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Concepción Domingo, A. del Olmo, Rafael Escribano, Dionisio Bermejo ...+1 more authors

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Fourier transform intracavity laser absorption spectra of the $6\nu_1$ band of CHD_3

C. Domingo, A. del Olmo, R. Escribano, D. Bermejo, and J. M. Orza

Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas Serrano 123 28006 Madrid, Spain

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Absorption spectra in the $16\,000\text{--}16\,320\text{ cm}^{-1}$ region have been recorded for gaseous CHD_3 at room temperature with 0.12 cm^{-1} resolution using a Fourier transform intracavity laser absorption technique. Two bands belonging to the $N = 6$ polyad, 6_1 ($6\nu_1$) and 6_2 ($5\nu_1 + 2\nu_5$), were identified and a rotational analysis for 6_1 including transitions up to $J = 13$, verified by means of ground-state combination differences, is reported. Comparison with rotational constants obtained from photoacoustic laser spectra at 77 K is discussed.

I. INTRODUCTION

The spectroscopy of high overtones of polyatomic molecules is one of today's fields of high interest, both as a probe for the local mode theory and as a tool to investigate molecular dynamics and, in particular, intramolecular vibrational distribution. The linewidth of the spectrum provides a clue to the type of molecular phenomena taking place in the sample: inhomogeneous structure is characteristic of spectra where the linewidth is basically Doppler, and the interpretation should be carried out in terms of the usual Fermi or Coriolis resonances. On the other hand, homogeneous structure is usually interpreted in terms of intramolecular vibrational relaxation and dephasing processes.

The isolated CH chromophore¹ is a selected example of this type of research, which has received considerable attention over the last few years.² In particular, spectra of high overtones of trideuterated methane CHD_3 have been recently investigated, both at high^{3,4} and medium resolution.⁵⁻⁷ We shall constrain ourselves here to the $N = 6$ polyad, centered around $16\,000\text{ cm}^{-1}$. When sufficiently high resolution is employed, the rotational structure of the spectrum of this polyad can be resolved, which allows a rotational analysis to be attempted. This analysis is, however, very complicated due to the presence of several Coriolis or Fermi perturbations, as will be discussed later.

The leading bands for this polyad are the 6_1 band, assigned as $6\nu_1$ in the standard normal-mode terminology, and the 6_2 band, which corresponds to $5\nu_1 + 2\nu_5$. Perry *et al.*⁵ recorded the spectra of these bands at 0.5 cm^{-1} resolution using a pulsed photoacoustic set up. Scherer *et al.*⁴ studied these bands on a cooled gas sample (77 K) at Doppler limited resolution ($\sim 0.015\text{ cm}^{-1}$), using a single mode cw dye laser as a source and intracavity laser photoacoustic detection. They obtained a refined set of rovibrational constants (band origin, rotational constants, and quartic centrifugal distortion constants) for each band, from a least-squares analysis of 51 transitions for 6_1 and 36 transitions for 6_2 , including data up to $J = 7$. They found that some of the data were perturbed for 6_1 and, consequently, the standard deviation of the fit was of the order of the experimental resolution only (0.02 cm^{-1}), whereas for 6_2 the fit proceeded satisfactorily yielding a sigma of 0.008 cm^{-1} . In the third

paper on these bands, Ben Kraiem *et al.*⁷ presented a rotational analysis of 6_2 recorded by means of an intracavity laser absorption technique, at 0.08 cm^{-1} resolution. They assigned over a hundred transitions and refined the corresponding rovibrational constants with an estimated standard deviation of 0.008 cm^{-1} .

In this paper we present a new study of the 6_1 and 6_2 bands of CHD_3 . We have recorded the spectra of these bands at 0.12 cm^{-1} resolution using a laser intracavity technique combined with Fourier transform (FT) detection. We have extended the range of observed transitions up to $J = 13$. We have tried several models to analyze our data, together with selected high-resolution observations of Scherer *et al.*⁴

II. EXPERIMENTAL

In our Fourier transform intracavity laser absorption spectroscopy (FT-ICLAS) spectrometer,⁸ an Ar^+ laser (Spectra Physics, model 2020) is used to pump a Spectra Physics 375-B dye laser with a folded cavity of 38 cm length (L). A tuning wedge is used to produce a spectral bandwidth of $\sim 8\text{ cm}^{-1}$ full width at half maximum. The output coupler has been substituted by a high-reflectivity mirror and the portion of the laser beam reflected out by the tuning wedge is analyzed using a Nicolet 170-SX FT-IR spectrometer, extended to operate in the visible region. The highest unapodized resolution of the spectrometer is 0.06 cm^{-1} . A 10 cm long intracavity cell (l) with Brewster angle windows, contains the gas sample to be studied. As it is known⁹ for this technique, the generation time, t_g , between the start of the laser action and the detection of the absorption, monitors the equivalent absorption path length outside the cavity, l_{eq} , through

