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The high-resolution FTIR spectrum of the v_6 band of C_2H_3D

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ABSTRACT

The absorption spectrum of the v_6 band of C_2H_3D centered near 1125.27674 cm^{-1} in the 1100–1250 cm^{-1} region was recorded with an unapodized resolution of 0.0063 cm^{-1} using a Fourier transform infrared (FTIR) spectrometer. A total of 947 infrared transitions of the *A*–*B* hybrid-type band were assigned and fitted to upper-state ($v_6 = 1$) rovibrational constants using a Watson's *A*-reduced Hamiltonian in the I^r representation up to eighth-order centrifugal distortion terms. The *b*-type infrared transitions of the band were analyzed for the first time. The root-mean-square deviation of the fit was 0.00062 cm^{-1}. The ground-state rovibrational constants up to eighth-order terms were also obtained by a fit of 617 combination differences from the present infrared measurements, simultaneously with 21 microwave frequencies with a root-mean-square deviation of 0.00055 cm^{-1}. From this work, the upper-state ($v_6 = 1$) and ground-state constants of C_2H_3D were derived with the highest accuracy, so far. The *a*- and *b*-type transitions of the hybrid v_6 band were found to be relatively free from local frequency perturbations. The ratio of the *a*- to *b*-type vibrational dipole transition moments (μ_a/μ_b) was found to be 1.05 ± 0.10. From the $v_6 = 1$ rovibrational constants obtained, the inertial defect Δ_6 was calculated to be 0.3570 ± 0.0008 μÅ^2.

1. Introduction

In the past few decades, infrared studies on the ethylene-*d* or C_2H_3D molecule were conducted with low to medium resolution [1–5] and with high resolution [6–10]. Furthermore, Hirota et al. [11] used microwave spectroscopy to measure 21 transitions and their analysis of the rotational spectra of C_2H_3D yielded accurate ground-state rotational and centrifugal distortion constants. Duncan et al. [1,2] did most of the assignments of the vibrational bands of C_2H_3D, in their comprehensive work on ethylene and its isotopic species. So far, most of the infrared measurements and analyses on C_2H_3D were carried out by Herbin and co-workers [4–8]. The v_{10} band in the 730–780 cm^{-1} region, and v_7 and v_8 bands in the 830–890 cm^{-1} regions of C_2H_3D were investigated separately [6,7] using a tunable diode laser spectrometer with a wavenumber accuracy better than 0.001 cm^{-1}. More recently, Tan et al. [9] and Lebron and Tan [10] collected the FTIR spectra of v_{12} and v_3 bands of C_2H_3D with a resolution of 0.004 and 0.0063 cm^{-1}, respectively in the 1240–1470 cm^{-1} region. From their work, accurate upper-state ($v_{12} = 1$ and $v_3 = 1$) rovibrational constants of C_2H_3D were obtained and ground-state constants were further improved. In 1988, Herbin et al. [8] recorded the Fourier transform infrared (FTIR) spectra of the v_6 band along with v_4, v_7, v_8, and v_{10} bands of C_2H_3D in the 725–1170 cm^{-1} region with a resolution of 0.003 cm^{-1}. Their analysis involving 494 transitions yielded upper-state rovibrational constants up to fourth-order terms and Coriolis interactions coupling terms for the five bands. Although the v_6 band is a hybrid *A*–*B* type, only *a*-type transitions of v_6 were studied in their work. The *b*-type transitions of v_6 in the 1150–1250 cm^{-1} region have yet to be done.

The aim of this paper is to measure and analyze both *a*- and *b*-type infrared absorption lines of the hybrid v_6 band of C_2H_3D at a resolution of 0.0063 cm^{-1} in the 1100–1250 cm^{-1} region using the single-state model. By assigning and fitting a large number of transitions, more accurate rovibrational constants of the $v_6 = 1$ state were obtained that include three rotational, five fourth-order, and four sixth-order, and five eighth-order centrifugal distortion constants. The accuracy of the rovibrational ground-state constants up to eighth-order terms has been improved by a simultaneous fit of numerous ground-state combination differences (GSCD) derived from the present v_6 infrared transitions, together with 21 microwave frequencies [11]. The upper-state ($v_6 = 1$) and ground-state constants of C_2H_3D derived from this work are the most precise to date.

2. Experimental details

The C_2H_3D gas sample of 98% atomic isotopical purity used in the experiments was purchased from Cambridge Isotope Laboratories in Cambridge, MA, USA. The spectra were recorded with an unapodized resolution of 0.0063 cm^{-1} using a Bruker IFS 125 HR Michelson Fourier transform spectrophotometer located at the

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Spectroscopy Laboratory of the National Institute of Education, Nanyang Technological University, Singapore. A globar infrared source together with a high-sensitivity liquid nitrogen cooled Hg–Cd–Te (MCT) detector and KBr beam splitter were used for all recordings. All spectral measurements were done at the ambient temperature of about 296 K. A gas pressure of about 5 torr in the cell was required to obtain strong absorption lines for the weak ν_6 band. A multiple-pass absorption cell with a 20-cm base path was used, and an absorption path of 8.0 m was achieved by adjusting for 40 passes in the cell.

A total of four runs of 200 scans each with a total scanning time of about 14 h were co-added to produce the final spectrum with a signal-to-noise ratio of about 35. The average full width at half maximum (FWHM) of the absorption lines in the spectrum was observed to be about 0.0065 cm^{-1} which was close to the spectral resolution of 0.0063 cm^{-1}. This gave an indication that pressure broadening was not significant. A background spectrum of the evacuated cell was recorded with a single run of 250 scans at a resolution of 0.0063 cm^{-1}. The ratio of the final C_2H_3D spectrum to the background spectrum yielded a transmittance spectrum with relatively smooth baseline.

