, the $\nu_7$ band is the strongest, indeed used for remote sensing measurements of ethylene.

Relying on high-resolution Fourier transform infrared (FTIR) spectra recorded in Brussels, the present work involved extensive measurements of individual line intensities and self broadening coefficients for the $\nu_7$ band of $^{12}$C$_2$H$_4$. Compared to the corresponding information available in the latest edition of the HITRAN spectroscopic database (HITRAN 2012 [2]), the measured line intensities were found to be higher by about 10 % for high J lines in the P branch and lower by about 5 % for high J lines of the R branch, varying between these two limits roughly linearly with the line positions. Test calculations performed in this work indicated that these discrepancies could result from the relative values of the transition moments of the $\nu_{10}$, $\nu_7$ and $\nu_{12}$ bands used when the information provided in HITRAN was generated (the transition moment of the $\nu_4$ band was set to zero). The measured self broadening coefficients exhibit a dependence on both J and K$_a$, which was modeled empirically. The spectroscopic information for ethylene available in HITRAN 2012 was modified to match the present observations. The impact of these modifications on retrievals of atmospheric ethylene was then evaluated via FTIR retrievals in the 949.0–952.0 cm$^{-1}$ microwindow, from a subset of ground-based high-resolution FTIR solar spectra recorded at the Jungfraujoch station. The new line intensities were found to lead to a reduction of the measured total columns of ethylene by $-4.1 \pm 0.1 \%$, compared to the use of HITRAN 2012.

Camphor is a bicyclic terpene. It can be naturally found in the wood of the camphor laurel tree mainly present in Asia, or it can be synthesized from α-pinene. It is mainly known from its strong aromatic smell in medicinal ointments. Camphor can be classified as a volatile organic compound (VOC) which can easily bind with water molecules. It may participate in the formation of aerosols when released in the atmosphere.

Camphor was studied by Kisiel et al. in 2003 [1]. They were able to obtain spectroscopic constants for the parent species, the ten $^{13}$C and the $^{18}$O isotopic species in natural abundance, from which they derived the $r_c$, $r_0$ and $r_m$ structures.

Our aim was to study the rotational spectra of the monohydrates and dihydrates of camphor. Ab initio calculations performed at the respectively M06-2X and MP2 levels using respectively the 6-311++G(2df,p) and 6-311++G(d,p) basis sets showed that two conformers of the monohydrate could be expected (see figure 1 below). Both should exhibit strong a-type spectra, weaker b-type spectra and very weak c-type spectra.

Using the MB-FTMW spectrometer in Lille, lines of the most stable conformer were easily found using the predictions made from ab initio calculations. Lines in the frequency range 5 – 20 GHz up to $J = 12$ were measured and fitted using the Pickett’s suite of programs using the Watson’s A-reduction Hamiltonian with the quartic centrifugal distortion constants included. In spite of careful search, we did not find any evidence of the presence of the less stable conformer in the supersonic expansion.

The search of lines of the dihydrate complex is still in progress.

![Figure 1 - The two conformers of camphor-H$_2$O, as predicted by ab initio calculations (MP2, 6-311++G(d,p)). The most stable is shown on the left.](image-url)

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DIODE-LASER SPECTROSCOPY: TEMPERATURE DEPENDENCE OF THE CO$_2$-BROADENING COEFFICIENTS IN THE $\nu_4$ BAND OF METHANE

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The study of planetary atmospheres is a hot topic and spectroscopy is a powerful tool to gain insight and new understanding of these atmospheres. Instruments on board various spacecrafts sound these atmospheres in different wavelength ranges, from the UV to the IR, under various geometry, solar or stellar occultation, limb and nadir to obtain detailed information on composition and even on dynamics. To retrieve physical properties, atmospheric spectra must be analyzed with accurate spectroscopic line parameters. In particular, broadening coefficients associated to their adequate line profile are of high importance [1].

The NOMAD instrument [2] on-board ExoMars mission, has been especially designed to observe CH$_4$. The determination of the densities of methane relies on the knowledge of accurate and adapted spectroscopic data, requiring, in particular for Mars, CO$_2$-broadening coefficients of high quality. Only one previous study about the CO$_2$-broadening coefficients has been performed, by our team, in the $\nu_4$ vibrational band at room temperature [3].

Using a tunable diode-laser spectrometer [4] equipped with a low or a high temperature absorption cell, we have measured CO$_2$-broadening coefficients of absorption lines in the $\nu_4$ fundamental band of methane. These coefficients have been determined by fitting three theoretical line profiles (Voigt, Rautian, Galatry) on the experimental line profiles. The measurements performed over a large range of temperatures (200 to 650 K) have permitted to deduce the temperature dependence of these collisional broadening coefficients. The experimental set-up and first results will be presented and discussed.

