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Location of the ν_1, ν_2, ν_3, and ν_5 Fundamental Vibrations of Ethylene-d_4

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Synopsis. The ^{Q}Q branch peaks of the ν_1, ν_2, and ν_3 Raman active bands of ethylene-d_4 were located at $\nu_1=2260.8\pm0.1$ cm^{-1}, $\nu_2=1518.3\pm0.1$ cm^{-1}, and $\nu_3=984.4\pm0.1$ cm^{-1}, respectively. The band center of the ν_5 band which does not have a ^{Q}Q branch was determined to be $\nu_5=2315.6\pm0.3$ cm^{-1} from the analysis in the symmetric top approximation.

While many Raman data have been presented for ethylene-d_0,[1-6] few Raman data have been published for ethylene-d_4. Though its pure rotational Raman spectrum was studied by Dowling *et al.*,[2] its vib-rotational Raman spectra have not been studied. Only the liquid state vibrational frequencies of the Raman active bands have been measured, by Hemptinne *et al.*[7] As a preliminary to the vib-rotational Raman study of ethylene-d_4, we report the ν_1, ν_2, ν_3, and ν_5 fundamental frequencies, since these data are considered to be important in the force constant calculation of this molecule.

Experimental

The experimental setup consisted of a He-Cd laser operated at 441.570 nm, a gas cell, and an Echelle grating monochromator. The scattered Raman radiation from a multi-reflection cell[8] placed inside the laser cavity was analyzed by the Echelle grating monochromator and detected by a cooled photomultiplier operated in conjunction with photon counting equipment. Ethylene-d_4 gas obtained from Merck, Sharp, and Dohme was used at a pressure of about 400 Torr. Wavelength calibration was made by using as standards the lines from an iron-neon hollow cathode lamp. A slit width of 0.4 cm^{-1} was used in the measurements of the ν_1 ^{Q}Q and the ν_2 ^{Q}Q branch peaks, and a slit width of 0.8 cm^{-1} was used in the measurements of the ν_3 ^{Q}Q branch peak and the ν_5 band.

Results

The ^{Q}Q branch peaks of the totally symmetric bands of ethylene-d_4 gas were determined to be $\nu_1=2260.8\pm0.1$ cm^{-1}, $\nu_2=1518.3\pm0.1$ cm^{-1}, and $\nu_3=984.4\pm0.1$ cm^{-1}. The ν_1 value is larger than that in liquid state by 10 cm^{-1}, but the ν_2 and ν_3 fundamental frequencies are nearly equal to those in liquid state, as obtained by Hemptinne *et al.*[7] These circumstances are similar to those in ethylene-d_0.[9]

As the rotational structure of the ν_5 band was observed under low resolution (about 1.0 cm^{-1}), as shown in Fig. 1, this band was analyzed in the symmetric top approximation. In order to enable the K-assignment to be done exactly we made use of the simulated spectrum which was caculated using the calculation program for the asymmetric rotor. As the rotational constants in the $v_5=1$ state can not be obtained at the present stage, we calculated the spectrum with $A_0=A_5=2.425$ cm^{-1}, $B_0=B_5=0.73630$ cm^{-1}, and $C_0=C_5=0.56355$ cm^{-1}, where the ground state constants for ethylene-d_4 were taken from the paper of Duncan *et al.*[10] In the symmetric top approximation the $^{P,R}Q_K$ branches form a series of lines at the origins of subbands, if $\bar{B}_0-\bar{B}_5$ is negligibly small. From the least squares fit of the observed data we obtained the following quadratic equation for the subband origins:

$$\nu^{\text{sub}} = 2317.4 + 3.601K - 0.006K^2.$$

This equation gives $\nu_5=2315.6\pm0.3$ cm^{-1} for the band

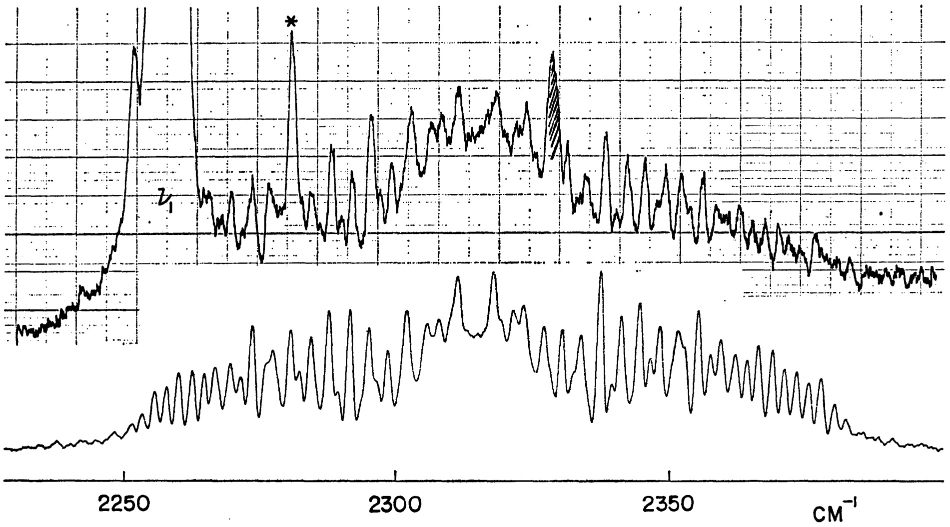

Fig. 1. Observed (top) and calculated (bottom) spectra of the ν_5 band of ethylene-d_4. The peak marked by * was attributed to ν_1 (C_2HD_3) and the peak with shadow was overlapped by N_2 line.

center, which is also about 11 cm^{-1} larger than that in liquid state. The negative value of the coefficient in K^2 is contradictory to $\mathrm{A}_5-\bar{\mathrm{B}}_5=1.801>\mathrm{A}_0-\bar{\mathrm{B}}_0=1.775$. It was perhaps caused by the circumstance that the correction for the term $(\bar{\mathrm{B}}_5-\bar{\mathrm{B}}_0)J(J+1)$ was not applied to the observed data and that the symmetric top approximation was used for an asymmetric top molecule.

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