

SYNCHROTRON HIGH-RESOLUTION FTIR SPECTROSCOPY SORTS OUT THE GROUND STATE AND LOW WAVENUMBER MODES OF KETENIMINE

D. McNaughton¹, M. K. Bane¹, C. D. Thompson¹, E. G. Robertson², D. R. T. Appadoo³, C. Medcraft¹

¹ School of Chemistry, Monash University, 3800, Victoria, Australia

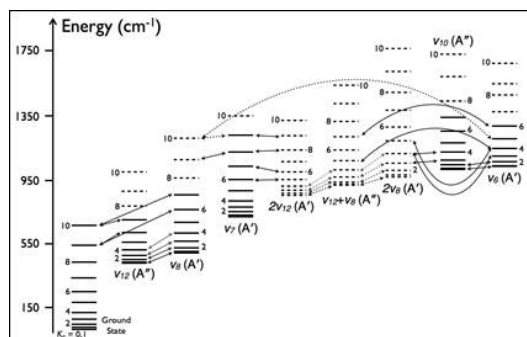
² Department of Chemistry, La Trobe University, 3083, Victoria, Australia

³ Australian Synchrotron, 800 Blackburn Rd, Clayton, 3168, Victoria, Australia

Ketenimine ($\text{CH}_2\text{C}=\text{NH}$) is a transient molecule that is of interest in interstellar chemistry and about which little is known. This tautomer of acetonitrile has been identified in the star forming region Sagittarius B2(N) via microwave emissions. In this study far- and mid-IR high resolution spectra were recorded using a Bruker HR125 coupled to the far-IR beam line of the Australian synchrotron and both pure ground state rotational transitions and ro-vibrational transitions were recorded.

The excited vibrational states exhibit complex ro-vibrational structure, due primarily to strong Coriolis interactions as shown in the figure. As a consequence of this dynamic coupling, some of these modes exhibit a novel intensity sharing effect, with the relatively weak ν_{10} and ν_{12} bands being analyzed completely using perturbation allowed transitions [1], which exhibit intensities independent of their natural dipole moment derivative.

The analysis of ν_7 [2], ν_{10} and ν_6 [3] were also complicated by the presence of local Fermi and Coriolis resonances with the higher order excitations of ν_{12} and ν_8 , which are themselves strongly Coriolis coupled. Analysis of ground state combination differences of ν_7 also uncovered second order Coriolis interactions between the ground state and both ν_{12} and ν_8 at high K_a , and a global fit including the ground state, ν_{12} , ν_8 , ν_7 , $2\nu_{12}$, $\nu_{12} + \nu_8$, $2\nu_8$, ν_{10} and ν_6 was achieved. The combination and overtones were included in the fit as dark-states, since they were too weak to be observed.



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**TEN-STATE FIT TO ACROLEIN LEVELS BETWEEN 850 AND 1020 cm^{-1} :
LOCATION OF THE ELUSIVE ν_{15} VIBRATION**

A.R.W. McKellar¹, B.E. Billinghurst², Li-Hong Xu³, R.M. Lees³

¹National Research Council of Canada, Ottawa, ON K1A 0R6, Canada

²Canadian Light Source, 101 Perimeter Road, University of Saskatchewan, Saskatoon, SK
S7N 0X4, Canada

³Department of Physics and Centre for Laser, Atomic, and Molecular Sciences, University of
New Brunswick, St. John, NB E2L 4L5, Canada

Acrolein (propenal, CH_2CHCHO) is an interstellar molecule, key atmospheric pollutant, and tobacco smoke byproduct. As well, it is a component in the chemical soups used for mining hydrocarbons by means of hydraulic fracturing (fracking). We have been studying acrolein (the lower energy *trans* rotamer) for a number of years, exploring to what extent complete and detailed rotational analysis is possible for a molecule of this size using very high resolution infrared spectra. The present results are based on new spectra obtained at the Canadian Light Source using synchrotron radiation to probe acrolein in a low temperature (200 K) long path (16 and 72 m) absorption cell.