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CO$_2$-BROADENING COEFFICIENTS IN THE $\nu_3$ FUNDAMENTAL BAND OF METHANE AT ROOM TEMPERATURE

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Methane is a minor component of our atmosphere, as well as of Jupiter, Saturn, Uranus, Neptune and Mars. Methane has been detected on Mars by many studies [1,2] and is the main driver for the future ESA mission ExoMars. The origin of methane on Mars is still uncertain: it can be produced through internal processes like volcanic or biological processes, or external ones like cometary impacts. The NOMAD instrument [3] on-board ExoMars mission, has been especially designed to observe CH$_4$ in the $\nu_3$ fundamental band. However, to retrieve CH$_4$ abundances, accurate spectroscopic line parameters are needed. The previous studies of methane collisional broadening coefficients in the $\nu_3$ fundamental band were devoted to the CH$_4$-CH$_4$, CH$_4$-He, CH$_4$-N$_2$, CH$_4$-O$_2$, CH$_4$-H$_2$, CH$_4$-Ar and CH$_4$-Xe mixtures [4-7]. These works are especially useful for Earth atmosphere. The main component of the Martian atmosphere is carbon dioxide. The CO$_2$-broadening coefficients are thus needed to determine precisely the quantity of methane present in this atmosphere. Very recently, we also determined the CO$_2$-broadening coefficients in the $\nu_4$ vibrational band [8].

In the present study, we have measured CO$_2$-broadening coefficients of absorption lines in the $\nu_3$ fundamental band of methane. Each line was recorded at room temperature (296 K) and for 4 different pressures, comprised between 20 and 60 mbar. The line profiles have been individually fitted, at each pressure, with two lineshapes: the Voigt profile and the Rautian and Sobel'man model which includes the Dicke narrowing. From these fits, we have obtained the collisional half-widths at each pressure and then determined accurately the CO$_2$-broadening coefficients.

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N₂-BROADENING STUDY IN THE ν₂ BAND OF METHYL CHLORIDE

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Since the diminution of utilization of the CFC gases following the Montreal Protocol [1], methyl chloride has become one of the main sources of chlorine ions in the atmosphere [2], as the main sources are not only anthropomorphic activities, but also tropical forests [2] and biomass burnings [3]. In order to monitor with enough reliability the importance of methyl chloride in our atmosphere, one needs to determine his spectral parameters with high precision.

In the present work, we have measured N₂-broadening coefficients in the ν₂ band of methyl chloride between 1335 and 1370 cm⁻¹. The measurements were performed with a high resolution tunable diode laser spectrometer [4], for 15 lines in the P and R branches, with J ranging from 4 to 20 and K varying from 2 to 7. For each line, four measurements of the collisional half-width were realized, with different nitrogen pressure, from around 15 to 55 mbar.

Collisional broadening coefficients were retrieved from the fit of Voigt [5], Rautian [6] and Galatry [7] line profiles on the experimental data. For the last two line-shapes, the Dicke narrowing effect [8] was taken into account. We analyzed the angular dependence and compared our results with previous studies in the ν₁ [9] and ν₃ [10] bands.

**TP32**

**O₂-BROADENING COEFFICIENTS IN THE ν₄ + ν₅ BAND OF ACETYLENE**

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Acetylene is a minor component of our atmosphere [1] as well as of the atmospheres of Mars [2], Jupiter [3], Titan [4], Uranus [5-6], and Neptune [7]. It has been suggested that by 2030 the concentration of C₂H₂ in the Earth’s atmosphere would reach 150% of its value in the 1990s due to increased use of automobiles worldwide [8]. Consequently, it has been the subject of several high resolution spectroscopic studies, especially on collisional broadening. To our knowledge, no O₂-broadening coefficients of ¹²C₂H₂ in the ν₄ + ν₅ band have been yet reported.

In this work, we have measured O₂-broadening coefficients for 21 absorption lines in the ν₄ + ν₅ band of ¹²C₂H₂ at room temperature using a diode-laser spectrometer [9]. These lines with J values up to 23 were located in spectral range from 1275 to 1380 cm⁻¹. For each studied line, the broadening spectra were recorded at four different pressures of oxygen ranging from 20.00 to 66.21 mbar.

The O₂-collisional broadening coefficients of C₂H₂ were retrieved by fitting the experimental profiles to the Voigt line-shape [10] as well as the Rautian [11], and Galatry [12] models which take into account the collisional narrowing due to molecular confinement (Dicke effect) [13]. Finally, our results are compared with a previous study realized in the ν₅ band of acetylene [14].

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Over the past years, chlorofluorocarbons (CFCs) were widely used as blowing agents, propellants, refrigerants and fire extinguishers. Since 1996 these compounds have been phased out by the Montreal protocol, given their capacity to destroy the stratospheric ozone layer. Hydro-fluorocarbons (HFCs) have been proposed as replacement gases because, given the absence of chlorine atoms, they do not contribute to the ozone loss. In addition, HFCs have shorter atmospheric lifetimes than CFCs because the C—H bond undergoes reaction toward hydroxyl radicals in the troposphere. On the other hand, the C—F chromophore strongly absorbs the infrared (IR) radiation in the atmospheric window around $9 \mu m$, making HFCs potential greenhouse gases.

