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Rovibrational constants of the ground state and $v_8 = 1$ state of $^{13}C_2HD_3$ by high-resolution FTIR spectroscopy

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ABSTRACT

The Fourier transform infrared (FTIR) spectrum of the *c*-type ν_8 band of $^{13}C_2HD_3$ was recorded for the first time at a unapodized resolution of 0.0063 cm^{-1} in the wavenumber region of 830–1000 cm^{-1}. Through the fitting of a total of 1057 assigned infrared transitions using Watson's *A*-reduced Hamiltonian in the I^r representation, rovibrational constants for the upper state ($v_8 = 1$) up to five quartic centrifugal distortion terms were derived for the first time with a root-mean-square (rms) deviation of 0.00073 cm^{-1}. The band center of ν_8 of $^{13}C_2HD_3$ was found to be 913.011021(55) cm^{-1}. Ground state rovibrational constants up to five quartic terms of $^{13}C_2HD_3$ were also determined from a fit of 453 ground state combination-differences from the present infrared measurements with an rms deviation of 0.00072 cm^{-1} for the first time. The uncertainty of the measured infrared lines was estimated to be ±0.0012 cm^{-1}. From the ground state rotational constants, the inertial defect of $^{13}C_2HD_3$ was calculated to be 0.06973(16) uÅ^2, showing the high planarity of the molecule.

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1. Introduction

For decades, spectroscopists have been recording and analyzing the rotational and vibrational spectra of the ethylene ($^{12}C_2H_4$) molecule and its isotopologues [1–13]. This is mainly because the naturally-occurring hydrocarbon is one of the simplest polyatomic asymmetric molecules. From the analysis of their infrared spectra, important rotation–vibrational information such as the band intensities, moments of inertia, equilibrium bond lengths and angles can be derived and extended to other classes of molecules. In Trace amount of the ethylene gas has been detected in planetary atmospheres of Jupiter, Saturn and Neptune, and that of Titan, the largest moon of Saturn [14–18] using the infrared spectra recorded by satellites. Therefore, accurate measurement and identification of the infrared transitions of the ethylene molecules leading to the determination of their rovibrational constants is crucial in fingerprinting them in highly complex infrared spectra which often contain numerous absorption lines of other molecules. In horticulture and agriculture, monitoring of natural ethylene concentration, especially in enclosed spaces, is of paramount importance since it has been found that ethylene is one of the main gases which can produce great damage to horticultural crops [19].

Advancements in infrared technology over the past few decades have allowed spectroscopists to study the infrared spectra of ethylene at high resolution and low noise conditions. This has provided molecular physicists and chemists greater insights into the rovibrational structures of the ethylene molecule and its isotopologues. Furthermore, as demonstrated by Duncan, McKean and co-workers [1,20–22], studies into the isotopic frequency shifts of isotopologues of a molecule were useful in the derivation of its empirical force field. In particular, an empirical general harmonic force field (GHFF) of ethylene was derived by Duncan et al. [1] in 1973 using ^{12}C frequency data, ^{13}C frequency shifts and Coriolis coupling constants (ζ). In that work, the ^{13}C frequency shift data of $H_2{}^{12}C^{13}CH_2$, $D_2{}^{12}C^{13}CD_2$, $H_2{}^{12}C^{13}CD_2$, $H_2{}^{13}C^{13}CH_2$, $D_2{}^{13}C^{13}CD_2$ and $H_2{}^{13}C^{12}CD_2$ were used. A number of infrared spectroscopic analyses on the ^{13}C-subtituted ethylene isotopologues were carried out since then using high-resolution infrared spectroscopy [3–10], although studies on the rovibrational structures of $^{13}C_2HD_3$ remain limited.

