

Analyses of High-Resolution Rotational and Rovibrational Spectra of C_{3v} Symmetric Top Molecules

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The effective rotational Hamiltonians of excited vibrational levels $\nu_t=1, 2,$ and 3 of molecules with C_{3v} symmetry are discussed, both for isolated vibrational levels as well as for polyads of interacting vibrational levels. The computer programs for generation of the corresponding Hamiltonians in the formalism of the 'Z-matrix', being the basis for the inverse eigenvalue problem, are described. Recent applications of the programs in simultaneous analyses of rotational and rovibrational spectra pertaining to the ν_5, ν_1 and $2\nu_2$ levels of the CDF_3 molecule will be shown.

J-DEPENDENCIES OF THE LINESHIFT COEFFICIENTS FOR THE ν_2 WATER VAPOR BAND

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Measured and calculated lineshift coefficients pressured by nitrogen in 1850 - 2230 cm^{-1} spectral region of water vapor are presented. Measurements were made with FT-spectrometer of Paris University at the spectral resolution 0.005 cm^{-1} and at three different pressures of sample at the room temperature. Special procedure have been used to minimize the errors connected with the asymmetry of the contours due to apparatus effects.

The two reduction procedures have been used to obtain the line shift coefficients. In the first one the shift was calculated as a difference between absorption maxima in the two spectra recorded without and in presence of the buffer gas. In the second one the line centers determination were made by nonlinear least square fitting of the Voight contour to the measured values of transmittance. In the case of line overlapping parameters of two or more lines were determining simultaneously. Accuracy of lineshift coefficient determination was better than 1 mk/atm . The lineshift coefficients have been determined for well resolved isolated lines of R-branch of ν_2 band with high quantum numbers J up to 18. Their values change from +14.4 to -14.5 mk/atm .

Calculations were made using ATC - theory and cut-of-free method. Dipole-quadrupole, quadrupole-quadrupole, induction and dispersive interactions was taken into account. There is one fitted parameter: polarizability in upper vibrational state (010), which has been determined from by least square fitting to experimental lineshift coefficients.

J-dependencies of lineshift coefficients for some type of transitions are investigated. This dependencies are accounted for scattering channels contributions compensation.

ν_2 BAND OF H₂O: LINE POSITION AND LINE INTENSITY ANALYSESL. H. COUDERT

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The somewhat successful treatment developed to account for the anomalous centrifugal distortion displayed by the water molecule¹ has been slightly altered in order to permit a calculation of the rotational energy in the ground and in the $\nu_2 = 1$ vibrational states using the *same* set of spectroscopic constants. This new treatment has been used to carry out two analyses of large bodies of data relevant to the water molecule. In the first analysis, in addition to the rotational levels of the ground² and $\nu_2 = 1^3$ vibrational states, infrared and microwave transitions within the ground and the $\nu_2 = 1$ vibrational states as well as infrared transitions belonging to the ν_2 band⁴ were considered. The unitless standard deviation of this first analysis is 1.2, the maximum J - and K_a -values considered being 25 and 20, respectively, and 80 spectroscopic constants were used. In the second analysis, the intensities published by Toth⁴ were included in a least squares fit procedure in which line-strengths were evaluated choosing a physically reasonable dipole moment function and computing its matrix elements with the spectroscopic constants of the first analysis.

In the paper, the results obtained in the two analyses will be presented. The potential energy and dipole moment functions derived from the analyses will be discussed. The latter function will be compared to that obtained by other authors.⁵

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³ C. CAMY-PEYRET, J.-M. FLAUD, J. P. MAILLARD, AND G. GUELACHVILI, *Mol. Phys.* **33**, 1641 (1977).

⁴ R. A. TOTH, *J. Opt. Soc. Am. B* **8**, 2236 (1991).

⁵ PER JENSEN, S. A. TASHKUN, AND VL. G. TYUTEREV, *J. Mol. Spectrosc.* **168**, 271 (1994).

