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Infrared spectra of C_2H_2 under jet-cooled and *para*-H_2 matrix conditions

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Abstract

In spectra of jet-cooled C_2H_2 recorded with an FTIR spectrometer, the ν_5, $\nu_4+\nu_5$, ν_3 and $\nu_2+\nu_4+\nu_5$ bands all exhibit an intensity distribution corresponding to ~6 K for rotation, with no evidence of nuclear spin conversion. Spectra of C_2H_2 isolated in solid *p*-H_2 show no evidence of rotation of C_2H_2. The strong interaction between ν_3 and $\nu_2+\nu_4+\nu_5$ in the gas phase is diminished in solid *p*-H_2. Lines associated with dimer, trimer and tetramer of C_2H_2 are identified. Spectral features characteristic of solid state acetylene are observed under jet-cooled conditions.

1. Introduction

Acetylene (C_2H_2) is an important species in planetary atmospheres and interstellar space. Its gas-phase spectra have been extensively investigated [1,2]. Clusters and crystalline C_2H_2 are expected also to be present in a planetary atmosphere [3]; their spectra are reasonably well characterized [4].

Infrared absorption spectra of C_2H_2 dispersed in various matrices have been reported [5–7]. Although several small non-diatomic molecules such as CH_4, NH_3, H_2O are known to rotate in matrices [8,9], no evidence of rotation of C_2H_2 in low-temperature matrices has been reported. Because of the 'softness' associated with the properties of *p*-H_2 as a quantum solid, guest molecules are expected to rotate more readily in solid *p*-H_2 than in other matrices. The rotational parameters of species isolated in *p*-H_2 are typically ~90% of those for the gas phase [10,11]. Internal rotation of CH_3OH is reported to occur in solid *p*-H_2, but not in solid Ne or Ar [12]. Because of the special properties associated with *p*-H_2, it would be interesting to discover whether C_2H_2 can rotate in this quantum solid. A direct comparison of spectra of jet-cooled C_2H_2 and matrix-isolated C_2H_2 not only helps in the assignments but also reveals spectral differences between C_2H_2 in the gas phase and in matrices.

2. Experiments

Spectra of jet-cooled C_2H_2 were measured under high resolution in Belgium. The jet-expansion system named FANTASIO is described elsewhere [13] and only the major features are presented here. The circular nozzle has a diameter 500 μm. Spectra are recorded with a Fourier-transform infrared spectrometer (FTIR) (Bruker IFS120HR) at

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0.0043 cm^{-1} resolution (defined as $0.9/\delta$, in which δ is the maximum optical path difference). Multipass optics around the expansion leads to an increase of signal to noise ratio ~5 times over single pass. The v_5 and $v_4 + v_5$ bands were recorded with a HgCdTe detector, and flow conditions were 0.08 L min^{-1} for C_2H_2 and 4.2 L min^{-1} for Ar, with injection and residual pressures of 700 and 1.6×10^{-2} torr, respectively. For the v_3 region, an InSb detector was used; flow conditions were 0.05 L min^{-1} for C_2H_2, and 2.8 L min^{-1} for Ar, with injection and stagnation pressures of 470 and 9×10^{-3} torr, respectively. The contribution of the residual gas in the cell, having higher temperature, could be eliminated from the spectrum by a subtraction procedure based on measurements of molecular density from a quadrupole mass filter with a retractable probe coupled to the chamber.

The matrix experiments were performed in Taiwan [12]. A nickel-plated copper plate, maintained at 3.6 K with a closed-cycle refrigerator, served both as a cold substrate for the matrix sample and as a mirror to reflect the incident infrared (IR) beam to the detector. IR absorption spectra were recorded with a FTIR (Bomem, DA8) with a HgCdTe detector. A gaseous mixture of C_2H_2/p-H_2 (1/5000 to 1/22000) was deposited over a period of 1–3 h. Typically, 200 scans at a resolution of 0.05 cm^{-1} were recorded. In some experiments the matrix sample was maintained ~4.5 K for 0.5–1.0 h for annealing, but all IR measurements were performed at 3.6 K.

C_2H_2 (99.6%) was degassed at 77 K before use. H_2 (99.9999%) was used after passage through a trap at 77 K before its conversion to p-H_2. The efficiency of conversion is controlled by the temperature of the catalyst; the concentration of o-H_2 is ~100 ppm at a conversion temperature of 15 K.

