Location of the 1/5 and 1/3 Fundamental Vibrations of Ethylene-H4

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Location of the ν_5 and ν_3 Fundamental Vibrations of Ethylene-H_4

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Abstract From the comparison between the observed and the simulated Raman spectrum, the band center of the ν_5 fundamental vibration of ethylene-H_4 was determined to be 3082.98 $\pm$0.12 cm^{-1} which is rather closer to the value of Duncan et al.

The Q branch maximum of the ν_3 fundamental vibration was also measured fairly accurately to be 1343.46$\pm$0.06 cm^{-1}.

Introduction

There are six vibrational bands in ethylene which are Raman active, and almost all of these bands have been studied by Feldman et al[1]. Though values of the fundamental frequency of ethylene obtained by them were accepted so far, the location of the ν_5 band center was corrected recently by Duncan et al[2].

With the aim of ascertaining the validity of the relocation of the ν_5 fundamental by Duncan et al. and of our simulating Raman spectrum with the use of asymmetric-rotor wave functions, Raman spectrum of this band was re-investigated. This paper reports the result for the ν_5 band, and also refers briefly to the location of Q branch maximum of the ν_3 fundamental for which the analysis is being carried out.

Experimental

The scattered Raman radiation from a multi-reflection cell[3] placed inside the He-Cd laser (4415.70 Å) cavity was analyzed by an Echelle grating monochromator and detected by a cooled photomultiplier operated in conjunction with the photon counting equipment. Wavelength calibration was made using as standards the lines from an iron-neon hollow cathode lamp. A commercial sample of ethylene-H_4 was used without purification and in gas pressure range of 500-900 torr.

Results

ν_5 band

The observed spectrum of the ν_5 band is given in Fig. 1. The spectrum was obtained with a spectral slit width of 0.5 cm^{-1} (in both the entrance and the exit slit). In order to enable the spectrum to be assigned, a band contour was calculated with the use of the computer program prepared previously[4], and on the basis of the rotational constants which were tabulated by Duncan et al[2]. The rotational constants in cm^{-1} employed in the calculation are as follows:

$A_0=4.86560$, $B_0=1.00098$, $C_0=0.82810$,

$\Delta_J=1.21\times10^{-6}$, $\Delta_{JK}=1.35\times10^{-5}$, $\Delta_K=9.27\times10^{-5}$,

$\delta_J=1.2\times10^{-7}$, $\delta_K=3.4\times10^{-6}$,

$A_5=4.8408$, $B_5=0.99925$, $C_5=0.82625$

Here the distortion constants in the $v_5=1$ state were assumed to be equal to those in the ground state.

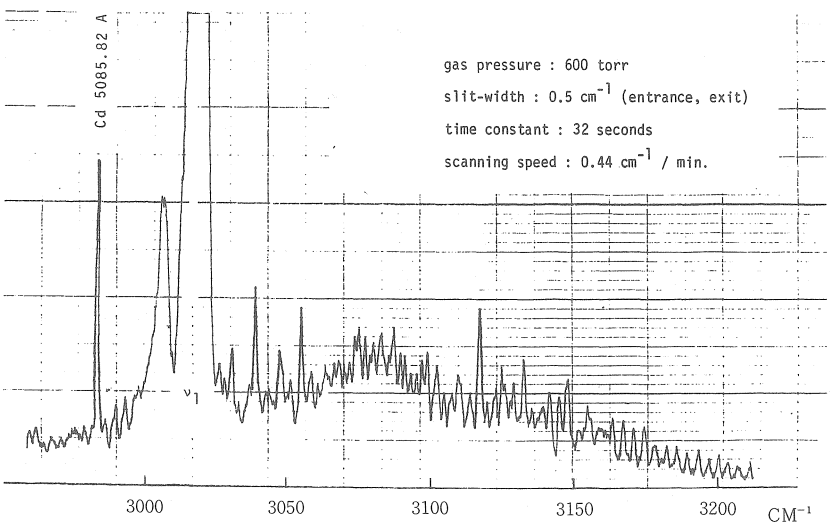

Fig. 1. Observed spectrum of the ν_5 band of ethylene-H_4

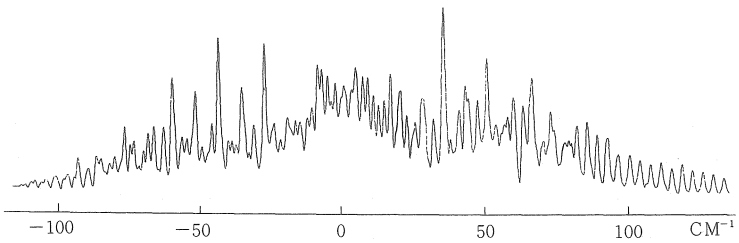

Fig. 2. Calculated spectrum of the ν_5 band of ethylene-H_4

The slit function included in the calculation was determined experimentally by means of the Raman band contour of the totally symmetric ν_1 band of methane. The calculated spectrum is given in Fig. 2. The agreement between the observed and the calculated band structures was fairly satisfactory. Since the observed spectrum was in low resolution, further refinement was not attempted. The location of the band center was determined by averaging the differences between the frequencies at the maxima in the observed spectrum and corresponding ones in the calculated spectrum.

