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# Rovibrational analysis of the ethylene isotopologue $^{13}C_2D_4$ by high-resolution Fourier transform infrared spectroscopy

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ABSTRACT

The Fourier transform infrared (FTIR) spectrum of the unperturbed *a*-type $\nu_{12}$ band of $^{13}C_2D_4$ was recorded at an unapodized resolution of 0.0063 $cm^{-1}$ between 1000 and 1140 $cm^{-1}$ for a rovibrational analysis. By assigning and fitting a total of 2068 infrared transitions using a Watson's *A*-reduced and *S*-reduced Hamiltonians in the $I^r$ representation, rovibrational constants for the upper state ($\nu_{12} = 1$) up to five quartic centrifugal distortion terms were derived for the first time. The root-mean-square (rms) deviation of the fits was 0.00034 $cm^{-1}$ both in the *A*-reduction and *S*-reduction Hamiltonian. The ground state rovibrational constants of $^{13}C_2D_4$ in the *A*-reduced and *S*-reduced Hamiltonians were also determined for the first time by a fit of 985 combination-differences from the present infrared measurements, with rms deviation of 0.00036 $cm^{-1}$. The $\nu_{12}$ band centre of $^{13}C_2D_4$ was at 1069.970824(17) $cm^{-1}$ and at 1069.970799(17) $cm^{-1}$ for the *A*-reduced and *S*-reduced Hamiltonians respectively. The ground state constants of $^{13}C_2D_4$ from this experimental work are in close agreement to those derived from theoretical calculations using the B3LYP/cc-pVTZ, MP2/cc-pVTZ, and CSSD(T)/cc-pVTZ levels of theory.

## 1. Introduction

Numerous studies of ethylene and its isotopologues have been initiated since the detection of ethylene $C_2H_4$ in the atmospheres of Jupiter [1], Neptune [2–4] and Titan [5,6] and the recognition of the need for accurate spectroscopic parameters to better understand this molecule. The vibrational structures of the $C_2H_4$ molecule and those of its isotopologues have been studied extensively by low-resolution infrared spectroscopy in the last two decades [7–10]. Furthermore, in order to understand their rovibrational structures by accurate determinations of their rotational and higher order centrifugal distortion constants, many recent high-resolution infrared investigations (resolutions better than 0.01 $cm^{-1}$) were made on $^{12}C_2H_4$ [11–13], $^{12}C_2H_3D$ [14], *trans*-$^{12}C_2H_2D_2$ [15], *cis*-$^{12}C_2H_2D_2$ [16,17], $^{12}C_2HD_3$ [18], and $^{12}C_2D_4$ [19]. However, high-resolution infrared spectroscopic measurement and analysis of $^{13}C_2D_4$ have not been reported so far. In 1973, Duncan et al. [7] identified the fundamental vibrational bands of $^{13}C_2D_4$ and assigned their band centres with an accuracy of 1 $cm^{-1}$. So far, no studies have been made on the rovibrational structure of $^{13}C_2D_4$ despite the requirement for the data at infrared spectral resolution better than 0.01 $cm^{-1}$.

In the last fifteen years, we have used high-resolution (0.0063 $cm^{-1}$ or better) FTIR spectroscopy to measure and analyse numerous fundamental and combination bands of $^{12}C_2H_4$ and its various isotopologues [11,12,14–19]. The main purpose was to improve or derive new ground state and upper state rovibrational constants for various isotopologues of ethylene to add to the pool of accurate data on the rovibrational structure of the ethylene molecule. The present investigation is aimed at the analysis of the *a*-type $\nu_{12}$ band of $^{13}C_2D_4$ which was measured using FTIR spectroscopy with a resolution of 0.0063 $cm^{-1}$. By assigning and fitting infrared transitions for the $\nu_{12}$ band, the rovibrational constants up to five quartic terms for the $\nu_{12} = 1$ state were obtained accurately for the first time. The ground state rovibrational constants for $^{13}C_2D_4$ up to quartic terms were also obtained for the first time by fitting ground-state combination differences (GSCDs) derived from the present infrared transitions. Furthermore, the ground state constants were calculated using the B3LYP/cc-pVTZ, MP2/cc-pVTZ, and CSSD(T)/cc-pVTZ levels of theory, and their values were compared to those derived using GSCDs from the present infrared transitions.