HFC-152a (1,1-difluoroethane, CHF$_2$CH$_3$) has been proposed as a valid replacement for CFCs to be used as aerosol propellant, foam expansion agent, and component of refrigerant blends. Due to its industrial and commercial applications, this molecule represents a potential atmospheric pollutant, which deserves spectroscopic investigations.

The present work deals with a combined experimental and theoretical study of the vibrational properties of HFC-152a. The vibrational analysis of the gas phase infrared spectrum has been carried out, in the far IR (FIR) and medium IR (MIR) regions, in terms of fundamentals, overtones, combination and hot bands up to three quanta of vibrational excitation. Accurate values of the absorption cross sections have been retrieved in the spectral range between 400 and 5000 cm$^{-1}$. MIR spectra have been recorded employing a Bruker Vertex 70 FTIR spectrometer equipped with a 13.4 ($\pm 0.1$) cm optical path length cell with KBr windows, while a Nicolet Magna 750 spectrometer and a 16 cm length cell (polyethene windows) have been used in the FIR region. For the vibrational analysis, resolutions of 0.2, 0.5 and 1 cm$^{-1}$ have been selected and the sample pressure has been varied between 0.5 and 2030 hPa. For the determination of absorption cross sections, spectra have been acquired at a resolution of 0.5 cm$^{-1}$, by using CHF$_2$CH$_3$ pressures in the range 0.54 - 220 hPa. All measurements have been carried out at 298 ($\pm 1$) K. The experimental work has been supported by quantum chemical calculations carried out at CCSD(T) and DFT levels of theory. In particular, CHF$_2$CH$_3$ equilibrium geometry and harmonic force field have been computed at the CCSD(T)/aug-cc-pVQZ level of theory, while the quartic semidiagonal force field has been evaluated employing the double hybrid B2PLYP functional coupled to the cc-pVTZ basis set. An hybrid CC/DFT force field has been devised with harmonic frequencies and anharmonic corrections computed at CCSD(T)/aug-cc-pVQZ and B2PLYP/cc-pVTZ levels, respectively. By performing a vibrational perturbative treatment (VPT2) of this hybrid force field, anharmonic frequencies, anharmonicity constants and coupling terms for Fermi and Darling-Dennison interactions have been derived in order to assist the quantum assignment. Details of the experimental and computational work and preliminary results will be presented.
The quantification of water vapour in the atmosphere is seen as an important contribution to the understanding of global atmospheric chemistry and issues relating to climate change effects. Fast and highly selective laser spectroscopic techniques such as tunable diode laser absorption spectroscopy (TDLAS) are important tools for atmospheric water monitoring and environmental applications [1-3]. In the atmosphere, the water content could vary between 40000 µmol/mol in the troposphere to about 3 µmol/mol (ppm) in the lower stratosphere, while the temperature and pressure could vary down to below -70 °C and down to a few 10 hPa, respectively. Hence, in order to accurately quantify the water vapour content in the atmosphere using these spectroscopic techniques, accurate and reliable line data such as pressure shifts, self and air collisional broadening coefficients as well as their temperature dependence are required to model spectra measured in the atmosphere.

In this work, we present accurate measurements of the temperature dependence, pressure shift, self and air broadening coefficients of a H\textsubscript{2}O absorption line at 1.4 µm. The measurements were performed using direct tunable diode laser absorption spectroscopy. For our temperature dependence measurements, we have used temperature-controlled gas cells which can be cooled or heated. With this setup, a temperature range from -40-300°C could be covered. The gas cells have been designed with special emphasis to achieve temperature homogeneity and to reduce temperature gradients across both ends to the mK range. For the pressure shift measurements, we stabilized the laser wavelength to better than 10\textsuperscript{-5} cm\textsuperscript{-1} (for 1σ at 1 Hz) resulting to accurate retrieval of the H\textsubscript{2}O line shift coefficients. Stable water in air mixtures generated by the German national humidity standard have been used to measure very smooth absorption profiles for the retrieval of air broadening coefficients to significantly reduce the measurement uncertainty. We further elaborate on the metrological challenges required to achieved data quality objectives that focus on issues such as the traceability of the results to the international system of units (SI) and an uncertainty analysis following the guidelines of the guide to the expression of uncertainty in measurements (GUM) [4]. We compared our results to data in literature (where available) and found good agreement, but our new results provide significantly improved uncertainties and thus will contribute to improved sensor accuracy in the future.