Our previous study of this region involved the ν_{11} (911 cm^{-1}), ν_{16} (959 cm^{-1}), and ν_{14} (993 cm^{-1}) fundamental bands [1]. Now we extend the analysis to include three additional nearby combination vibrations. And, most crucially, we locate the weak ν_{15} fundamental, which has not previously been observed. Our analysis includes these seven vibrational states together with three more which are not directly observed but which perturb the observed states. They are combined in a large ten-state (!) simultaneous fit. These ten states are as follows: four fundamentals already mentioned; directly observed combinations $\nu_{12} + 2\nu_{18}$ (878 cm^{-1}), $\nu_{17} + 2\nu_{18}$ (899 cm^{-1}), $\nu_{17} + \nu_{13}$ (917 cm^{-1}); and indirectly observed perturbers $\nu_{12} + \nu_{13}$ (≈ 889 cm^{-1}), $6\nu_{18}$ (≈ 920 cm^{-1}), $3\nu_{13}$ (≈ 976 cm^{-1}).

Does a ten-state fit make any sense? It is computationally quite feasible, even just using an ordinary (modern) PC. The largest matrices to diagonalize (for $K < 20$, with factorization) are 200 x 200. But there are certainly difficulties, as will be discussed here. These include the problem of labeling the rotational levels, and of dealing with a large number of vibrationally off-diagonal parameters (≈ 50 , at the moment). Even if the ten-state analysis is ultimately a bit impractical, it is still interesting to explore.

It turns out that the weak ν_{15} fundamental band origin is located at 1002 cm^{-1} , somewhat higher than we expected (for example, Hamada *et al.* [2] report 972 cm^{-1}). Since this lies *above* the known ν_{14} origin at 993 cm^{-1} , it seems that we should exchange the labels and say that the 1002 vibration is really ν_{14} , and the 993 vibration is ν_{15} (both are out-of-plane bends, with A'' symmetry).

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HIGH-RESOLUTION MOLECULAR BEAM SPECTROSCOPY OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE 3 μM REGION

Elena Maltseva¹, Annemieke Petrigani^{2,3}, Alessandra Candian², Xander Tielens², Jos Oomens^{1,3}, Wybren Jan Buma¹

¹University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

²Leiden Observatory, Niels Bohrweg 2, 2333 CA Leiden, The Netherlands

³Radboud University, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands

Strong infrared emission features at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.7 μm referred to as the unidentified infrared bands are observed in different types of space objects. These features are basically attributed to polycyclic aromatic hydrocarbons (PAHs), although the exact molecular identification of the carriers of these infrared features has not been possible yet [1]. We present a high-resolution IR absorption study of a number of jet-cooled polycyclic aromatic hydrocarbons in the 3.3 micrometer region. The experimental spectra display many more bands than expected (Fig. 1), and lead to the conclusion that the appearance of the spectrum is dominated by fourth-order vibrational coupling terms. This has far-reaching consequences since up till now the assignment of infrared emission features observed in different types of space objects in this wavelength region -and the conclusions drawn from these assignments on the evolution of interstellar gas- has heavily relied on harmonic quantum chemical calculations [2].

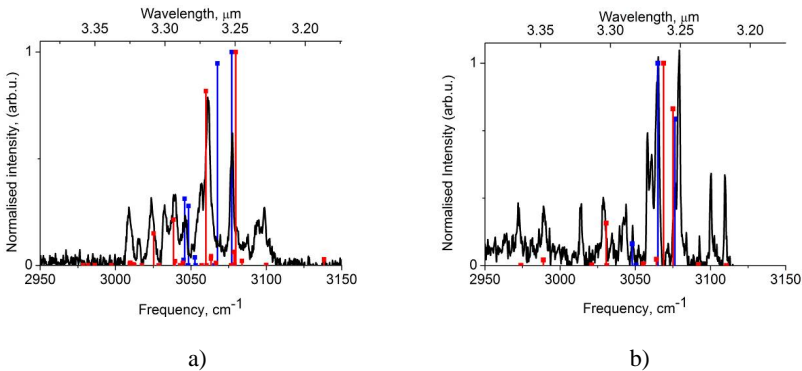


Figure 1. High-resolution 3 μm absorption spectra (black line) of naphthalene (a) and tetracene (b) plotted with stick spectra from harmonic (blue) and anharmonic (red) DFT calculations.