Thus the band center was determined to be 3082.98 ± 0.12 cm^{-1} which is in good agreement with that of Duncan et al. but 19.5 cm^{-1} lower than that of Feldman et al. In Table 1, the observed and the calculated maxima are tabulated together with single transitions included in the maxima. Slight differences between the observed and the calculated wavenumber shifts in the maxima are probably due to inaccuracy in wavelength measurement.

ν_3 band

The observed spectrum of the ν_3 band is given in Fig. 3. Before the complete analysis of this band is attempted, the location of Q branch maximum was measured carefully using only the international standard lines from an iron-neon hollow cathode lamp.

As a result, the location of Q branch maximum was determined to be 1343.46 ± 0.06 cm^{-1} which is 1.2 cm^{-1} lower value than the previously accepted one[1].

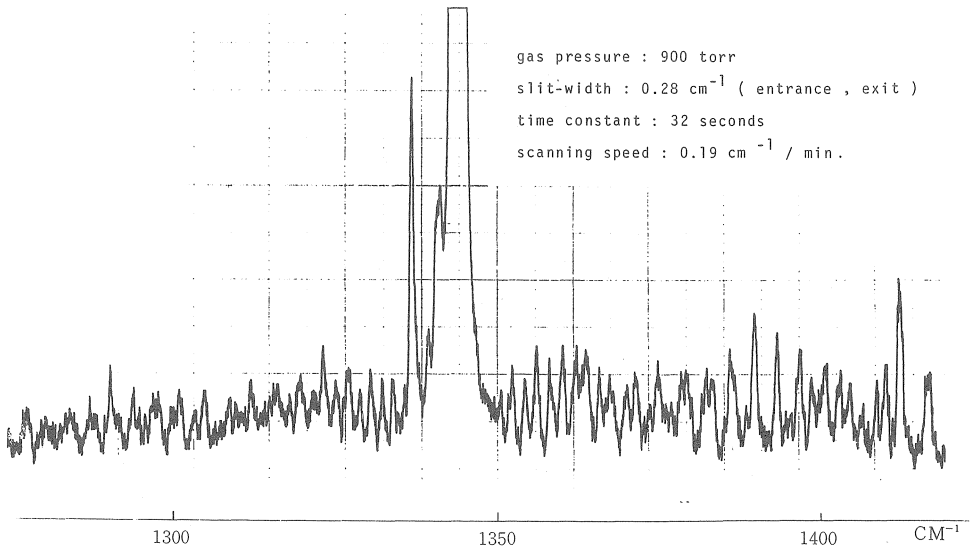

Fig. 3. Observed spectrum of the ν_3 band of ethylene-H_4

Table 1. Raman shifts of lines in the ν_5 band of ethylene-H_4

obs. max.	calc. max.	transition $J, K_p, K_o \rightarrow J', K'_p, K'_o$	$\Delta\nu_{calc}$	obs. max.	calc. max.	transition $J, K_p, K_o \rightarrow J', K'_p, K'_o$	$\Delta\nu_{calc}$
3028.21(07)	3027.82	6, 6, 0 5, 5, 0	3027.99	3105.18(06)	3105.03	4, 0, 4 6, 1, 6	3105.14
		6, 6, 1 5, 5, 1	3027,99			7, 0, 7 8, 1, 7	3104.91
3030.92(06)	3030.79	13, 2,12 11, 1,10	3030.88	3110.06(07)	3110.35	5, 3, 3 5, 4, 1	3110.18
		10, 2, 8 8, 1, 8	3030.81			5, 3, 2 5, 4, 2	3110.18
3036.82(08)	3036.64	14, 0,14 12, 1,12	3036.79	3110.87(07)	3110.75	7, 1, 7 9, 0, 9	3110.81
		11, 2,10 9, 1, 8	3036.54			12, 6, 6 11, 7, 4	3110.83
3038.92(06)	3038.88	13, 1,13 11, 0,11	3038.98	3117.73(04)	3117.67	6, 4, 2 6, 5, 2	3117.83
		8, 6, 2 8, 5, 4	3038.91			7, 4, 4 7, 5, 2	3117.80
3042.50(12)	3042.48	9, 2, 8 7, 1, 6	3042.43	3120.12(07)	3120.21	9, 0, 9 11, 1,11	3120.26
		13, 1,12 11, 2,10	3042.66			6, 1, 5 8, 2, 7	3120.16
3047.37(07)	3047.12	12, 1,11 10, 2, 9	3047.00	3123.47(11)	3123.14	10, 0,10 12, 1,12	3123.29
		6, 5, 1 6, 4, 3	3047.03			7, 1, 6 9, 2, 8	3123.16
3050.16(09)	3049.84	12, 2,10 11, 1,10	3049.81	3125.37(10)	3125.21	11, 1,11 13, 0,13	3125.03
		6, 2, 4 4, 1, 4	3049.73			11, 2,10 12, 3,10	3125.29
3051.26(06)	3051.36	9, 1, 9 7, 0, 7	3051.42	3126.47(08)	3126.24	11, 0,11 13, 1,13	3126.36
		11, 1,10 9, 2, 8	3051.36			5, 2, 4 7, 3, 4	3126.34
3058.50(14)	3058.55	8, 0, 8 6, 1, 6	3058.62	3129.49(04)	3129.49	12, 0,12 14, 1,14	3129.46
		13, 2,12 11, 3, 8	3058.48			6, 2, 4 8, 3, 6	3129.63