Acknowledgement: Part of this work has been carried out within the framework of the European Metrology Research Programme (EMRP) project ENV07 MeteoMet on Metrology for pressure, temperature, humidity and air speed in the atmosphere. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

MEASUREMENTS AND MULTISPECTRUM FITTING ANALYSIS OF OXYGEN B-BAND SPECTRA

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We recorded spectra of self- and foreign-broadened P-branch transitions of the oxygen B band occurring near 689 nm using the optical frequency comb-assisted Pound-Drever-Hall-locked frequency-stabilized cavity ring-down spectrometer (OFC-assisted PDH-locked FS-CRDS) [1, 2]. High frequency resolution and long-term stability as well as high sensitivity of the experimental setup allowed us to perform detailed line-shape analysis, where we took into account both the Dicke narrowing and the speed-dependent collisional broadening. The multispectrum fitting technique was used to minimize numerical correlations between fitted line-shape parameters. The relation between the parameters describing Dicke narrowing with the use of the soft- and hard-collision models is discussed and verified experimentally in the self-broadened case at the low pressure regime (below 5 kPa). We report absolute line positions with uncertainties of about 170 kHz, whereas intensities and the collisional broadening coefficients with subpercent uncertainty [3]. We compare these results to the data available in the literature.

The research is part of the program of the National Laboratory FAMO in Toruń, Poland, and is supported by the Polish National Science Centre Projects no. DEC-2011/01/B/ST2/00491 and UMO-2012/05/N/ST2/02717. The research is also supported by the Foundation for Polish Science TEAM and HOMING PLUS Projects co-financed by the EU European Regional Development Fund. A. Cygan is partially supported by the Foundation for Polish Science START Project.

Carbon dioxide CO\textsubscript{2} is the leading anthropogenic gas contributing to the greenhouse effect in the Earth’s atmosphere. Atmospheric CO\textsubscript{2} concentration is frequently monitored via satellites (e.g. GOSAT or in the future OCO2) as well as via ground-based FTIR networks (e.g. NDACC or TCCON) [1].

CO\textsubscript{2} lines near 2 \mu m are frequently used for remote sensing applications. In any case, spectroscopic monitoring closely depends on accurate input of line-by-line spectral data like line strength or air-broadening coefficients. Such data are frequently taken from the major databases like HITRAN or GEISA [2]. The CO\textsubscript{2} 2 \mu m HITRAN 2012 data are based on mid-resolution (0.010-0.015 cm\textsuperscript{-1}) FTIR measurements [3] as well as on approximations and calculations [3,4].

Here, we present new line strength measurements of the 50+ strongest CO\textsubscript{2} lines of the 2 \mu m band (20012-00001) measured with a high-resolution FTIR spectrometer (Bruker IFS 125HR, resolution: 0.002 cm\textsuperscript{-1}). Total integration times of 6-24 hours per spectrum ensured a high signal-to-noise ratio of typically 10\textsuperscript{3} and beyond. All measurements were performed with 99.9995% purity CO\textsubscript{2}. We employed two different gas cells, a 20 cm single-pass cell and a 3.2 m-40 m White cell, both temperature-stabilized to 296 K \pm 0.15 K by an active liquid cooling/heating system. The measurements were conducted at pressure levels from 1 mbar to 10 mbar. Several metrologically calibrated pressure sensors (1/10/100/1000 Torr) were used simultaneously to ensure consistent and reliable results.

A crucial issue for accurate CO\textsubscript{2} measurements is the suppression of background CO\textsubscript{2} present in the interferometer light path outside the measurement cell. Significant CO\textsubscript{2} and H\textsubscript{2}O absorption lines in the background signal can impair the results or even prevent reliable measurements [3]. We therefore modified the vacuum system of our spectrometer to reduce the background pressure by three orders of magnitude down to 10\textsuperscript{-5} mbar and less, such that despite the long interferometer section no background CO\textsubscript{2} absorption was detectable even in a 30 hours co-added background spectrum.

The presentation describes the instrumental setup used, presents the line strengths of CO\textsubscript{2} lines derived from the measurements and discuss the effects that determine the uncertainty of the retrieved line strengths.

Acknowledgement: We gratefully acknowledge the valuable advice by Pascale Roy and Laurent Manceron (SOLEIL) who shared their experiences with the setup of the vacuum system at the AILES beamline [6].

VERY HIGH RESOLUTION HETERODYNE DETECTION TECHNIQUE FOR SYNCHROTRON RADIATION IN THE THz RANGE

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The AILES beamline at synchrotron SOLEIL has been designed to provide a light source covering the complete infrared (IR) range with an extension in the THz domain. Since 2006, the AILES beamline has been exploited with a high resolution Fourier transform (FT) interferometer which provides spectra covering a broad spectral range with a resolution limited to about 30MHz. The synchrotron SOLEIL operates different storage modes where parameter such as the spatial distribution or the size of the electron bunches can be modified to achieve particular effects on the synchrotron radiation. Amongst the available operating modes coherent synchrotron radiation (CSR) is of notable interest as the power levels obtained in the THz region is orders of magnitude greater compared to a standard operating mode\cite{1,2}.

We have performed the first heterodyne study which consists of mixing (on Schottky diode mixer) the broadband synchrotron source with a well-defined electronic signal (harmonics of a local oscillator) and detecting the intermediate frequency (IF) in the low frequency range using a spectrum analyser. Preliminary tests in the 200 GHz and 400 GHz band have demonstrated that a greatly improved spectral resolution (typically down to few KHz) can be achieved.

