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Note

High-resolution FTIR spectroscopic analysis of the Coriolis interaction in the $v_7 + v_8$ band of ethylene-*cis*-d_2 (*cis*-$C_2H_2D_2$)

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ABSTRACT

The spectrum of the $v_7 + v_8$ band of ethylene-*cis*-d_2 (*cis*-$C_2H_2D_2$) was recorded with a unapodized resolution of 0.0063 cm^{-1} in the 1525–1675 cm^{-1} region using a Fourier transform infrared (FTIR) spectrometer. Assignments of 536 transitions were made for this band centred at 1599.42009 ± 0.00038 cm^{-1}. The $v_7 + v_8$ band was found to be perturbed by the v_2 band through a *c*-type Coriolis resonance. Both perturbed and unperturbed transitions were fitted to give 12 rovibrational constants with high accuracy for the $v_7 + v_8 = 1$ state with a standard deviation of 0.00099 cm^{-1} using a Watson's *A*-reduced Hamiltonian in the I^r representation. From an analysis of the Coriolis interaction between the $v_7 + v_8$ band and the v_2 band of *cis*-$C_2H_2D_2$, the band centre of v_2 at 1572.795 ± 0.025 cm^{-1} was derived. Furthermore, the first-order *c*-type Coriolis coupling constant between the two bands was accurately obtained.

1. Introduction

Ethylene (C_2H_4) is a well-known molecule of tropospheric interest [1,2], and has been detected in the atmospheres of Jupiter, Saturn, and Neptune [3–5]. Accurate infrared data on ethylene and its isotopomers has been continuously updated in the HITRAN spectroscopic database [6]. The twelve fundamental vibrational frequencies of ethylene-*cis*-d_2 (*cis*-$C_2H_2D_2$) were measured and assigned by Crawford et al. [7]. Furthermore, Hirota et al. [8] obtained the ground state rotational and all five quartic centrifugal distortion constants using 15 microwave transitions. Infrared studies were continued by Hegelund and Nicolaisen [9–11] who did extensive studies on the several fundamental and combination bands of *cis*-$C_2H_2D_2$ at a resolution of 0.030 cm^{-1} in the 750–3100 cm^{-1} region. They [10] studied the $v_7 + v_8$ and $v_4 + v_7$ bands of *cis*-$C_2H_2D_2$ in the infrared region, 1500–1900 cm^{-1}. Recently, the *c*-type Coriolis interaction of v_{12} band with $2v_{10}$ of *cis*-$C_2H_2D_2$ has been investigated by Goh et al. [12] at a resolution of 0.004 cm^{-1} by FTIR spectroscopy. In 2010, Tan and Lebron [13] extended the high resolution studies on the *cis*-$C_2H_2D_2$ molecule to the v_7 band with the derivation of accurate ground state and excited $v_7 = 1$ rovibrational constants. More recently, the Coriolis interaction between v_6 and v_4 bands of *cis*-$C_2H_2D_2$ has been investigated by Tan and Gabona [14]. So far, infrared investigation on the $v_7 + v_8$ band of *cis*-$C_2H_2D_2$ has been limited to a resolution of 0.03 cm^{-1} [10].

In this paper, we present the measurements and results of our investigation on the $v_7 + v_8$ band of *cis*-$C_2H_2D_2$ measured at a resolution of 0.0063 cm^{-1}. Since the $v_7 + v_8$ band is perturbed by the nearby v_2 band by *c*-type Coriolis interaction, a simultaneous rovibrational analysis of both bands was made. By assigning and fitting a total of 536 *a*-type transitions of $v_7 + v_8$, the band centre, three rotational, five quartic, and four sextic centrifugal distortion constants of the $v_7 + v_8 = 1$ state were determined accurately. The band centre and rotational constants *B* and *C* of v_2 of *cis*-$C_2H_2D_2$ and first-order *c*-type Coriolis coupling constant were also derived in the analysis.