## 2. Experimental details

A Bruker IFS 125HR Michelson Fourier transform spectrophotometer in the National Institute of Education, Nanyang

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Technological University, Singapore, was used to record the spectrum of $^{13}C_2D_4$ in the 1000–1140 $cm^{-1}$ region with an unapodized resolution of 0.0063 $cm^{-1}$ for the rovibrational analysis of the $\nu_{12}$ band of $^{13}C_2D_4$. A globar infrared source, and a high-sensitivity liquid nitrogen cooled Hg–Cd–Te detector, and KBr beamsplitter were used. The final spectrum was produced by coadding five runs of 200 scans each with the total scanning time of about 18 h for all 1000 coadded scans. The linewidth (FWHM) in the spectrum was observed to be about 0.0065 $cm^{-1}$.

The $^{13}C_2D_4$ gas samples of 98 atom% purity in D used in the measurements were supplied by Cambridge Isotope Laboratories in Cambridge, MA, USA. For the spectral measurements at the ambient temperature of about 296 K, we used a multiple-pass absorption cell with 80 cm of total absorption path length. The vapor pressure of $C_2D_4$ of about 2 mbar in the cell which was measured using a capacitance pressure gauge, allowed the intensity of the $\nu_{12}$ band of $^{13}C_2D_4$ to be sufficiently high for the present study. A background spectrum of the evacuated cell was recorded using 400 scans at a resolution 0.0063 $cm^{-1}$. The ratio of the sample spectrum of $^{13}C_2D_4$ to that of the background gave a transmittance spectrum with relatively smooth baseline.

Calibration of the absorption lines of $\nu_{12}$ band of $^{13}C_2D_4$ was carried out using the unblended $N_2O$ lines which were measured before recording the $^{13}C_2D_4$ spectrum. The selected $N_2O$ calibration wavenumber values were taken from Guelachvili and Rao [20]. From the line fitting involving 36 wavenumber values in the 1260–1300 $cm^{-1}$ region, the resulting precision obtained was 0.0001 $cm^{-1}$. It is reasonable to estimate the absolute accuracy of the measured $^{13}C_2D_4$ lines to be approximately ±0.00060 $cm^{-1}$ after accounting for small systematic errors in the experiments.

Theoretical calculations were performed using GAUSSIAN09 [21] at the CSSD(T)/cc-pVTZ, MP2/cc-pVTZ, and B3LYP/cc-pVTZ levels of theory to predict the equilibrium rotational and quartic centrifugal distortion constants of the ground state of $^{13}C_2D_4$. The quantum mechanical calculations of the ground state rovibrational constants were then used to compare with the GSCD-fitted values.

## 3. Results and discussion

The $^{13}C_2D_4$ molecule is a simple asymmetric top planar molecule with $D_{2h}$ symmetry. Its asymmetry parameter $\kappa$ is about −0.83. The $\nu_{12}$ vibrational mode of $^{13}C_2D_4$ is ascribed to the antisymmetrical DCD in-plane bending [22]. The $\nu_{12}$ band is typically *A*-type with a prominent *Q* branch at about 1070 $cm^{-1}$. A high-resolution (0.0063 $cm^{-1}$) compressed plot of the $\nu_{12}$ spectrum of $^{13}C_2D_4$ in the 1000–1140 $cm^{-1}$ region, showing the *P*, *Q* and *R* branches and its band centre, is shown in Fig. 1. The rotational structure of the $\nu_{12}$ band of $^{13}C_2D_4$ is similar to that of the $\nu_{12}$ band $^{12}C_2D_4$ [19]. Fig. 2(a) shows a detailed section of the dense *Q*-branch region of 1070.3–1071.4 $cm^{-1}$ with assignments of the well-resolved *a*-type transitions in $K_a = 4$–7 clusters. The simulated spectrum in this region is shown in Fig. 2(b). A detailed section of transitions in a *P* branch region, with the corresponding simulations is shown in Fig. 3. The absorption lines were simulated by convolving with a Gaussian line shape with appropriate FWHM of 0.0065 $cm^{-1}$.