3060.78(08)	3060.79	6, 1, 6 4, 0, 4	3060.69	3132.90(07)	3132.75	13, 0,13 15, 1,15	3132.58
		11, 6, 6 12, 5, 8	3060.82			9, 6, 4 9, 7, 2	3132.91
3068.14(15)	3067.74	6, 4, 2 7, 3, 4	3067.93	3135.73(04)	3135.92	14, 0,14 16, 1,16	3135.72
		14, 1,13 13, 2,11	3067.60			16, 3,14 18, 2,16	3136.06
3070.06(17)	3070.29	12, 1,11 11, 2, 9	3070.29	3137.65(07)	3137.82	4, 4, 0 6, 5, 2	3137.98
		5, 0, 5 3, 1, 3	3070.10			8, 2, 7 10, 3, 7	3137.72
3071.85(08)	3071.89	11, 1,10 10, 2, 8	3071.94	3138.87(03)	3138.85	15, 2,14 17, 1,16	3138.93
		17, 6,12 18, 5,14	3071.87			15, 0,15 17, 1,17	3138.89
3073.76(07)	3073.96	12, 0,12 11, 1,11	3073.83	3140.05(11)	3139.96	21, 2,19 22, 3,19	3140.03
		14, 0,14 13, 1,13	3073.89			14, 7, 7 14, 8, 7	3140,14
3075.31(09)	3075.40	8, 0, 8 7, 1, 6	3075.54	3145.29(07)	3145.34	17, 0,17 19, 1,19	3145.26
		10, 4, 6 11, 3, 8	3075.53			6, 4, 2 8, 5, 4	3145.25
3080.23(09)	3080.19	4, 0, 4 3, 1, 2	3080.17	3148.21(05)	3148.35	18, 0,18 20, 1,20	3148.45
		13, 2,12 12, 3,10	3080.15			18, 1,18 20, 0,20	3148.30
3082.90(12)	3082.42	10, 2,10 9, 3, 6	3082.34	3151.95(08)	3152.23	10, 3, 8 12, 4, 8	3152,18
		7, 2, 6 8, 1, 8	3082.33			21, 1,21 22, 2,21	3152.23
3087.24(06)	3087.36	16, 4,12 15, 5,12	3087.49	3154.99(07)	3154.85	20, 0,20 22, 1,22	3154.86
		17, 4,14 18, 3,16	3087.21			20, 1,20 22, 0,22	3154.78
3089.73(08)	3089.75	8, 2, 6 9, 1, 8	3089.84	3170.90(11)	3170.97	11, 5, 6 13, 6, 8	3170.96
		7, 2, 6 6, 3, 4	3089.79			11, 5, 7 13, 6, 7	3170.96
3091.33(09)	3091.50	14, 4,10 13, 5, 8	3091.56	3174.36(10)	3174.60	12, 5, 7 14, 6, 9	3174.57
		10, 1, 9 11, 0,11	3091.49			12, 5, 8 14, 6, 8	3174.57
3093.35(09)	3093.43	10, 2, 8 11, 1,10	3093.48	3182.30(07)	3182.26	12, 6, 6 14, 7, 8	3182.11
		13, 4,10 12, 5, 8	3093.59			12, 6, 7 14, 7, 7	3182.11
3095.39(11)	3095.32	12, 4, 8 11, 5, 6	3095.50	3185.70(07)	3185.81	13, 6, 8 15, 7, 8	3185.71
		1, 0, 1 3, 1, 3	3095.51			13, 6, 7 15, 7, 9	3185.71
3097.34(06)	3097.31	4, 0, 4 5, 1, 4	3097.34	3189.38(10)	3189.36	14, 6, 8 16, 7,10	3189.30
		11, 4, 8 10, 5, 6	3097.45			14, 6, 9 16, 7, 9	3189.30
3099.29(06)	3099.38	16, 2,14 17, 1,16	3099.55	3193.13(09)	3193.06	15, 6,10 17, 7,10	3192.89
		10, 4, 6 9, 5, 4	3099.35			15, 6, 9 17, 7,11	3192.89
3102.60(06)	3102.64	3, 2, 2 3, 3, 0	3102.50	3196.57(09)	3196.77	14, 7, 7 16, 8, 9	3196.78
		5, 2, 4 5, 3, 2	3102.52			14, 7, 8 16, 8, 8	3196.78

* Wave-numbers are in units of cm^{-1} .

* Numbers in parentheses are the values of the uncertainty (last two decimals) .

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