2. Experimental details

The *cis*-$C_2H_2D_2$ gas sample (98% purity) used in the experiment was purchased from Cambridge Isotope Laboratories in Cambridge, MA, USA. The spectra were collected using a Bruker IFS 125HR Michelson Fourier transform spectrophotometer at FTIR laboratory of the National Institute of Education, Nanyang Technological University, Singapore. The measurements were done in the 1460–1740 cm^{-1} region with a unapodized resolution of 0.0063 cm^{-1} at the ambient temperature of about 296 K using a globar infrared source together with a high-sensitivity liquid nitrogen cooled Hg-Cd-Te detector. A *cis*-$C_2H_2D_2$ vapour pressure of about 10 mbar (measured using a capacitance pressure gauge) in a multiple-pass absorption cell with a total path-length of 80 cm was sufficient to give strong infrared absorption. About 18 h of scanning time was enough to give a signal-to-noise ratio of about 50 for the final spectrum.

The H_2O infrared lines present as an impurity in the 1464–1734 cm^{-1} wavenumber region of the spectrum were used in the

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calibration of the absorption lines of the $\nu_7 + \nu_8$ band of *cis*-$C_2H_2D_2$. The standard wavenumbers of H_2O were taken from Guelachvili and Narahari Rao [15]. By fitting a total of 39 H_2O lines in the calibration of the wavenumber scale of the spectrum, a relative precision for all observed transitions was 0.0005 cm^{-1}. It is reasonable to approximate the absolute accuracy of the measured *cis*-$C_2H_2D_2$ lines to be ±0.001 cm^{-1}, accounting for small systematic errors in wavenumber calibration and the noise level in the spectra.

3. Rovibrational analysis and discussion

Ethylene-*cis*-d_2 (*cis*-$C_2H_2D_2$) is an asymmetric top molecule with an asymmetry parameter (κ) = −0.869, belonging to the point group C_{2v} with the C_2-axis coincident with the *b*-axis [9]. It has twelve fundamental modes of vibration. The ν_8 band at 759 cm^{-1} has A_2 symmetry while the ν_7 band at 842 cm^{-1} has B_1 symmetry [9]. According to Hegelund and Nicolaisen [10], the $\nu_7 + \nu_8$ band at 1599 cm^{-1} has B_2 symmetry and the nearby ν_2 band at 1573 cm^{-1} is of A_1 symmetry. The $\nu_7 + \nu_8$ band has been analysed to be an *A*-type band [10]. The survey spectrum of the $\nu_7 + \nu_8$ band of *cis*-$C_2H_2D_2$ in the 1525–1675 cm^{-1} region at the resolution of 0.0063 cm^{-1} is shown in Fig. 1. In the band centre region, strong *Q* branch (^QQ_K) clusters with a separation of about 0.5 cm^{-1} were observed. In each cluster, the lines were close to one another but clearly isolated allowing the strong lines in the cluster to be assigned with accuracy. The strong lines in the *P* and *R* branches could be assigned to the $^QP_K(J)$ and $^QR_K(J)$ clusters respectively, and since the clusters of lines overlapped, individual clusters could not be seen separately. Fig. 2 shows a sample of the well resolved lines with assignments for transitions of J' = 6 and 7 in the *R* branch (1607.6–1609.5 cm^{-1}) region.

In the rovibrational analysis, we found that transitions of K'_a = 5 and 6 for J' = 6 or more, gradually deviate from their unperturbed positions, to as low as −0.08 cm^{-1}. As stated by Hegelund and Nicolaisen [10], the perturbation is due to an interaction of the $\nu_7 + \nu_8$ band at 1599.4 cm^{-1} with the ν_2 band at 1572.8 cm^{-1} of *cis*-$C_2H_2D_2$. Deviations (observed–calculated) of line positions in cm^{-1} as a function of J' for the transitions of J' = 5 onwards, with K'_a = 5 in the *P* and *R* branches are shown in Figs. 3 and 4 respectively. Deviations up to −0.08 cm^{-1} for the perturbed transitions at J' = 13 in Figs. 3 and 4 were observed.

The preliminary assignments of the $\nu_7 + \nu_8$ band were assisted by the precise rovibrational ground state constants obtained from ground state combination differences of the relatively unperturbed ν_7 band of *cis*-$C_2H_2D_2$ [13] and rovibrational constants of the excited $\nu_7 + \nu = 1$ state previously reported [10]. In the nonlinear fit, each infrared transition was given an uncertainty of 0.0005 cm^{-1} which is the estimated precision of the measured line. A Watson Hamiltonian [16] with an I^r representation in an *A*-reduction was applied in the fit with inclusion of first-order *c*-type Coriolis interaction terms described using the following matrix elements:

$$\langle \nu_2, J, K \pm 1 | H | \nu_7 + \nu_8, J, K \rangle = \pm W_{2,7,8} F(J,K)$$

where $F(J,K) = \frac{1}{2}[J(J+1) - K(K \pm 1)]^{1/2}$, and $W_{2,7,8}$ is the first-order *c*-Coriolis coupling constant respectively between $\nu_7 + \nu_8$ and ν_2 bands.