$$l_{\text{eq}} = \frac{l}{L} ct_g. \quad (1)$$

In our experiment we control t_g in the following way. The Ar^+ laser pumping the dye is intensity modulated, above and below the threshold of the dye, by means of a transverse gate electro-optical modulator (EOM), and the modulation is synchronized with the sampling of the interferogram. In this way the interferogram of the He-Ne reference laser of the FT apparatus, converted into a square wave,

provides the clock for sampling the interferogram of the dye laser and, conveniently phase delayed and amplified, also drives the EOM.

400 torr of CHD₃ (Merck, Sharp, and Dome) were placed in the intracavity cell. The generation time was 100 μ sec. Rhodamine 6G was used as a dye for recording the absorption spectra of the CHD₃ in the 16 100–16 320 cm^{-1} region.

Figure 1 shows, as an illustration, the spectrum of CHD₃ at room temperature in the region of the Q branch of the 6₁ band, with an unapodized resolution of 0.12 cm^{-1} . The figure presents four pieces of spectra of the region 16 218–16 234 cm^{-1} taken consecutively, and corresponding to slightly different emission frequencies of the dye laser. We normally followed this scheme of work which allows the measurement of absorption lines of the sample as an average of several independent observations. The experimental line position accuracy of our measurements is then of the order of 0.05 cm^{-1} .

These spectra correspond to the Q-branch region of the 6₁ component of the polyad. The strongest features are the

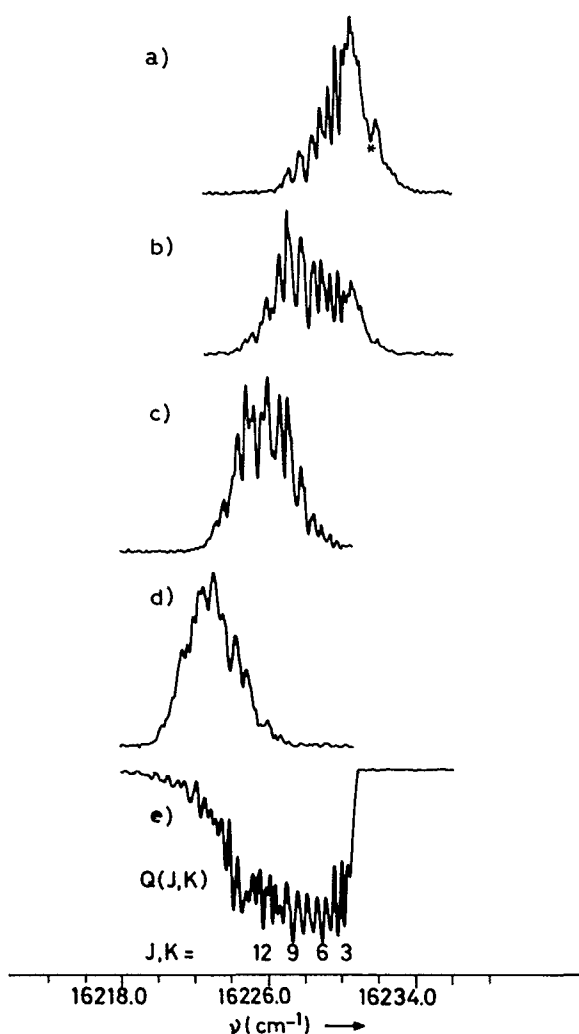


FIG. 1. Spectra of the Q branch region of the 6₁ band of CHD₃. Peak marked with an asterisk correspond to 6₂.

Q(J,K = J) lines, with K = J multiple of 3. The bottom trace is a computed simulation of this region carried out with the refined parameters of Table I. The flat background of the synthetic spectrum contrasts with the observations where the absorptions appear superimposed on the power curve of the dye laser. A few assignments are indicated on the calculated spectrum.