3. Results and discussion

3.1. Spectra of jet-cooled C_2H_2

The region 700–1400 cm^{-1} contains the v_5 (729.163 cm^{-1}) and $v_4 + v_5$ (1328.081 cm^{-1}) bands. The v_5 band, corresponding to excitation of the *cis*-bending motion, is of $\Pi_u \leftarrow \Sigma_g^+$ type, thus with P, R and prominent Q branches (Fig. 1a). The weaker $v_4 + v_5$ band, of $\Sigma_u^+ \leftarrow \Sigma_g^+$ type with P and R branches (Fig. 2a), corresponds to simultaneous excitation of *cis*- and *trans*-bending motions [2].

The region 3270–3310 cm^{-1} contains the v_3 and $v_2 + v_4 + v_5$ (3281.899 and 3294.839 cm^{-1}) bands, both are of $\Sigma_u^+ \leftarrow \Sigma_g^+$ type with P and R branches (Fig. 3a) and are already reported under jet-cooled conditions using FTIR [14]. A strong anharmonic resonance connecting the two upper vibrational states is responsible for the observation of $v_2 + v_4 + v_5$ that hence acquires intensity similar to that of the v_3 [15].

The rotational temperature was determined to be 6.1 and 7.0 K, respectively, from relative intensities of rovibrational lines in v_3 and $v_4 + v_5$. The latter value therefore also characterizes v_5, which was recorded simultaneously with $v_4 + v_5$ but suffers from saturation. The intensity conforms to nuclear-spin statistics 1:3 in favor of odd J-lines, as confirmed by spectral simulations. An example is presented in Fig. 2 for $v_4 + v_5$. It thus indicates the absence of nuclear-spin conversion during cooling processes to reach 6 K; these results are similar to those reported previously for C_2H_2 at 31 K in the literature [14].

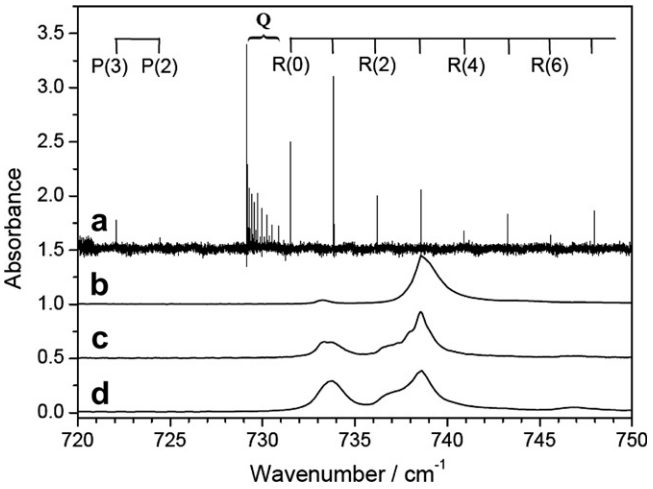

Fig. 1. IR absorption spectra of C_2H_2 in the region 720–750 cm^{-1}. (a) Under jet-cooled conditions (see Section 2), with rotational assignments indicated; (b) annealed C_2H_2/p-H_2(1/22000) matrix; (c) C_2H_2/p-H_2 (1/10000) matrix; (d) C_2H_2/p-H_2 (1/5000) matrix.

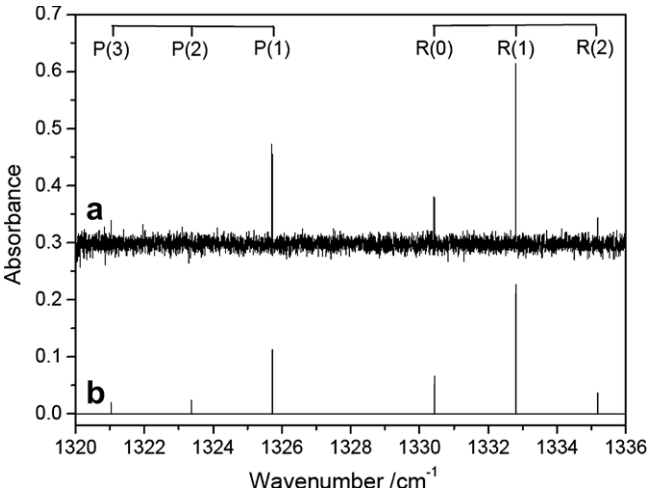

Fig. 2. IR absorption spectra of C_2H_2 under jet-cooled conditions in the region 1320–1340 cm^{-1}. (a) Observed, with the P(2) line within the experimental noise limit and P(3) barely identifiable; (b) simulated for $T_{rot} = 7$ K with no nuclear-spin conversion; rotational assignments are indicated.