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FREQUENCY COMB ASSISTED MIR SPECTROSCOPY OF H_3^+ and CD_2H^+

Oskar Asvany, Pavol Jusko, Sandra Brünken, Stephan Schlemmer

I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln, Germany

Cryogenic ion traps, narrow band infrared radiation sources, and accurate frequency calibration via a frequency comb are ideal tools for high-resolution vibrational spectroscopy of molecular ions [1]. In this work, we use the action spectroscopic techniques LIR (laser induced reactions, [2]) and LIICG (laser induced inhibition of complex growth, [3]) in a 4 K 22-pole ion trap to record spectra of H_3^+ and CD_2H^+ . While the high-resolution vibrational data on CD_2H^+ allow to predict pure rotational transitions with sub-MHz accuracy, and thereby tremendously facilitate their mm-wave detection (see contribution S. Brünken), accurate data on H_3^+ (see Figure) are important as it is an ab initio benchmark system [4]. With our measurements on H_3^+ we hope to resolve some recent disagreements of the high-resolution data found in the literature [5].

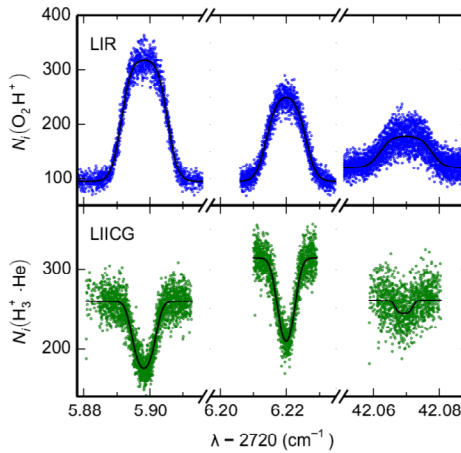


Figure 1. Measurement examples of H_3^+ transitions in the ν_2 fundamental band recorded with the methods of LIR (upper panel) at a nominal temperature of 40 K and LIICG (lower panel) at 4 K.

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CRDS OF ACETYLENE NEAR 1.6 μm

O. M. Lyulin ^{1,2}, D. Mondelain ¹, S. Kassi ¹, J. Vander Auwera ³, A. Campargue ¹

¹Université Grenoble 1/CNRS, UMR5588 LIPhy, Grenoble, F-38041, France

²Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS, 1, Academician Zuev square, Tomsk 634021, Russia

³Service de Chimie Quantique et Photophysique, C.P. 160/09, Université Libre de Bruxelles, 50 Avenue F. D. Roosevelt, B-1050 Brussels, Belgium

The absorption spectrum of acetylene has been recorded at room temperature (297 K) using high sensitivity Cavity Ring Down Spectroscopy ($\alpha_{\text{min}} \sim 5 \times 10^{-11} \text{ cm}^{-1}$) in the 5851 and 6341 cm^{-1} interval corresponding to a region of very weak absorption. A list of about 10700 absorption features with estimated absolute line intensities was constructed. The smallest intensities are on the order of $5 \times 10^{-29} \text{ cm/molecule}$. The line list includes about 2500 absorption lines of ethylene present at the ppm level in the acetylene sample and identified on the basis of a high resolution Fourier transform spectrum specifically recorded. A total of more than 2700 lines of $^{12}\text{C}_2\text{H}_2$ were rovibrationally assigned by comparison with accurate predictions provided by a global effective operator model. Overall, the present effort adds about 2260 new assignments to the set of about 500 assigned transitions available in the literature. The new assignments correspond to 45 new bands and 17 already known bands, for which additional *J*-lines were assigned. 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 0.001 cm^{-1}). A few of the analyzed bands were found to be affected by rovibrational perturbations, which are discussed. The new data will be valuable to refine the parameters of the global effective Hamiltonian and dipole moments of $^{12}\text{C}_2\text{H}_2$.