III. RESULTS AND DISCUSSION

Our data for the 6₂ band coincide with those of Ben Kraiem *et al.*,⁷ these being obtained at a higher resolution than in our case, and will not be commented further. The 6₁ band corresponds to the 6th overtone of the CH stretch and therefore has A₁ symmetry in the C_{3v} point group which represents the CHD₃ molecule. Rovibrational energy levels can be expressed up to fourth-order approximation, assuming absence of perturbations, by the usual equation,

$$E(J,K) = \nu_0 + BJ(J+1) + (C-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4. \quad (2)$$

Using this expression and values for the ground-state parameters from Tarrago and Dupré-Maquaire,¹⁰ we have assigned over 100 lines of this band. With these data, and the higher-resolution data of Scherer *et al.*,⁴ we have tried to perform the refinement of the excited-state parameters. However, as noted earlier, some perturbations have been detected among the excited-state levels of this band, which could easily cause misassignments. To minimize the risk of polluting the results of the analysis through the use of wrongly assigned transitions, we have included in our fits only those data that could be checked by ground-state combination differences. For example, the pair of lines P(12,6) and R(10,6) have been used in the refinement, although their observed minus calculated deviation is $\delta = \sim -0.045 \text{ cm}^{-1}$; the line R(9,8), for which $\delta = -0.021 \text{ cm}^{-1}$, has not been included since its partner P(11,8) has not been detected. Thus, our data set has been reduced to only 37 transitions. In a similar manner, only 16 data from Scherer *et al.* have been taken into consideration for our fits. Data from each source have been weighted as the reciprocal of the squared of their estimated uncertainty. These are estimated as 0.002 cm^{-1} for the higher-resolution data, and 0.05 cm^{-1}

TABLE I. Refined values of the rovibrational parameters of the 6₁ band of CHD₃, in cm^{-1} . The ground-state constants were fixed to the values of Ref. 10: $B_0 = 3.279 16$; $C_0 = 2.628 96$; $D_J^0 = 4.945 \times 10^{-5}$; $D_{JK}^0 = -3.83 \times 10^{-5}$; $D_K^0 = 1.38 \times 10^{-5}$, all in cm^{-1} .

Constant	This work
ν_0	16 230.667 (1) ^a
ΔB	-0.0557 (1)
ΔC	-0.0428 (1)
ΔD_J	-2.9(2) $\times 10^{-5}$
ΔD_{JK}	-10.4(7) $\times 10^{-5}$
ΔD_K	-5.8(9) $\times 10^{-5}$

^aUncertainties are one standard deviation in units of the last digit.

for our Fourier transform data. Then, in practice, we used relative weights of 1 and 0.0016, respectively.

The simplest model to try is to consider the band as unperturbed and the energy levels as given by Eq. (2). A fit of the band origin and the rotational parameters of the excited state gives the results shown in Table I. The standard deviation of the fit is 0.0018 cm⁻¹. The rotational constants agree well with the values of Scherer *et al.*,^{4,11} the only difference worth mentioning being the D_{JK} constant, which we estimate slightly smaller than the value reported in their paper. The uncertainty in our parameters is slightly reduced in comparison to their work, possibly as a result of having included combination differences checked data only, and also

higher quantum number transitions which increase the accuracy of the centrifugal distortion parameters. Table II lists the whole set of observed data, with indication of those transitions that have been used in the fit, and the deviations between the observed wave numbers and those calculated with the parameters of Table I.

We have also tried several other models. First, the obvious Fermi interaction between 6_1 and the A component of 6_2 ($5\nu_1 + 2\nu_5^0$) has been considered. Second, a perpendicular $\Delta K = \pm 1$, $\Delta l = \mp 2$ Coriolis interaction between 6_1 and the $l = \pm 2$ degenerate component of the 6_2 band has also been studied. Last, we have refined this latter model by taking into account the effect on the energy levels of the

TABLE II. Observed transitions in the 6_1 band of CHD₃ and (observed minus calculated) deviations with respect to values calculated with the parameters of Table I.