3.2. Spectra of C_2H_2 in solid p-H_2

IR spectra of samples of C_2H_2/p-H_2 (1/5000 to 1/22000) at 3.6 K exhibit intense features near 738 and 3279 cm^{-1}, as shown in Traces B–D of Figs. 1 and 3, respectively, for var-

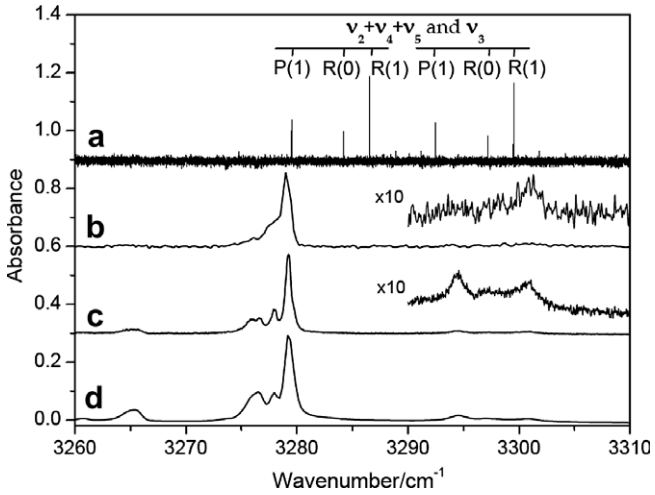

Fig. 3. IR absorption spectra of C_2H_2 in the region 3250–3310 cm^{-1}. (a) Under jet-cooled conditions (see Section 2), with rotational assignments indicated for the two observed bands (ν_3 and $\nu_2+\nu_4+\nu_5$); (b) annealed C_2H_2/p-H_2(1/22000) matrix; (c) C_2H_2/p-H_2 (1/10000) matrix; (d) C_2H_2/p-H_2 (1/5000) matrix.

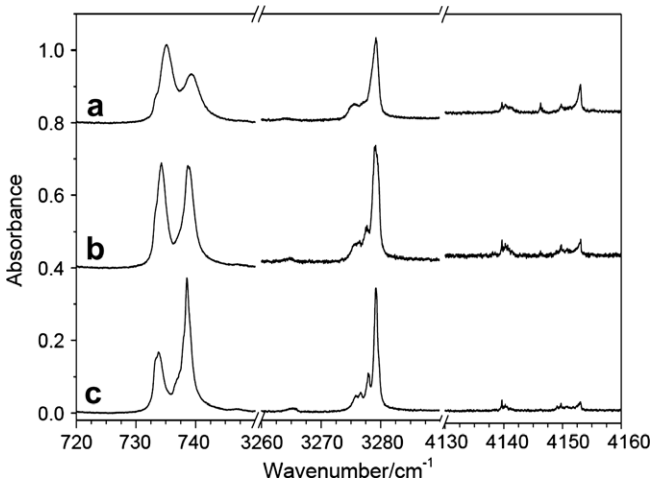

Fig. 4. IR absorption spectra of C_2H_2 in the region 720–750, 3260–3290 and 4130–4160 cm^{-1} for solid C_2H_2/p-H_2 (1/10000); impurity levels of o-H_2 are (a) 1.21%, (b) 0.51% and (c) 0.28%. The intensity of the band at 4153 cm^{-1}, corresponding to the $Q_1(0)$ line of H_2, indicates the relative concentration of o-H_2 in various samples.

ious molar ratios. At such a low temperature, if rotation were feasible and nuclear spin conserved, one would expect to observe absorption lines originating only from ground-state levels $J''=0$ (*para*) and 1 (*ortho*) of C_2H_2 in solid p-H_2. If rotation of C_2H_2 does not occur in the p-H_2 matrix, only a single line corresponding to the purely vibrational transition is predicted to appear.