This experiment allowed us to characterize the synchrotron beam with a resolution never achieved before. We show that in the case of CSR, the so-called “continuum” synchrotron radiation is actually composed of several discrete features having ultra-fine structures resembling a well-defined THz frequency comb. As shown by Billinghurst et al.\cite{2}, intense radiation spaced by 352 MHz (corresponding to the bunch frequency at SOLEIL) is observed. The new findings come from the observation of 846 KHz discrete features which have never been resolved previously. It corresponds to a periodic signal of \textasciitilde 1.18\mu s corresponding to the revolution period of the electron bunches in the ring.

This new detection scheme has also been applied to high resolution gas phase spectroscopy. Several pure rotational lines of acetonitrile (CH\textsubscript{3}CN) around 200 GHz have been recorded and compared to a 30 MHz convoluted spectrum.

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\end{thebibliography}
MEASUREMENT OF N$_2$-COLLISIONAL SHIFT COEFFICIENTS OF METHANE LINES IN THE $\nu_3$ BAND AT HIGH TEMPERATURES

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The study of the spectral parameters, and their variations with temperature and pressure, of methane lines is important for the remote sensing of atmospheres [1]. Methane is a minor component of the terrestrial atmosphere and his impact is important (methane is the third most abundant greenhouse gas [2]). Furthermore, methane is also present in the atmosphere of others planets [3-5] and stellar objects [6,7].

In this work, the collisional shift of absorption lines in the $\nu_3$ band of methane has been measured for several high temperatures (up to 600 K). This study has been made with a two-beams tunable diode-laser spectrometer.

The collisional line shift has been determined using a procedure described elsewhere [8]. So far we know, there is not a general law for the temperature dependence of the collisional line shift commonly used in the literature [9]. Knowing that, different laws have been tested to determine the temperature dependence of the line shift. The observations will be discussed.

A HYBRID VARIATION-PERTURBATION METHOD FOR CALCULATING ROVIBRATIONAL ENERGY LEVELS OF POLYATOMIC MOLECULES

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A procedure for calculation of ro-vibration states of medium sized molecules is presented. It combines the advantages of the variational calculations and perturbation theory. The vibrational problem is solved by diagonalizing a Hamiltonian matrix \cite{1}, which is partitioning into two sub-blocks. The first, smaller sub-block includes matrix elements with the largest contributions to the energy levels targeted in the calculations. The contributions from the matrix elements in the second, significantly larger sub-block, on these energy levels are generally small and are evaluated via perturbation theory, numerically implemented as a Jacobi rotation. Only the first sub-block needs to be stored in memory and diagonalized. The product of vibrational ($J=0$) eigenfunctions and rigid rotors wave functions are then used to construct the ro-vibrational basis set for the ro-vibrational eigen-problem, where the hybrid approach is also employed. The Hamiltonian matrix is partitioned into sub-blocks, each of which is associated with a single vibrational state. Such partitioning is especially efficient for systems where the Coriolis coupling between different vibrational energy levels is small. The cross-contributions from different vibrational states are included using the perturbation theory. The separate individual sub-blocks are then diagonalized, thus replacing the diagonalization of the large Hamiltonian matrix with a number of small eigen-problems.

Numerical examples show that the proposed hybrid variational-perturbation method significantly speeds up the solution of the eigen-problem without significant loss of precision both in ro-vibrational energies and transition intensities. With this hybrid scheme ro-vibrational energy levels of large molecules with up to 20 atoms can be treated.

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

Several monoterpenes and terpenoids are biogenic volatile organic compounds which are emitted in the atmosphere, and react with OH, O₃, NOₓ, etc. to give rise to several oxidation and degradation products. Spectroscopic information on these atmospheric species are still very scarce. Meanwhile we have demonstrated that combining quantum chemical calculations to microwave spectroscopy led to the unambiguous characterization of the most stable conformers for perillaldehyde [1], limonene and carvone [2]. This information can be used to subsequently model accurately the vibrational signature for atmospheric purposes [3]. We have recorded the pure rotational spectra of nopinone (C₉H₁₄O), using the MB-FTMW spectrometer of Lille, in the 2-20 GHz range at temperatures varying between 340 and 380 K. For this bicyclic molecules only one conformer can be observed, and the rotational structure was observed up to J, K_a = 10. All the spectra were modeled with a semi-rigid rotor Hamiltonian and fitted to obtain an rms value of about 1 kHz using a-, b- and c- type transitions. A hyperfine structure was observed. It was associated with the spin-spin interaction of the hydrogen nuclei of the three CH₂ groups of the molecule and modeled to reproduce the observed splittings.

All the experimental results were supported by several quantum calculations performed at different levels of theory (DFT and \textit{ab initio}). In particular no experimental evidence of internal rotation motion was found (methyl groups), in good agreement with the calculated barriers.

