

M1

VIBRATION-ROTATION SPECTROSCOPY OF ^{13}C CONTAINING ACETYLENE

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The high-resolution vibration-rotation spectra of $^{13}\text{C}_2\text{H}_2$ have been recorded in selected regions between 50 and 10000 cm^{-1} as part of an EC funded collaboration among several european laboratories on the SADOVEM project (Spectra and Dynamics of Vibrationally Excited Molecules). Path lengths up to 42 m were used with pressures from 0.25 to 3900 Pa, at nearly Doppler or pressure limited resolution (from 0.002 to 0.030 cm^{-1}).

A large number of cold bands, originating from the ground state, and of hot bands arising mainly from the low-lying bending excited states have been observed and analysed. The hot bands originating from the $\nu_5 = 1$ (Π_u) or $\nu_4 = \nu_5 = 1$ (Σ_u and Δ_u) levels provided information on the states of gerade symmetry.

Several bands of $^{12}\text{C}^{13}\text{CH}_2$, which was present as an impurity in our sample, were also analysed, providing a complete set of spectroscopic parameters for the fundamental levels of this isotopomer.

Vibrationally excited states involving pure stretching or bending excitations as well as stretching-bending combinations have been spectroscopically characterized through simultaneous or band-by-band least-squares fits of the assigned transitions. Both vibrational and rotational l -type resonances within a given $\nu_4 + \nu_5$ manifold have been explicitly taken into account. Several ro-vibrational perturbations have been evidenced in the spectra; among these the most relevant anharmonic resonances in the dyads $\nu_1 / \nu_2 + 2\nu_5$ and $\nu_3 / \nu_2 + \nu_4 + \nu_5$ have been treated rigorously at the fundamental levels and followed up to higher energies. Deperturbed values for the energies of the interacting vibrational levels have been obtained and a number of anharmonicity constants x_{ij} , which may be used to improve the anharmonic force field of this molecule, have been derived.

M2

ROTATIONAL AND VIBRATIONAL RELAXATION OF THE $\nu_1 / 2\nu_2$ FERMI DYAD IN CO₂ GAS FROM RAMAN-INFRARED DOUBLE RESONANCE EXPERIMENTS

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Time-resolved Raman-infrared double resonance experiments have been carried out on CO₂ gas in order to determine collisional relaxation rates of energy levels. The total depopulation rates are determined in a three levels double resonance scheme. A pulsed stimulated Raman excitation populates the studied state over a brief time interval. The ensuing collisional depopulation of this level is monitored by a cw probe CO₂ laser which transition originates in the same level. The transient absorption on the probe laser gives the time dependent population behavior. The high selectivity of the lasers allows the study of vibrational and rotational levels. The relaxation rates, of the (10⁰) vibrational state and, for the first time, of the J = 14 to 34 rotational levels of the (02⁰) vibrational state, have been measured. Derived broadening coefficients have been compared to those calculated by a semi-classical model. State-to-state rotational energy transfer rates are studied in a four levels double resonance scheme and compared with the fitting and scaling laws MEG and ECS-P.

M3

GROUND STATE ROTATIONAL CONSTANTS AND THE LOWEST FUNDAMENTAL BANDS OF PROPYNE -D4

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The structure of the propyne molecule was recently studied by Le Guennec et al. [1]. This investigation showed that the information concerning the spectra of different isotopic species of this molecule is inadequate. We have started a series of studies concerning propyne-d₄ and we had to determine first the ground state rotational and centrifugal constants. With the aid of the Fourier spectrometer Bruker IFS-120HR in Oulu we measured four bands in the infrared spectrum of the molecule: ν_7 (1050 cm⁻¹), $2\nu_9$ (950 cm⁻¹), ν_9 (500 cm⁻¹) and ν_{10} (290 cm⁻¹). After assigning several thousands of rotational lines in these bands we could form more than 4000 ground state combination differences. The maximum values of the quantum numbers J and K were 82 and 18, respectively. The following results were obtained (all the values are in cm⁻¹ and the error limits are one standard deviation): $B = 0.22463339(11)$, $D^J = 57.636(38) \times 10^{-9}$, $D^{JK} = 3.0786(28) \times 10^{-6}$, $H^J = 13.4(37) \times 10^{-15}$, $H^{JK} = 14.53(44) \times 10^{-12}$, and $H^{KJ} = 62.5(82) \times 10^{-12}$.

The lowest fundamental bands ν_9 and ν_{10} were measured using a liquid helium cooled bolometer as the detector. The spectra are congested because the separation of the adjacent Q branches are about 0.5 cm⁻¹ only and also due to the strong hot bands.

The range of the ν_{10} band is from 260 to 325 cm⁻¹. Altogether about 2500 lines were assigned, the maximum values of J and K were 69 and 15, respectively. As ν_{10} band is the lowest fundamental, the only perturbation mechanism is *l*-resonance. It has remarkable effects on the structure of the band and it makes the assignments more difficult. In the analysis the program MILLI [2] and the ground state constants determined above were used. In the fit with 14 adjustable parameters a standard deviation of 0.00019 cm⁻¹ was attained for 2292 lines with nonzero weight. Some results (in cm⁻¹): $\nu_0 = 291.842074(11)$, $\alpha^A = 0.29307(27) \times 10^{-3}$, $\alpha^B = -0.572101(14) \times 10^{-3}$, and $A\zeta = 2.1811098(13)$.

The ν_9 band extends from 460 to 535 cm⁻¹. Its structure is unusual. Because $A\zeta$ is nearly equal with A, the Q branch spacing is almost 2B and P_{QK} branches are on higher wavenumber side. The maximum J and K values were 82 and 15, respectively. There is a Fermi resonance between the levels $\nu_9 = 1$, $l_9 = \pm 1$ and $\nu_{10} = 2$, $l_{10} = \mp 2$ which perturbs mainly on the *-l* side. In addition there are *l*-resonance effects. Some preliminary results: $\nu_0 = 498.92153(3)$, $\alpha^A = 0.523(2) \times 10^{-3}$ and $\alpha^B = -0.29054(3) \times 10^{-3}$.

[1] M.Le Guennec, J. Demaison, G. Wlodarczak, and C.J. Marsden, J. Mol. Spectrosc. 160, 471-490 (1993).

[2] C. Betrencourt-Stirnmann, G. Graner, D.E. Jennings, and W.E. Blass, J. Mol. Spectrosc. 69, 179-198 (1978).