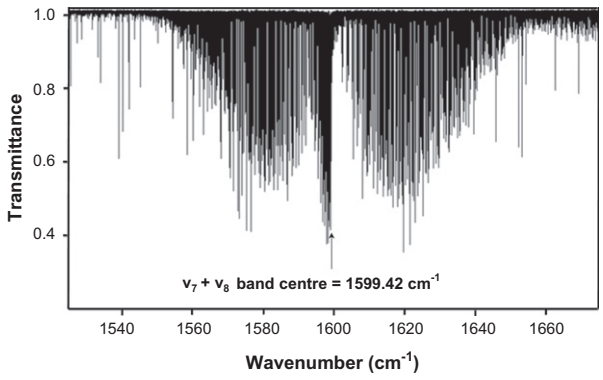

Fig. 1. The high-resolution (0.0063 cm^{-1}) survey spectrum of the $\nu_7 + \nu_8$ band of *cis*-$C_2H_2D_2$. Strong lines in the 1525–1560 cm^{-1} and 1640–1675 cm^{-1} regions are H_2O lines.

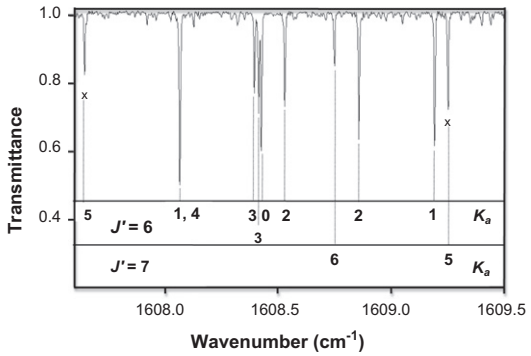

Fig. 2. Detail of the $\nu_7 + \nu_8$ *R*-branch region for *cis*-$C_2H_2D_2$ showing the assignments of transitions in the 1607.6–1609.5 cm^{-1} region. Perturbed lines are indicated by "x".

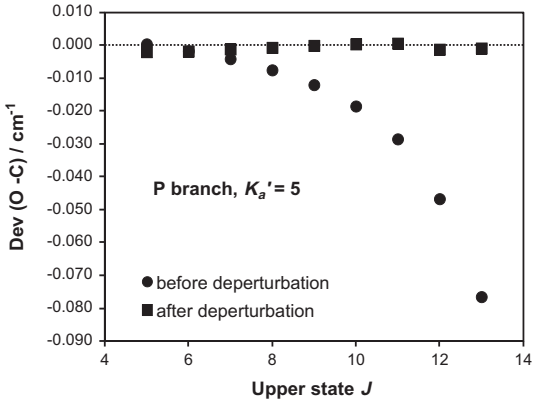

Fig. 3. Deviations (obs.–calc.) in cm^{-1} of K'_a = 5 plotted as a function of upper state *J* in the *P* branch of $\nu_7 + \nu_8$ of *cis*-$C_2H_2D_2$.

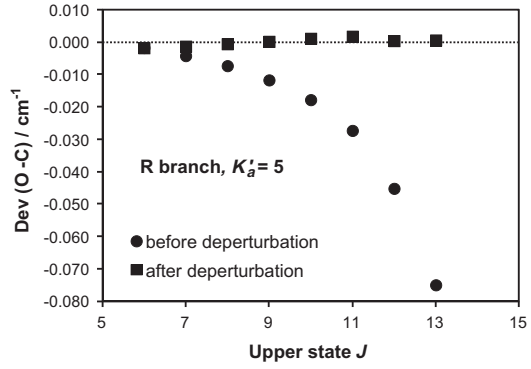

Fig. 4. Deviations (obs.–calc.) in cm^{-1} of K'_a = 5 plotted as a function of upper state *J* in the *R* branch of $\nu_7 + \nu_8$ of *cis*-$C_2H_2D_2$.