Support from the French Laboratoire d’Excellence CaPPA (Chemical and Physical Properties of the Atmosphere) through contract ANR-10-LABX-0005 of the Programme d’Investissements d’Avenir is acknowledged.

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Our work is focused to the study of the rotational spectra of the monohydrates and dihydrates of nopinone, which is one of the major oxidation products of β-Pinene. For this task, DFT and \textit{ab initio} calculations performed at the respectively M06-2X and MP2 levels using the respectively 6-311++G(2df,p) and 6-311++G(d,p) basis set showed that two conformers of the monohydrate could be expected. Both should exhibit strong \textit{a}-type spectra, weaker \textit{b}-type spectra and very weak \textit{c}-type spectra.

Using the MB-FTMW spectrometer in Lille, lines of the most stable conformer were found using the predictions made from \textit{ab initio} calculations. These spectra were recorded in the 2-20 GHz range at 343 K. Lines up to $J = 10$ and $K_a = 3$ were measured and fitted using the Pickett’s fit program with a semi-rigid rotor Hamiltonian model. The search of lines of the less stable monohydrate conformer and the dihydrate complex is still in progress. Moreover, no experimental evidence of internal rotation motion was found (methyl groups), in good agreement with the calculated barriers.

The CaPPA project (Chemical and Physical Properties of the Atmosphere) is funded by the French National Research Agency (ANR) through the PIA (Programme d'Investissement d'Avenir) under contract ANR-10-LABX-005.

THE INTERNAL ROTATION OF THE METHYL GROUP IN METHACROLEIN CHARACTERIZED BY MILLIMETER-WAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

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Methacrolein (MAC), CH$_2$=C(CH$_3$)CHO, is a molecule of atmospheric interest. Indeed it is a major product of the reaction between isoprene (C$_5$H$_8$) and the OH radical. Meanwhile spectroscopic information on MAC is still very scarce [1-2].

On the theoretical side, we have performed quantum chemical calculations at different levels of theory (DFT and \textit{ab initio}) to model the structure of the two conformers and the large amplitude motion associated with the methyl top. In particular the barrier height to internal rotation of the most stable conformer was calculated as being 500 cm$^{-1}$ at the MP2/aug-cc-pVTZ level.

On the experimental side, we have characterized the millimeter-wave spectrum of the most stable conformer of MAC. Spectra were recorded in the 150-465 GHz range using the Lille frequency multiplication chain spectrometer. In particular the ground state has been analyzed up to $J, K_a = 50, 17$, and the first excited state is currently investigated. The internal rotation has been treated using the Rho-axis-method (RAM) and the computer program RAM36, developed by V. Ilyushin. It should be noted that owing to molecular structure and particularity of the RAM the rotational Hamiltonian for MAC is established in II$^l$ coordinate representation. The spectrum analysis is in progress, and the global fit includes the ground and the first excited torsional states.

Support from the French Laboratoire d’Excellence CaPPA (Chemical and Physical Properties of the Atmosphere) through contract ANR-10-LABX-0005 of the Programme d’Investissements d’Avenir is acknowledged. OZ acknowledges the Région Nord-Pas-de-Calais (IRENI programme) and the CNRS for her doctoral fellowship.

The field of exoplanetary science is now a prominent area of research with the discovery of around 1800 exoplanets to date. The need to characterize the composition of these planets has led to a huge demand for spectroscopic data, the majority of which has yet to be catalogued. Unlike spectra recorded in the laboratory at room temperature, exoplanets are likely to be much hotter objects with temperatures up to 1500 K. Here we present work on the calculation of a hot rotation-vibration line list for methyl chloride. Interest for such a line list has increased due to the proposal of CH$_3$Cl as an observable biosignature gas in the search for life outside the Solar System [1]. A new nine-dimensional potential energy surface and dipole moment surface have been generated using the highest level of modern *ab initio* theory. The potential energy surface incorporates a range of higher-level additive energy corrections to account for scalar relativistic effects, core-valence electron correlation, higher-order coupled cluster methods, and the Born-Oppenheimer approximation. Variational calculations of the rotation-vibration energy levels and corresponding transition intensities of CH$_3$Cl have utilized the computer program TROVE [2], whose functionality has been extended to handle molecules of the form XY$_3$Z. To approach experimental accuracy in rovibrational calculations, the potential energy surface must be empirically refined to existing experimental spectroscopic data. This combination of first principles quantum mechanical methods and empirical tuning can produce highly accurate and extensive line lists applicable for elevated temperatures.

This work is part of the ExoMol project [3], which is actively providing key spectroscopic data on all molecular transitions necessary for the study and modelling of exoplanet and other hot atmospheres. S. Yurchenko and A. Yachmenev acknowledge the support from ERC Advanced Investigator Project 267219.