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ACCURATE HIGH RESOLUTION FTIR MEASUREMENTS OF THE SELF- AND AIR-BROADENING COEFFICIENTS IN THE $2\nu_3$ -BAND OF N_2O

Viktor Werwein, Jens Brunzendorf, Olav Werhahn, Volker Ebert

Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

One of the main contributors to the atmospheric greenhouse effect is nitrous oxide. Spectral line data of this atmospheric trace gas – especially line-broadening coefficients – with well-defined uncertainties are of high importance for remote sensing applications, modelling of earth atmosphere composition and therefore for prediction of climate development.

The self-broadening coefficients of nitrous oxide documented in the HITRAN [1] and GEISA [2] databases rely on an extensive line set measured by Toth [3] over a pressure range of 87-533 mbar using FTIR spectroscopy in the spectral range from 1800 to 2360 cm^{-1} . In this study the measured coefficients were averaged for the same rotational quantum numbers over different vibrational bands and smoothed afterwards. During the implementation process into the HITRAN database numerous self-broadening coefficients were determined via an interpolation between Toth's data. The situation for N_2O -air-broadening coefficients is similar. The HITRAN values, for example, originate from FTIR measurements made by various groups [4, 5, 6] each using different treatment of uncertainties. Also in this case broadening coefficients of a considerable number of lines were implemented into the HITRAN database using a third order polynomial fit to the mentioned measurements. So far, no direct high resolution experimental validation of these interpolated data have been reported, e.g., for the self- and air-broadening coefficients. This is in parts the case for the N_2O ν_3 -fundamental and the $2\nu_3$ -overtone band.

In the framework of the EUMETRISPEC project [7] we used high resolution FTIR spectroscopy for measurements of self- and air-broadening coefficients for the $2\nu_3$ -overtone band of N_2O under improved experimental conditions (i.e. improved N_2O -sample purity of 99.999 %, a metrologically validated standard air mixture, a set of traceably calibrated pressure and temperature sensors as well as a precisely temperature-stabilized copper absorption cell for compensating temperature fluctuations). The corresponding infrared spectra were taken at the temperature of 296 K in the spectral range from 3800 to 5200 cm^{-1} with a nominal resolution of 0.002 cm^{-1} . While the lowest measured pressures were 200 mbar, the upper pressure ranges for both self- and air-broadening measurements were extended up to 1300 mbar. Broadening coefficients for the rotational levels from $J=1$ to $J=40$ are reported and compared to literature values.

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[7] www.eumetrispec.org.

FTS STUDIES OF THE ISOTOPOLOGUES OF CO₂ TOWARD CREATING A COMPLETE AND HIGHLY ACCURATE REFERENCE STANDARD

Ben M. Elliott, Keeyoon Sung, Charles E. Miller

NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive,
M/S 233-300, Pasadena, CA 91109 USA

The proliferation and increased abilities of remote sensing missions for the monitoring of planetary atmospheric gas species has spurred the need for complete and accurate spectroscopic reference standards. As a part of our ongoing effort toward creating a global carbon dioxide (CO₂) frequency reference standard, we report new FTS measurements of the isotopologues of CO₂. The first measurements were taken of the ¹⁷O-enriched isotopologues in the ν_3 region (2200 - 2450 cm⁻¹, ~65 - 75 THz), and have absolute calibration accuracies of 100 kHz (3x10⁻⁶ cm⁻¹) or better, comparable to the uncertainties for typical sub-millimeter/THz spectroscopy. Similarly high quality data have also been produced for the ¹⁸O- and ¹³C-substituted species. Such high absolute calibration accuracy has become regular procedure for the cases of linear molecules such as CO₂ and CO for FTS measurements at JPL, and enables us to produce measured transition frequencies for entire bands with accuracies that rival those of early heterodyne measurements for individual beat notes. Additionally, by acquiring spectra of multiple carbon dioxide isotopologues simultaneously, we have begun to construct a self-consistent frequency grid based on CO₂ that extends from 20 – 200 THz. These new spectroscopic reference standards are a significant step towards minimizing CO₂ retrieval errors from remote sensing applications, especially those involving targets with predominantly CO₂ atmospheres such as Mars, Venus and candidate terrestrial exoplanets where minor isotopologues will make significant contributions to the radiance signals.