INFRARED DIODE LASER SPECTROSCOPY OF ACETYLENE IN VIBRATIONALLY EXCITED STATE

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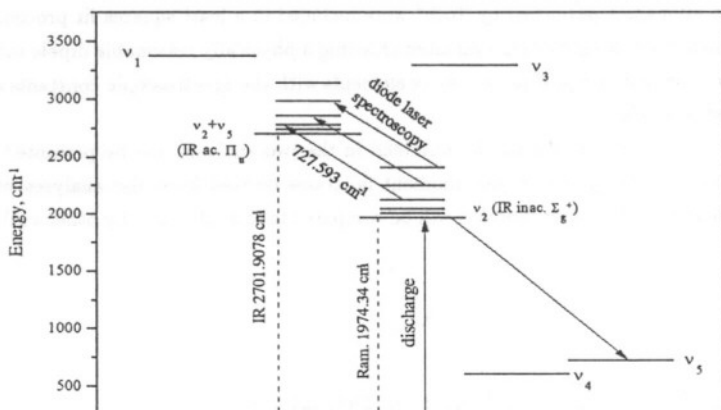
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The infrared spectrum of the new $\nu_2 + \nu_5 - \nu_2$ short-living band of acetylene has been studied in the 14 μm region of the fundamental ν_5 band of C_2H_2 using two complementary techniques: hollow cathode concentration modulation discharge, and kinetic study of the formation and decay process of the same acetylene discharge using the diode laser spectrometer and digital oscilloscope technique.

We observed 46 transitions including P, R and Q transitions between IR inactive ν_2 level (Σ_g^+) and IR active $\nu_2 + \nu_5$ (Π_u) of acetylene. The resulting $\nu_2 + \nu_5 - \nu_2$ band origin lies at $727.59322(93) \text{ cm}^{-1}$.

Collisional quenching of vibrationally excited metastable ν_2 state of acetylene has been investigated by a fast high-voltage discharge modulation technique. We measured the rate constant of quenching by helium: $4.94(11) \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$.



THE INFRARED SPECTRUM OF H_2Te BETWEEN 12 AND 2.4 μm

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High resolution Fourier transform spectra of a natural sample of H_2Te and of monoisotopic $H_2^{130}Te$ have been recorded in the 700-4300 cm^{-1} spectral domain. The analysis of the ν_2 , $2\nu_2$, ν_1 , ν_3 , $3\nu_2$, $\nu_1+\nu_2$, $\nu_2+\nu_3$, $2\nu_1$, $\nu_1+\nu_3$ and $2\nu_3$ bands has been carried out and the experimental upper states have been calculated to within the experimental uncertainty using an Hamiltonian which takes explicitly into account the relevant interactions i.e. the strong Coriolis interactions coupling the rotational levels of the vibrational states $(\nu_1\nu_2\nu_3)$ and $(\nu_1-1 \nu_2 \nu_3+1)$, the strong Darling Dennison interaction between $(\nu_1\nu_2\nu_3)$ and $(\nu_1-2 \nu_2 \nu_3+2)$, and the weak Coriolis-type interaction between $(\nu_1\nu_2\nu_3)$ and $(\nu_1 \nu_2-2 \nu_3+1)$. In this way precise vibrational energies and rotational and coupling constants were determined for (010) , $\{(020)(100)(001)\}$, $\{(030)(110)(011)\}$ and $\{(200)(101)(002)\}$. Finally, from the rotational constants determined in this work, it has been possible to derive an accurate equilibrium structure for H_2Te .

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DETECTION OF SILENE $\text{CH}_2=\text{SiH}_2$ IN THE GAS PHASE BY MILLIMETER WAVE SPECTROSCOPY

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Although CH_2SiH_2 (I) has been shown by numerous trapping reactions to exist as a transient and was detected in an Ar matrix at 10 K [1] and by photoelectron spectroscopy [2] the free molecule has never been observed and characterized in the gas phase. We have generated I by pyrolysis of 5,6-bis(trifluoromethyl)-2-silabicyclo[2.2.2]-octa-5,7-diene (SBO) at 600°C, and at 1000°C of silacyclobutane and, in traces, disilacyclobutane in a flow of Ar. The search for millimeterwave transitions in the 180 - 473 GHz frequency range was guided by novel ab initio calculations of the rotational parameters at different levels. Eventually 139 α -type lines of the planar ethene-shaped I corresponding to $6 \leq J \leq 16$ and $K_a \leq 11$ were observed and fitted to ground state parameters with $\sigma = 16.9$ kHz. The assignment was confirmed by observation of lines belonging to isotopic varieties. Photolytic generation of I from SBO was achieved with an Ar excimer Laser. The 1/e lifetime of I at room temperature was determined from the exponential decay of the $7_{1,6} - 6_{1,5}$ rotational line to be 30 ± 2 ms.

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