The recent discovery of the water dimer signatures in the microwave spectrum of equilibrium water vapour [1,2] encourages more detailed than previous characterization of how thermally excited weakly bound dimers interact with electromagnetic radiation. As stated in a number of previous studies (see e.g. [3,4]), near room temperature is high enough to have many rovibrational states of H$_2$O-H$_2$O pairs heavily populated in an intermolecular potential well. The role of quasi-bound thermally excited H$_2$O-H$_2$O states is thus becoming extremely important at least starting from about room temperature. When spectroscopically probed, these quasi-bound pair states may give rise to a continuum which can be associated with an absorption underlying individual dimer lines seen in [1,2]. Present paper aims at giving illustrative examples of how the formation of highly-excited quasi-bound dimers might affect the observed continuum-like absorption and how rotationally-resolved dimer features should manifest themselves in absorption. In particular, the effect of finite quasi-bound dimer lifetime on absorbance of radiation in various spectral ranges is discussed. The results of a model classical computation of the true dimer partition function and the relevant equilibrium constant are presented. The correspondence of these results to experimental observations in [1,2] is discussed.

The role of the solvent polarity on the molecule stability, the optimized geometry, atomic charges (for charge distribution), dipole moments (for molecular charge transfer) and vibrational spectra belonging to title molecule was discussed in detail. Solvent effects on theobromine molecule in different solvents (toluene, DMSO and water) were studied theoretically at the DFT/B3LYP level in combination with the conductor polarizable continuum model (CPCM). The variation of dipole moments and charges on atoms were studied in the gas phase and in water. Additionally, information about the size, shape, charge density distribution and site of chemical reactivity of the molecules has been obtained by mapping electron density isosurface with electrostatic potential surfaces (ESP). All calculations were performed at the DFT/B3LYP computational level (with the 6–311++G(d,p) basis set) by using Gaussian 09 program and Gauss View molecular visualization program package [1,2].

To gain an insight into the structure of different species of hydrogen bonds between caffeine and water and their relative stability, the equilibrium geometry and the vibrational frequencies are calculated, using DFT calculations. The results of calculations show that formation of complexes with water molecule will affect the structures of the molecule. Comparison with gas phase results reveal that hydrogen bonding induces small changes in the bond lengths. The computed IR spectra show that the some stretching vibrational bands of caffeine are changed due to the hydrogen bond formation. The frequency shifts in IR spectra and changes in the bond lengths are interpreted as the hydrogen bonding interactions between caffeine and water.

The total electron density and molecular electrostatic potential surfaces of the molecule were constructed by using B3LYP/6–311++G** method to display electrostatic potential (electron + nuclei) distribution. The electronic properties HOMO and LUMO energies were also measured. All calculations were performed at the DFT/B3LYP computational level (with the 6–311++G(d,p) basis set) by using Gaussian 09 program and Gauss View molecular visualization program package [1,2]. The parameters most sensitive to the complexation are the stretching vibrations of title molecule involved in hydrogen bonding.

THEORETICAL INVESTIGATIONS OF α, α, α-TRIFLUORO-3, -P AND O-NITROTOLUENE BY MEANS OF DENSITY FUNCTIONAL THEORY

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We study the optimized molecular structures, vibrational frequencies including Infrared intensities and Raman activities, corresponding vibrational assignments, 1H and 13C NMR chemical shifts, the magnitudes of the JCH and JCC coupling constants, Ultraviolet–visible (UV–vis) spectra, thermodynamic properties and atomic charges of the title compounds, α, α, α-trifluoro-3, -p and o-nitrotoluene, in the ground state by means of the density functional theory (DFT) with the standard B3LYP/6-311++G(d,p) method and basis set combination for the first time. Theoretical vibrational spectra were interpreted by normal coordinate analysis based on scaled density functional force field. The results show that the vibrational frequencies and chemical shifts calculated were obtained to be in good agreement with the experimental data. Based on the comparison between experimental results and theoretical data, the calculation level chosen is powerful approach for understanding the identification of all the molecules studied. In addition, not only were frontier molecular orbitals (HOMO and LUMO), molecular electrostatic potential (MEP) and electrostatic potential (ESP) simulated but also the dipole moment, softness, electronegativity, chemical hardness, electrophilicity index, transition state and energy band gap values were predicted. According to the investigations, all compounds were found to be useful to bond metallically and interact intermolecularly; however, the thermodynamic properties confirm that the α, α, α-trifluoro-p-nitrotoluene was more reactive and more polar than the others.
THE SPECTRAL LINE CONTOUR SHAPE IN THE LINE WING FOR DIFFERENT BANDS OF H$_2$O AND CO$_2$

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There are situations when the spectral line contour shape at the offset frequencies (at large distances from the line center) can manifest itself in a wide spectral regions - namely in the transparency windows of the atmosphere. One of such regions is the 8-12 microns interval of H$_2$O. It is an example of a so-called continuous absorption. Let us assume the interpretation of continuous absorption as determined by total absorption of the line wings of H$_2$O monomer. The most accepted approximation that is widely used in the atmospheric radiation models is MT_CKD. According to it, the contour shape is assumed uniform for all lines of any of the bands in the IR-range. During experimental and theoretical researches the focus was on the spectral trend and temperature dependence of the absorption coefficients and the role of bath gas in experimental and theoretical studies of the absorption behavior in the wings of the H$_2$O and CO$_2$ bands. There has been no comparison of the line contours of different bands. However, it’s possible to detect indirect evidence of such dependence in the literature. Thus, in [1] the function characterizing the deviation of the contour in the wing from Lorentzian line shape was determined numerically for bands 4.3, 2.7 and 1.4 microns of CO$_2$. This deviation function occurs to be different for different bands. Different empirical line contours for rotational, $v_2$ and $v_1$ $v_3$ - bands of H$_2$O were obtained in [2]. These results also show that deviations from Lorentzian line shape are different for different bands.