THE WATER SELF CONTINUUM NEAR 1.6 μm D. Mondelain^{1,2}, S. Kassì^{1,2}, A. Campargue^{1,2}¹Université Grenoble Alpes, LIPhy, F-38000 Grenoble, France
²CNRS, LIPhy, F-38000 Grenoble, France

Since its discovery one century ago, a deep and, up to now, unresolved controversy remains on the nature of the water vapor continuum. Several interpretations are proposed: accumulated effect of the distant (non-Lorentzian) wings of many individual spectral lines, metastable or true bound water dimers, collision-induced absorption [1-3]. The atmospheric science community has largely sidestepped this controversy, and has adopted a pragmatic approach: most radiative transfer codes used in climate modelling, numerical weather prediction and remote sensing use the MT_CKD model which is a semi-empirical formulation of the continuum [4]. The MT_CKD cross-sections were tuned to available observations in the mid-infrared but in the absence of experimental constraints, the extrapolated near infrared (NIR) values are much more hazardous. Due to the weakness of the broadband absorption signal to be measured, very few measurements of the water vapor continuum are available in the NIR windows especially for temperature conditions relevant for our atmosphere. This is in particular the case for the 1.6 μm window where the very few available measurements show a large disagreement. Here we present the first measurements of the water vapor self-continuum cross-sections in the 1.6 μm window [5,6] by cavity ring down spectroscopy (CRDS) at different temperatures (from room temperature to 340 K). The real time pressure dependence of the absorption continuum was investigated during pressure cycles up to 12 Torr for fifteen selected wavenumber values. The continuum absorption coefficient measured between 5875 and 6450 cm^{-1} shows a minimum value around 6300 cm^{-1} and ranges between 1×10^{-9} and 8×10^{-9} cm^{-1} for 8 Torr of water vapor, to be compared to a baseline stability of the order of 10^{-10} cm^{-1} in routine. The continuum level is observed to deviate significantly from the expected quadratic dependence versus the pressure. This deviation is interpreted as due to a significant contribution of water adsorbed on the super mirrors to the cavity loss rate. The pressure dependence is well reproduced by a second order polynomial. We interpret the linear and quadratic terms as the adsorbed water and vapor water contribution, respectively. The derived self-continuum cross sections, $C_s(T=296\text{ K})$, ranging between 3×10^{-25} and 3×10^{-24} $\text{cm}^2 \text{ molec}^{-1} \text{ atm}^{-1}$ are found in reasonable agreement with the last version of the MT_CKD 2.5 model, except for the temperature dependence in the center of the window which is found significantly smaller than predicted. Comparison with other existing experimental data and models will be discussed.

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**AN ACCURATE AND COMPLETE EMPIRICAL LINE LIST FOR WATER VAPOR
BETWEEN 5850 AND 7920 cm⁻¹**

A. Campargue^{1,2}, S. N. Mikhailenko^{3,4}, D. Mondelain^{1,2}, S. Kassì^{1,2}

¹Université Grenoble Alpes, LIPhy, F-38000 Grenoble, France

²CNRS, LIPhy, F-38000 Grenoble, France

³Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB,
Russian Academy of Science, 1, Akademician Zuev square, 634021, Tomsk, Russia