Calibration of the absorption lines of ν_6 band of C_2H_3D were carried out using the N_2O lines in the 1235–1325 cm^{-1} region, taken from Guelachvili and Rao [12]. The N_2O transitions were recorded just before those of the C_2H_3D. A correction factor of 1.000000922 was required to bring the observed wavenumbers into agreement with the calibrated frequencies. A relative precision of 0.000283 cm^{-1} for all observed transitions was achieved by fitting 64 N_2O

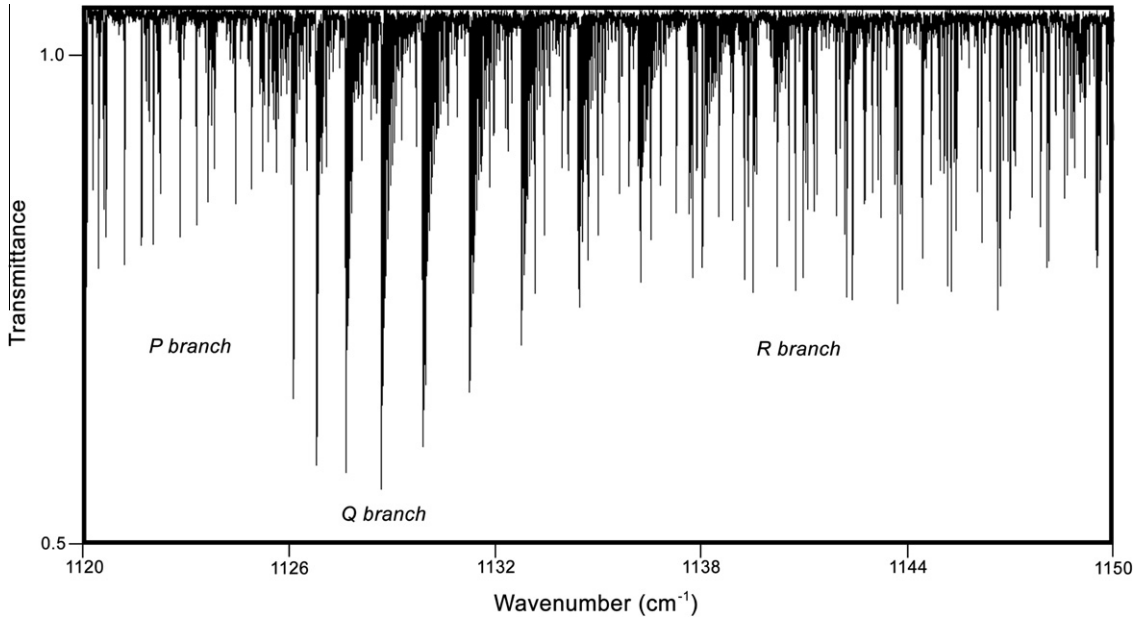

Fig. 1. High-resolution (0.0063 cm^{-1}) plot in the 1120–1150 cm^{-1} region of ν_6 band of C_2H_3D showing *a*-type transitions in the *P*, *Q*, and *R* branches.

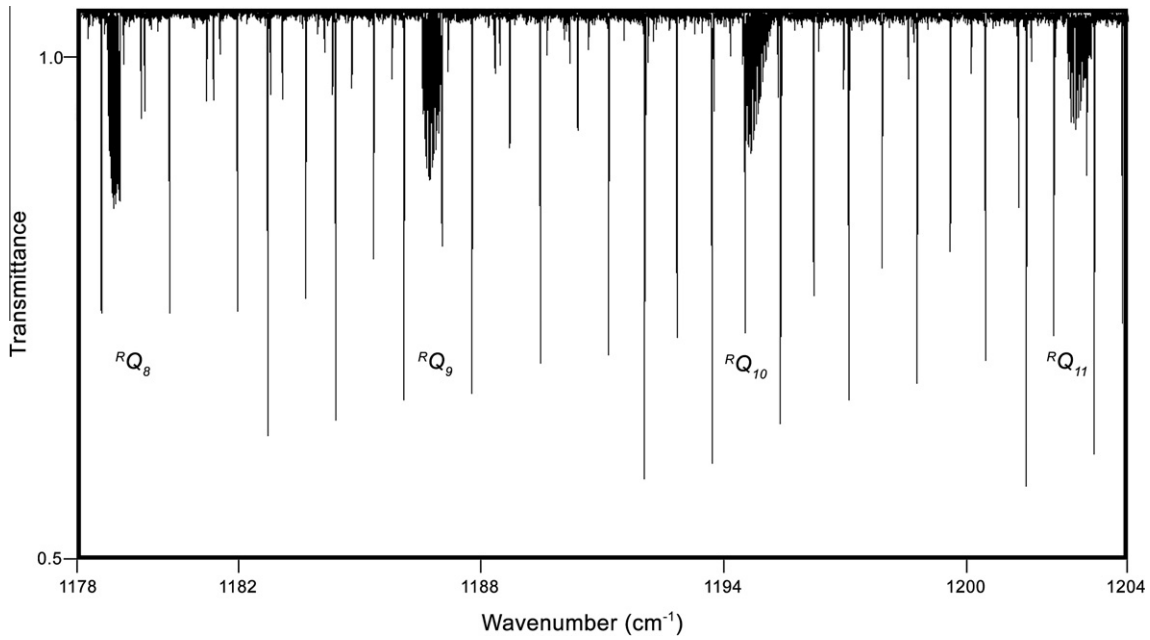

Fig. 2. High-resolution (0.0063 cm^{-1}) plot in the 1178–1204 cm^{-1} region of ν_6 band of C_2H_3D showing *b*-type transitions in the *R* branch, with $^RQ_3$ to $^RQ_7$ clusters.