Assignment	$\nu_{\text{obs}}/\text{cm}^{-1}$	$\nu_{\text{obs}} - \nu_{\text{cal}}/\text{cm}^{-1}$	Assignment	$\nu_{\text{obs}}/\text{cm}^{-1}$	$\nu_{\text{obs}} - \nu_{\text{cal}}/\text{cm}^{-1}$
P(14,2)	16 130.32	(-0.02) ^a	Q(7,2)	227.70 ^c	-0.01
P(14,6)	131.27	0.02	Q(8,7)	227.70 ^c	(0.03)
P(14,10)	132.86	(-0.14)	Q(7,5)	228.08	0.01
P(13,2)	137.91	-0.06	Q(7,6)	227.30	(0.06)
P(13,6)	138.87	(0.07)	Q(6,3)	228.5305 ^b	-0.0010
P(13,8)	139.43	(0.00)	Q(6,5)	228.7774 ^b	0.0010
P(12,2)	145.55	-0.02	Q(6,6)	228.85	(-0.07)
P(12,6)	146.27	-0.05	Q(5,2)	229.0877 ^b	0.0008
P(12,7)	146.58	-0.01	Q(5,3)	229.1597 ^b	-0.0035
P(11,2)	153.09	(-0.02)	Q(5,5)	229.3878 ^b	0.0001
P(11,6)	153.73	(-0.05)	Q(4,3)	229.71 ^c	0.01
P(10,2)	160.59	-0.02	Q(4,4)	229.71 ^c	(-0.08)
P(10,7)	161.37	(-0.05)	Q(3,3)	230.09	(-0.04)
P(9,2)	168.01	0.03	Q(2,2)	230.34	(-0.05)
P(9,5)	168.47	0.08	Q(1,1)	230.53	(-0.04)
P(8,2)	175.37	0.02	R(0,0)	16 237.14	0.03
P(8,5)	175.71	0.02	R(1,0)	243.4480 ^b	-0.0018
P(7,2)	182.56	-0.05	R(2,0)	249.6769 ^b	0.0034
P(6,2)	189.7775 ^b	-0.0002	R(2,2)	249.7312 ^b	0.0012
P(6,3)	189.8474 ^b	-0.0040	R(3,2)	255.84	-0.01
P(6,5)	190.0672 ^b	-0.0018	R(4,2)	261.79	-0.06
P(5,2)	196.87	0.01	R(5,3)	267.8444 ^b	0.0015
P(4,0)	203.7858 ^b	0.0026	R(5,5)	268.0980 ^b	0.0032
P(4,2)	203.8375 ^b	-0.0001	R(6,2)	273.57	0.01
P(3,0)	210.6639 ^b	-0.0012	R(7,2)	279.30	0.04
P(2,0)	217.43	-0.01	R(7,5)	279.73	0.07
Q(14,6)	16 221.49	(0.06)	R(8,3)	284.94	-0.04
Q(15,9)	221.72	(0.05)	R(8,7)	285.83	(0.07)
Q(14,8)	222.27	(0.02)	R(9,2)	290.35	(-0.03)
Q(14,9)	222.79	(0.10)	R(9,4)	290.70	(0.03)
Q(13,8)	223.36	(0.06)	R(9,6)	291.05	(-0.06)
Q(13,9)	223.80	(0.10)	R(9,7)	291.34	(-0.03)
Q(15,14)	224.20	(0.02)	R(9,8)	291.63	(-0.02)
Q(11,6)	224.64 ^c	-0.07	R(10,2)	295.81	-0.00
Q(12,9)	224.64 ^c	(-0.03)	R(10,3)	296.02	0.07
Q(11,7)	225.06 ^c	0.07	R(10,6)	296.57	-0.05
Q(12,10)	225.06 ^c	(0.02)	R(10,7)	297.00	0.09
Q(13,13)	225.26	(0.04)	R(10,9)	297.47	-0.08
Q(11,9)	225.53	-0.07	R(10,10)	297.90	0.03
Q(11,10)	225.88	-0.03	R(11,2)	301.20	0.03
Q(10,9)	226.50	(0.01)	R(11,6)	302.20	(0.14)
Q(8,3)	227.02 ^c	0.03	R(11,8)	302.83	(0.09)
Q(9,8)	227.02 ^c	(-0.06)	R(12,2)	306.36	(-0.10)
Q(8,5)	227.32 ^c	0.04	R(12,6)	307.50	0.07
Q(9,9)	227.32 ^c	(0.00)	R(12,10)	309.27	(0.24)

^a Values in parentheses are given for transitions that have not been used in the fit.

^b Observed values from Ref. 4.

^c Unresolved blended lines.

perturbing 6_2 band of the $\Delta K = \Delta l = \pm 2$ doubling between its two components, $5\nu_1 + 2\nu_3^0$ and $5\nu_1 + 2\nu_2^{\pm 2}$, plus also the effect of the $\Delta K = \pm 2, \Delta l = \mp 4$ Coriolis interaction between 6_2 and 6_3 ($4\nu_1 + 4\nu_3^{\pm 4}$). In all these cases, initial estimates of the parameters for the candidate bands have been obtained by adequate scaling of the corresponding values of fundamental or lower-energy bands (for example, constants for 6_2 have been derived from those of ν_1 and $2\nu_5$,³ or from force-field estimations¹²).

Regretfully, none of these models has succeeded in providing a satisfactory explanation for the perturbations found among the energy levels of the $6\nu_1$ state. In general, improvement of the situation has been prevented by the lack of observation of transitions to the perturbing bands. Measurements over an extended region and with an even higher spectral sensitivity should therefore be carried out to permit a complete understanding of this problem.

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- ¹¹ In Table II of the paper of Scherer *et al.* (Ref. 4), there is an erratum in the sign of ΔD_J . It should read -2.9 instead of $+2.9$. We have been authorized by the authors to point this out.
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