Among the experiments conducted by the Duncan and co-workers on ethylene and its isotopologues to derive the GHFF [1] were the identification and assignment of the twelve fundamental bands of $^{12}C_2HD_3$ to an accuracy of 1 cm^{-1}. This was followed two decades later with the measurement of the infrared spectrum of $^{12}C_2HD_3$ at a resolution of about 0.5 cm^{-1} [2]. In that work, the vibrational band centers of $^{12}C_2HD_3$ in the 2000–6200 cm^{-1} region were assigned. Furthermore, Tan and co-workers analyzed the ν_8

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band of $^{12}C_2HD_3$ in 2011 [11] and again in 2015 [12]. In the latest work on $^{12}C_2HD_3$ [12], precise rovibrational constants for the ground state and the $\upsilon_8 = 1$ state were derived from fitting 568 ground state combination differences (GSCDs) and 1249 infrared transitions using Watson's A-reduced Hamiltonian in the I^r representation.

In the present investigation, we continue our studies on the rovibrational structures of ethylene and its isotopologues with the spectroscopic study on the ethylene isotopologue $^{13}C_2HD_3$ (as shown in Fig. 1 with the I^r representation) using high-resolution FTIR spectroscopy. From the non-linear least-squares fitting of assigned infrared transitions of the ν_8 band of $^{13}C_2HD_3$ using Watson's A-reduced Hamiltonian in the I^r representation, accurate rovibrational constants of the $\upsilon_8 = 1$ state were determined for the first time. In addition, the ground state constants of $^{13}C_2HD_3$ up to 5 quartic constants were derived accurately for the first time from a ground state combination difference (GSCD) fit of the infrared transitions obtained from this work.

2. Experimental details

The spectrum of the ν_8 band of $^{13}C_2HD_3$ was measured at an unapodized resolution of 0.0063 cm^{-1} with the Bruker IFS 125R Michelson Fourier transform spectrometer in the Spectroscopy Laboratory of the National Institute of Education, Nanyang Technological University in Singapore. A Globar infrared source, a high-sensitivity Hg–Cd–Te detector cooled with liquid nitrogen, and a KBr beamsplitter were used in the spectral measurements, which were collected at an ambient temperature of about 296 K with a multiple-pass absorption cell of total absorption path length of 0.80 m.

The $^{13}C_2HD_3$ gas sample used in the measurement was actually the 2% impurity in $^{13}C_2D_4$ gas that was supplied by Cambridge Isotope Laboratories, Massachusetts, USA. The final spectrum was produced by a total of co-added 560 scans with the total scanning time of about 9.3 h. The mean vapor pressure of 684 millibar measured by a capacitance pressure gauge was required so that the intensity of the ν_8 band of $^{13}C_2HD_3$ was sufficiently high for the present investigation. As the background spectrum of the evacuated cell comprising a total of 500 scans was recorded at a resolution 0.0063 cm^{-1}, zero-filling was not required. A transmittance spectrum with relatively smooth baseline was obtained from the ratio of the sample spectrum of $^{13}C_2HD_3$ to that of the background. The line widths measured at half the maximum intensity of the absorption peaks in the transmittance spectrum were found to be approximately 0.012 cm^{-1} mainly due to pressure-broadening.

A total of 30 N_2O lines in the 1135–1200 cm^{-1} region were used in the calibration of the absorption lines of the ν_8 band of $^{13}C_2HD_3$. The spectrum of the N_2O gas was measured before recording the $^{13}C_2HD_3$ spectrum. Standard wavenumber values of the selected N_2O lines were taken from Guelachvili and Rao [23]. The relative precision of the wavenumbers obtained from the line fitting of the 30 wavenumber values was 0.0001 cm^{-1}. The absolute uncertainty of the measured $^{13}C_2HD_3$ lines was estimated to be ±0.0012 cm^{-1} (1/10th of the measured line width).