The line shape dependence in the line wing from the reference band is natural for Asymptotic line wing theory formalism [3] that we used for our calculations. In this work the deviations of the line contours from the Lorentzian line shape for bands in the intervals of 800-1000, 2000-2600 and 4000-5000 cm$^{-1}$ of H$_2$O (see also [4]) were numerically defined on the basis of experimental data [5]. Similar deviations were numerically defined in the wings of the bands 1.2, 1.2195, 1.4, 2.7, 4.3 micron of CO$_2$. These deviations are in good agreement with that obtained in [1] for bands 1.4, 2.7, 4.3 microns.

Available in the literature experimental data on the continuous absorption of H$_2$O and CO$_2$ in the transparency windows can be described as a total absorption of the line wings of the neighbor bands with the special contour shape in the wing. While the line contour in the wing detects a dependency on the considered spectral range, in other words, is different for different bands.

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Classical ro-vibrational trajectories for a model water-like molecule are analyzed to investigate how a well-known bifurcation in its rotational dynamics is influenced by vibrational excitation. It is demonstrated that even when rotation around new stationary axes is clearly visible for a molecule exhibiting small-amplitude vibrations, such new type of rotational motion may disappear completely as a vibrational excitation increases. As the result corresponding changes in quantum rotational multiplets should not be visible in case of highly excited rotational states.

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CONFORMATIONAL FLEXIBILITY OF LIMONENE OXIDE STUDIED BY MICROWAVE SPECTROSCOPY

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It is well established that biogenic volatile organic compounds (BVOCs) play a major role in atmospheric chemistry. Besides methane and isoprene, large quantities of monoterpenes are emitted by a variety of plants and coniferous forests and are atmospheric pollutants [1]. These molecules and their oxidation and degradation products may participate in the formation of aerosols.

The title molecule, limonene oxide, is an atmospheric pollutant product of oxidation of other terpenes, as limonene and α-pinene, among others [2]. This molecule has already been studied theoretically and experimentally in liquid phase by chiroptical (Vibrational Circular Dichroism) and non chiroptical (IR, Raman) techniques [3]. Our aim was to study the rotational spectra of limonene oxide. DFT and ab initio calculations were performed, i.e. B3LYP/6-311++G(2df,p), M062X/6-311++G(2df,p), MP2/aug-cc-pVTZ and MP2/6-311++G(d,p) methods. The G3 methodology was also used to predict the relative energies. All these calculations showed six conformers with an energy less than 5kJ/mol. The four most stable conformers of limonene oxide should be expected in the jet, since the fifth and sixth ones could relax to other conformers [4]. All of them should exhibit strong c-type transitions while b-type and a-type transitions are expected to be weaker.

Using the MB-FTMW spectrometer in Lille, the three most stable conformers were observed. The spectra were recorded in the 4-20 GHz range at 343 K. Lines up to \(J = 12\) and \(K_a = 3\) were measured and fitted using the Pickett’s fit program. The search of lines of the fourth conformer is still in progress. Moreover, no experimental evidence of internal rotation motion was found (methyl groups), in good agreement with the calculated barriers.

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FROM THE GAS TO CONDENSED PHASES: MICROWAVE AND VIBRATIONAL STUDY OF $\gamma$-TERPINENE

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It is well established that biogenic volatile organic compounds (BVOCs), as monoterpenes, play a major role in atmospheric chemistry [1]. From the gas phase, they may participate in the formation of aerosols which are found as particles in the condensed phase. The target of this work is focused on the structural analysis in the gas and condensed (liquid and solid) phases of $\gamma$-Terpinene. Thus, our methodology is the following: 1) In the first step of this work, theoretical calculations and microwave spectroscopy were used in order to evidence the most stable conformers and their relative energies [2]. To this end MB-FTMW spectra were recorded and analysed in the 4-20 GHz region at Lille; 2) For the gas phase, the infrared spectra have been recorded on the FTIR spectrometer of the AILES beamline at synchrotron SOLEIL, using a long path cell. Special attention was given to the 700–1300 cm$^{-1}$ atmospheric window, to the CH vibration region, and to the “fingerprint” FIR region [3]; 3) For the condensed phases, the IR, FIR and Raman spectra have been recorded using the spectrometers available at the University of Jaen.

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