⁴Mathematical Physics Department, Tomsk Polytechnic University 30, Lenin av., 634050,
Tomsk, Russia

An empirical line list has been constructed for “natural” water vapor at 296 K in the 5850 – 7920 cm⁻¹ region. It was obtained by gathering separate line lists recently published on the basis of spectra recorded by high sensitivity Continuous Wave Cavity Ring Down Spectroscopy (CW-CRDS) of natural water, complemented with literature data for the strongest lines. The list includes 38318 transitions of four major water isotopologues (H₂¹⁶O, H₂¹⁸O, H₂¹⁷O and HD¹⁶O) with an intensity cut-off of 1×10⁻²⁹ cm/molecule at 296 K. The list is made mostly complete over the whole spectral region by including a large number of weak lines with positions calculated using experimentally determined energy levels and intensities obtained from variational calculations. In addition, we provide HD¹⁸O and HD¹⁷O lists in the same region for transitions with intensities larger than 1×10⁻²⁹ cm/molecule. The HD¹⁸O and HD¹⁷O lists (1972 lines in total) were obtained using empirical energy levels available in the literature and variational intensities. The global list (40290 transitions) for water including the contribution of the six major isotopologues will be adopted for the next edition of the GEISA database in the region.

The advantages and drawbacks of our list are discussed in comparison with the list provided for the same region in the 2012 edition of the HITRAN database. The direct comparison of the CRDS spectra to simulations based on the HITRAN list has revealed some insufficiencies which could easily be corrected: missing HDO lines, duplicated lines, inaccurate line positions or line intensities from variational calculations.

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**SPECTROSCOPY OF $^{14}\text{NH}_3$ AND $^{15}\text{NH}_3$ IN THE RANGE 6369 TO 6578 cm^{-1} .
DETERMINATION OF LOWER STATE ENERGY TRANSITIONS USING
TEMPERATURE DEPENDENCE FROM 134K TO 296K**

J. EL Romh^{1,2}, P.Cacciani¹, J.Cosléou¹, M. Khelkhal¹, F.Taher²

¹Physical Laboratory of Lasers, Atoms and Molecules , Lille1University ,France

²Molecular Quantum Mechanics and modeling, Lebanese University(Beirut-Hadath),
Lebanon

The spectroscopy of ammonia was known up to 5600 cm^{-1} in the database (HITRAN 2008) including the ground state fundamental vibration absorption bands (v_1 : symmetric stretch, v_2 : symmetric bend, v_3 : asymmetric stretch, v_4 : asymmetric bend) and several combination and overtone bands. Recently, collecting available information, Sung and al [1] proposed a list for main isotopologue $^{14}\text{NH}_3$ in the range 6300-7000 cm^{-1} , which have been included in the updated database (HITRAN 2012). For the $^{15}\text{NH}_3$ isotopologue, only attributions of transitions belonging to $v_1 + v_3$, $v_1 + 2v_4$, $v_3 + 2v_4$ [2-4] bands have been performed by Lees and al in the range 6412 to 6819 cm^{-1} , furthermore line positions and line strengths of the several lines have been measured by Lins and al [5]. In our work the spectra of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ have been recorded with an External Cavity Diode Tunable Laser spectrometer (ECDTLS) from 6369 cm^{-1} to 6578 cm^{-1} at four temperatures (134K, 180K, 220K, 296K). The spectra has been calibrated and each transition fitted to Voigt profile by the help of dedicated software (Labview, Fityk) [6]. Lines positions and intensity ratio temperature dependence have been used to derive the energy of lower state for each transition. A specific treatment has been developed considering pairs of transitions intensities removing pressure dependence. For $^{14}\text{NH}_3$ a transition list has been proposed including position, intensity and lower state energy. Comparison with the Sung one shows new lines, confirms the Sung assignments for many transitions but exhibits disagreement for several components. For $^{15}\text{NH}_3$, a list similar to the Sung's one for $^{14}\text{NH}_3$ has been proposed at 296K for the first time in the range 6367-6578 cm^{-1} and work on lower state energy is in progress.