3. Rovibrational analysis, results and discussion

The ν_8 band of $^{13}C_2HD_3$, having an A'' symmetry in the C_s point group using the numbering of normal modes by Herzberg [24], is a c-type band arising from the out-of-plane ^{13}C–H/^{13}C–D bending [25] as illustrated in Fig. 1 of Ref. [11]. With an asymmetry parameter $\kappa \approx -0.858$, $^{13}C_2HD_3$ is a near-prolate asymmetric rotor. The high-resolution (0.0063 cm^{-1}) spectrum of the ν_8 band in the wavenumber range of 830–1000 cm^{-1} (Fig. 2) shows a profile characteristic of a c-type band. A broad central Q branch of the band, made up mostly of transitions belonging to $^PQ_1$ and $^RQ_0$, is located at about 913.03 cm^{-1}. The other absorption lines of $\Delta J = J' - J'' = 0$ are situated in the P and R branches, with distinct Q clusters observed for $K_a' \geqslant 4$ located at regular wavenumber intervals of approximately $2A - (B + C) \approx 4\ cm^{-1}$. Besides the Q clusters, the P and R branches are made up of overlapping series located about $2A$ ($\approx$6 cm^{-1}) apart and each series of transitions shares the same K_a but differing in quantum number J. Within each series, absorption lines of unresolved asymmetry doublets are well-separated by about $B + C$ ($\approx$1.4 cm^{-1}). As with the ν_8 band of $^{12}C_2HD_3$, asymmetric splitting begins at a higher J value as K_a increases. The assignment of J-series of $^PP_2$ to $^PP_4$ in the P branch and $^RR_1$ to $^RR_5$ in the R branch are shown in Figs. 3(a) and 4(a) respectively. Several ^PQ clusters in the P branch, such as the $^PQ_5$ as shown in Fig. 3(a), are unresolved.

In the preliminary analysis of the spectrum, rovibrational constants belonging to the ground state of $^{13}C_2HD_3$ were estimated by adding the difference between each of the ground state parameters of $^{12}C_2D_4$ [13] and of $^{13}C_2D_4$ [10] to the corresponding ground state rovibrational constants of $^{12}C_2HD_3$ [12]. Alpha constants of the fundamental ν_8 band of $^{12}C_2HD_3$ (i.e. $\alpha = A'' - A'$) [12] were then added to the estimated ground state constants of $^{13}C_2HD_3$ to derive the rovibrational constants of the $\upsilon_8 = 1$ state of

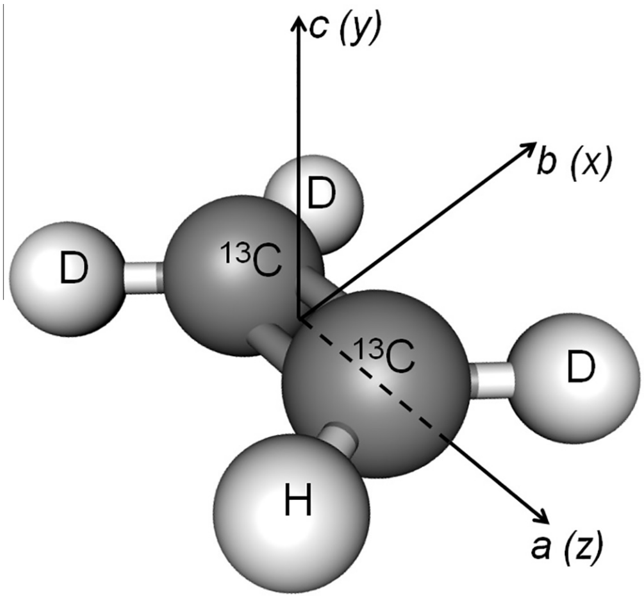

Fig. 1. The molecular structure of $^{13}C_2HD_3$ (I^r representation).

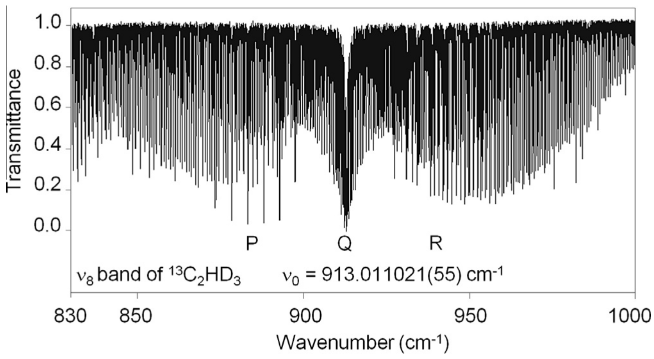

Fig. 2. High-resolution (0.0063 cm^{-1}) FTIR spectrum of the c-type ν_8 band of $^{13}C_2HD_3$ showing P, Q, and R branches.

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