In the initial assignments of the low *J* values of the band, cluster patterns of about 1.2 $cm^{-1}$ separation ($\approx B + C$) was observed for both the *P* and *R* branches with the strongest transitions attributed to $J = K_c$ and $K_a = 0$ or 1. The same nonlinear least-squares program previously employed for the $\nu_{12}$ band of $^{12}C_2D_4$ was used to fit the assigned transitions of the $\nu_{12}$ band of $^{13}C_2D_4$ [19]. As initial values for the fit, we used the constants from the theoretical calculations since there are no previous measurements available on the ground state constants for $^{13}C_2D_4$ in the literature. No microwave data for a rotational analysis is available due to the symmetry of $^{13}C_2D_4$. The initial band centre was estimated using the value from Duncan et al. [7]. Initial assignments of the transitions were made starting with the low *J* transitions in the *P*- and *R*-branches. The quantum number assignments were verified by using ground state combination differences. These low *J* transitions were fit to obtain refined upper state constants that were used to predict higher *J* transitions. The higher *J* transitions were assigned and the process was repeated to extend the assignments to even higher *J* values until no new lines could be confidently assigned. This bootstrap procedure allowed us to accurately assign all the IR transitions.

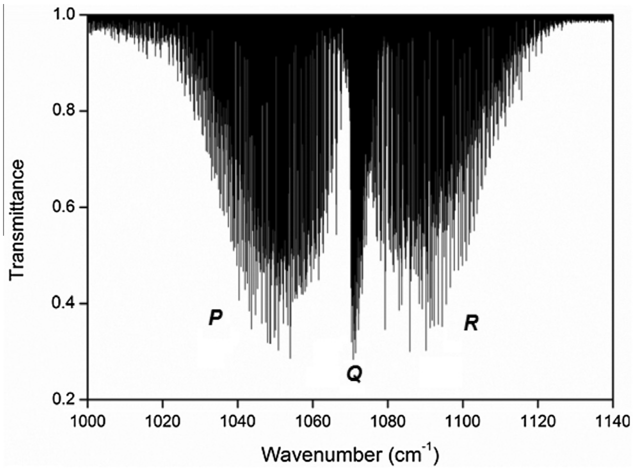

**Fig. 1.** High-resolution (0.0063 $cm^{-1}$) FTIR spectrum of $\nu_{12}$ band of $^{13}C_2D_4$.

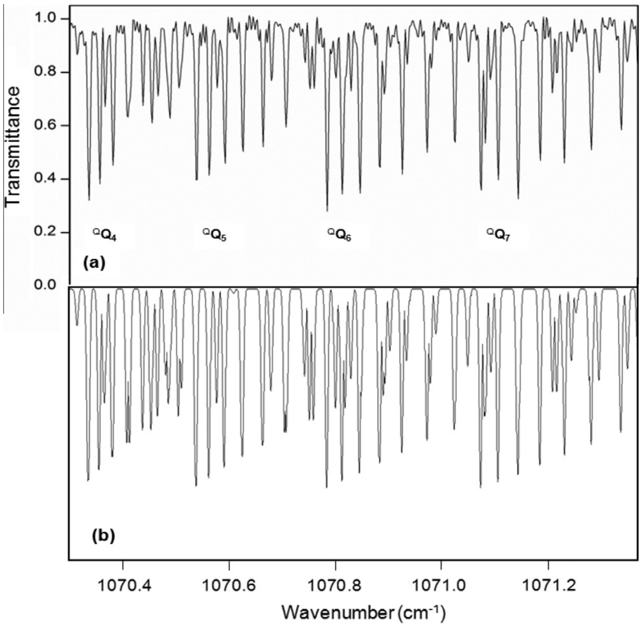

**Fig. 2.** (a) A detailed section of the *Q* branch region of the $\nu_{12}$ band of $^{13}C_2D_4$ with assignments of $K_a = 4$ to 7 clusters, and (b) its corresponding simulation.

Ground state constants were improved using ground state combination differences from the present infrared measurements of $\nu_{12}$ of $^{13}C_2D_4$. The improved ground state constants were then fixed in the fitting program to determine the upper state ($\nu_{12} = 1$) constants. The ground state constants were further refined and expanded to higher orders as more newly assigned IR transitions were gradually included in the fitting procedure to expand the set of data. A total of 985 ground state combination differences (GSCDs) from the present infrared transitions of the $\nu_{12}$ band were