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INFRARED SPECTROSCOPY OF ^{17}O -ENRICHED CARBON DIOXIDE IN THE 3200-5340 cm^{-1} RANGE. IMPROVEMENT OF THE GLOBAL MODELING OF THE LINE POSITIONS AND INTENSITIES OF RARE CO_2 ISOTOPOLOGUES

Yu.G. Borkov¹, D. Jacquemart^{2,3}, O.M. Lyulin¹, S.A. Tashkun¹, V. I. Perevalov¹

¹Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Academician Zuev square, 634021, Tomsk, Russia

²Sorbonne Universités, UPMC Univ Paris 06, UMR 8233, MONARIS, F-75005, Paris, France

³CNRS, UMR 8233, MONARIS, F-75005, Paris, France

The line positions and intensities of carbon dioxide isotopologues have been retrieved in the 3200-5340 cm^{-1} region from Fourier transform spectra recorded in MONARIS (Paris, France) with the Bruker IFS 125-HR [1]. In total 17930 line positions and intensities of 242 bands of 12 isotopologues $^{16}\text{O}^{12}\text{C}^{16}\text{O}$, $^{16}\text{O}^{13}\text{C}^{16}\text{O}$, $^{16}\text{O}^{12}\text{C}^{18}\text{O}$, $^{16}\text{O}^{12}\text{C}^{17}\text{O}$, $^{16}\text{O}^{13}\text{C}^{18}\text{O}$, $^{16}\text{O}^{13}\text{C}^{17}\text{O}$, $^{18}\text{O}^{12}\text{C}^{18}\text{O}$, $^{17}\text{O}^{12}\text{C}^{18}\text{O}$, $^{18}\text{O}^{13}\text{C}^{18}\text{O}$, $^{17}\text{O}^{12}\text{C}^{17}\text{O}$, $^{17}\text{O}^{13}\text{C}^{18}\text{O}$, and $^{17}\text{O}^{13}\text{C}^{17}\text{O}$ have been retrieved. 98 bands were assigned for the first time. All studied bands belong to the $\Delta P = 5$, 6 and 7 series of transitions, where $P = 2V_1 + V_2 + 3V_3$ is the polyad number (V_i are vibrational quantum numbers). The accuracy of the line position measurement is about $0.3 \times 10^{-3} \text{ cm}^{-1}$ for the unblended and not very weak lines. The accuracy of the line intensities varies from 4% to 15% depending on the isotopologue, on the intensity of the line and on the extent of the line overlapping. The spectroscopic constants have been derived for the majority of the observed bands. The observed line positions together with those collected from the literature were used to improve the effective Hamiltonian parameters of the above listed isotopologues. The fitted sets of parameters for all isotopologues reproduce the measured line positions within the measurement uncertainties (rms values are around 0.001-0.002 cm^{-1}). The measured intensities were used to fit the effective dipole moment parameters for the $\Delta P = 5$ and $\Delta P = 6$ series of transitions of $^{16}\text{O}^{12}\text{C}^{17}\text{O}$, $^{17}\text{O}^{12}\text{C}^{17}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ isotopologues and for $\Delta P = 7$ series of transitions of $^{16}\text{O}^{12}\text{C}^{18}\text{O}$, $^{16}\text{O}^{12}\text{C}^{17}\text{O}$, $^{16}\text{O}^{13}\text{C}^{17}\text{O}$, $^{17}\text{O}^{12}\text{C}^{18}\text{O}$, $^{17}\text{O}^{12}\text{C}^{17}\text{O}$, $^{17}\text{O}^{13}\text{C}^{18}\text{O}$ and $^{17}\text{O}^{13}\text{C}^{17}\text{O}$ isotopologues.

[1] D. Jacquemart, F. Gueye, O. M. Lyulin, E.V. Karlovets, D. Baron, V.I. Perevalov, JQSRT **113**, 961 (2012).