3.2.1. The ν_5 band

An experiment with an annealed sample of C_2H_2 in highly pure p-H_2 (o-H_2 less than 0.23% and a slight H_2O impurity) yielded a spectrum showing side bands much diminished relative to the main band at 738.5 cm^{-1} (Fig. 1b). The observed spectral pattern is inconsistent with that expected for Q(1), R(0) and R(1), with no nuclear-spin conversion (similar to Fig. 1a). These observed features of C_2H_2 in p-H_2 are therefore unlikely to be attributable to rotational lines of ν_5. The feature at 738.5 cm^{-1} is thus assigned to a purely vibrational – thus rotationless – transition of ν_5.

It should be pointed out that at higher concentrations two lines at 733.7 and 738.5 cm^{-1} were observed (Fig. 1c and d); their separation of 4.8 cm^{-1} is near that, 4.7 cm^{-1}, between Q(1) and R(1) lines in the jet-cooled spectrum (Fig. 1a) and might lead to some confusion. Similarly, two lines were observed when substantial o-H_2 impurity was present, as shown in Fig. 4; the intensity of the feature near 733.7 cm^{-1} increased relative to that near 738.5 cm^{-1} as the concentration of o-H_2 increased from 0.28% (trace C) to 0.51% (trace B) and to 1.21% (trace A), and the maximum also shifted from 733.8 cm^{-1} to 735.0 cm^{-1}. The feature near 733.7 cm^{-1} can therefore be ascribed, at least in part, to C_2H_2 with nearby o-H_2. The observation in Fig. 4 that ν_5 (*cis*-bending) but not ν_3 (C–H stretching) is affected by the presence of o-H_2 indicates that o-H_2 might be attached at the side of C_2H_2. A doublet structure was also observed in ν_5 for T-shaped complexes of C_2H_2 with HX (X = F, Cl, Br) in solid Ar [16], and for C_2H_2 in solid N_2 [7].

3.2.2. The ν_3 band

The matrix spectrum in highly pure p-H_2 shows an intense line at 3279.2 cm^{-1} and some unresolved weak features in the ν_3 region (Fig. 3b); the spectral pattern also indicates that there is no rotation for C_2H_2. At higher concentrations, three subsidiary features at 3278.0, 3276.6 and 3275.9 cm^{-1} increase in intensity (Fig. 3c and d). These features are unlikely to be associated with rotational structure of ν_3. Furthermore, they are unlikely to arise from any other vibrational transition of the monomer. An exhaustive survey of possible vibrational energy states in $^{12}C_2H_2$ indicates that no accessible state other than $\nu_2+\nu_4+\nu_5$ exists within 100 cm^{-1} of ν_3 [1]. In the gas phase, the two bands are separated by ~13 cm^{-1} and have nearly identical intensities (Fig. 3a) [15]. In the matrix, the observed weak features are separated from ν_3 by less than 4 cm^{-1}. Assigning one of them to $\nu_2+\nu_4+\nu_5$ would imply a significantly reduced intramolecular anharmonic coupling between $\nu_2+\nu_4+\nu_5$ and ν_3 in the p-H_2 matrix.

The weak feature at 3300.9 cm^{-1} (Fig. 3b) might correspond to the $\nu_2+\nu_4+\nu_5$ assignment. A 2 by 2 interaction matrix model reproducing the anharmonic coupling between ν_3 and $\nu_2+\nu_4+\nu_5$ using the parameters in Ref. [15] shows that, with a splitting ~20 cm^{-1}, the intensity ratio for bands $\nu_2+\nu_4+\nu_5$ to ν_3 is expected to decrease from ~1 in the gas phase to ~0.056 if the interaction matrix element is assumed to be unchanged from the gas to the matrix. An observed intensity ratio of 0.04 ± 0.01 for these two features is consistent with this prediction. The intensity of the $\nu_2+\nu_4+\nu_5$ band relative to the ν_3

band was observed to be reduced to ~0.5 in an Ar matrix with energy splitting ~14 cm^{-1} [5], and to <0.03 in an N_2 matrix with energy splitting ~28.4 cm^{-1} [7].

3.2.3. The $v_4 + v_5$ band

Two broad features at 1331.6 and 1340.1 cm^{-1} were observed in the $v_4 + v_5$ region. Similar to that observed for v_5, the intensity of the former increases relative to that of the latter as the concentration of o-H_2 increases from 0.28% to 1.21%. Hence, we assign the feature at 1340.1 cm^{-1} to C_2H_2 and the feature at 1331.6 cm^{-1} to C_2H_2 with nearby o-H_2.

Table 1 compares observed wavenumbers of the various spectral features assigned to monomer absorption in various environments.

3.3. Absorption bands of clusters

Three intense lines at 3272, 3266 and 3261 cm^{-1} were reported in the literature for clusters of C_2H_2 produced under jet-cooled conditions and are assigned to the T-shaped dimer, trimer and tetramer of C_2H_2; these lines are separated from the monomer band by 17, 23 and 28 cm^{-1}, respectively [4]. They were also observed using FANTASIO (Fig. 5, flow conditions $C_2H_2 = 0.35$ L min^{-1} and Ar = 7 L min^{-1}) but are not specifically analyzed yet. Upon dilution of C_2H_2 in solid p-H_2, we observed that lines at 3265.8, 3260.9 and 3254.8 cm^{-1} have reduced intensities relative to that of the main feature at 3279.2 cm^{-1} (Fig. 3b–d); the separations of 13.6, 18.5 and 24.6 cm^{-1} are slightly smaller but parallel to those observed in the gas phase. We tentatively assign these lines to absorption of dimer (perhaps also the line at 3275.9 cm^{-1}), trimer and tetramer of C_2H_2, respectively. Analogously, we assign the observed line at 746.5 cm^{-1} (and perhaps a line overlapping the feature at 733.7 cm^{-1}) to a dimer of C_2H_2. A band due to solid state acetylene near 3235 cm^{-1}, similar to the one reported in a pulsed-jet experiment [17] was also observed here in the jet (Fig. 5), but not in the matrix, at molar ratios of acetylene/p-$H_2 \leqslant 1/400$. At this concentration, direct deposition of a flowing (not jet-cooled) mixture of acetylene in p-H_2 cannot form solid acetylene on the cold support.

Table 1
Origin/cm^{-1} of C_2H_2 bands observed under jet conditions and in matrices

Band	Jet	p-H_2 matrix	Ar matrix [5]	Kr matrix [6]	N_2 matrix [7]
v_5	729.163	738.5	736.8	732	742.0, 747.4
$v_4 + v_5$	1328.081	1340.1	1334.5	1325.5	–
v_3[a]	3281.899	3279.2	3288.9	3280	3282.6
$v_2 + v_4 + v_5$[a]	3294.839 (~1.0)	3300.9 (~0.04)	3302.9 (~0.5)	3293 (~1.0)	3311.0 (<0.03)

[a] The v_3 and $v_2 + v_4 + v_5$ states are connected by anharmonic resonance. The intensities of the $v_2 + v_4 + v_5$ band relative to that of the v_3 band are listed in parentheses.

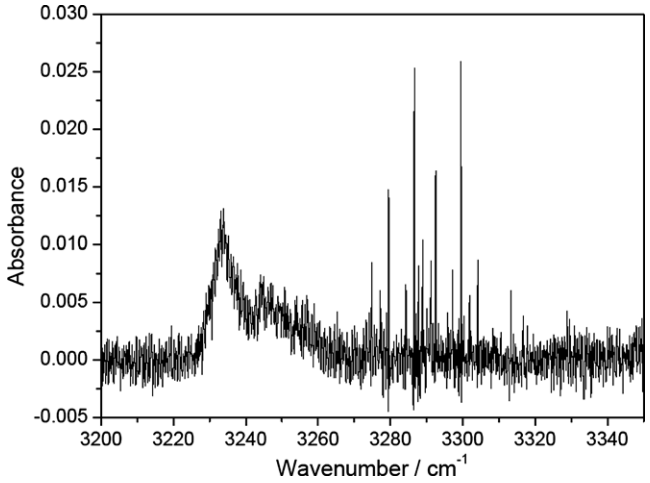

Fig. 5. IR absorption spectra of solid-state C_2H_2 under jet-cooled conditions (see Section 2) in the region 3200–3350 cm^{-1}.

4. Conclusion

Infrared absorption spectra of C_2H_2 under jet-cooled conditions and in solid p-H_2 were compared. No evidence for rotation of C_2H_2 in solid p-H_2 has been detected. The interaction between the v_3 and $v_2 + v_4 + v_5$ states of C_2H_2, known to be strong in the gas phase, is much weaker, if not absent, in solid p-H_2. Additional features associated with bending modes of C_2H_2 were ascribed to C_2H_2 with nearby o-H_2. Bands due to dimer, trimer and tetramer of C_2H_2 were tentatively assigned for C_2H_2 in solid p-H_2, whereas evidence for solid acetylene was obtained in the expansion.

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