Infrared Spectrum of the $\nu_2 + \nu_6$ Band of $C^{13}C^{12}H_6$ *

Walter J. Lafferty and Earle K. Plyler

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The infrared spectrum of the $\nu_2 + \nu_6$ band of $C^{13}C^{12}H_6$ has been analyzed and a value of $B_0 = 0.64865 \pm 0.00005$ cm^{-1} determined. When this value is combined with that found in recent work on isotopically normal ethane, a "r_s" value of 1.527 ± 0.004 A for the carbon-carbon bond distance is obtained. (Uncertainties are probable errors.)

1. Introduction

From recent infrared studies of ethane and ethane-d_6, a ground state carbon-carbon bond distance of 1.536 with probable error 0.002 A has been obtained [1, 2].[1] This bond distance is considerably higher than the C—C bond lengths, 1.526 with limits of error ± 0.002 A, obtained for the saturated hydrocarbons propane and isobutane by the "r_s" or "substitution" method in the microwave studies of Lide [3, 4]. Since the two methods of determining bond distances are only approximately equivalent due to rotation-vibration effects, this difference is not surprising.

The purpose of this work was to examine the spectrum of $C^{13}C^{12}H_6$ in an attempt to obtain a "r_s" value for the C—C bond distance of ethane for comparison with these bond lengths reported for the more complex molecules. In addition other rotational constants would be obtained which would be of use to future investigators of this molecule.

2. Experimental Procedure

The sample, which contained 59.5 percent $C^{13}C^{12}H_6$, was purchased from Merck Sharp & Dohme of Canada, Ltd. The spectra were taken with a pressure of 3.2 mm Hg total pressure (1.9 mm $C^{13}C^{12}H_6$) and an optical path of 24 m.

The spectrometer, used in this study as well as for the normal ethane work [2], has been described previously. Because of the small amount of costly sample available, a threefold longer optical path (24 m) was required than was used for ethane. This resulted in the loss of some resolution; however, lines separated by about 0.035 cm^{-1} could be resolved. The spectra were measured by using rare gas emission lines as standards. The regions between the standard lines were measured from the fringe system formed by a Fabry-Perot interferometer [5].

3. Rotational Analysis

As in the case of normal ethane, the only parallel band of $C^{13}C^{12}H_6$ that could be resolved sufficiently well with the instrumentation available was the $\nu_2 + \nu_6$ band at 2749 cm^{-1}. Substitution of one C^{13} in ethane results in a shift of about 4.1 cm^{-1} for the origin of this band. Since the sample contained about 40 percent normal ethane, the resulting spectrum consisted of a complicated mixture of lines from the two overlapping bands together with their accompanying "hot bands" arising from excited levels of the torsional vibration. The lines of ethane were easily identified when the spectra were compared with those obtained from the earlier studies on ethane. The vibrational shift was such that most of the P and R branch lines fell between those of the normal ethane. There was, however, some blending of the lines. Since blending can result in an apparent change of the frequency of a line, all blended lines were marked as such when assigned and given a weight of $\frac{1}{2}$ in the following calculations. Badly overlapped lines were not used in the analysis.

As in the case of normal ethane, the quantity $(A'-B')-(A''-B'')$ was sufficiently large so that transitions from the substates $K=2$ and higher were resolved. The unresolved lines from the substates $K=0$ and 1 were not used in the calculations. The ground state rotational constants were calculated by means of combination differences from the equation

$$\Delta_2 F'' = R(J-1, K) - P(J+1, K)$$
$$= (4B'' - 6D_J'' - 4D_{JK}''K^2)\ (J+\tfrac{1}{2})$$
$$- 8D_J''(J+\tfrac{1}{2})^3. \quad (1)$$

Since no substates with K greater than 6 were identified, the value of D_{JK}'' obtained was highly uncertain. The assumption was then made that this constant is equal to that found for ethane times the ratio of the B values of the substituted ethane to that of the normal molecule or 5.8×10^{-6} cm^{-1}. With this assumed constant, the resulting ground state rotational constants found by least squares

were $B''=0.64865\pm0.00005$ cm^{-1} and $D_J''=8.4\pm1.4\times10^{-7}$ cm^{-1} where the uncertainties cited are probable errors. The values of D_J'' calculated is in good agreement with that found for normal ethane ($D_J''=7\pm2\times10^{-7}$ cm^{-1}).

The upper state rotational constants were determined using the equation

$$\nu=\nu_0+[B'+B''-(D'_{JK}+D''_{JK})K^2]m+[B'-B''$$
$$-D'_J+D''_J-(D'_{JK}-D''_{JK})K^2]m^2-2(D'_J+D''_J)m^3$$
$$-(D'_J-D''_J)m^4+[(A'-B')-(A''-B'')]K^2. \quad (2)$$

The values of B'', D_J'', D_{JK}'' obtained above were inserted into the equation, and the data were subjected to a least squares fit. As in the case of normal ethane, the $K=5$ substate was found to be perturbed. The origin of this state fell 0.03_2 cm^{-1} above the calculated value. While this difference is small, it is 3.1 times the standard deviation of the fit taken without including this substate and is therefore significant. Any changes in the other rotational constants of this state were too small to be detected. Because of this perturbation, the observed frequencies were again fit to eq (2) with the frequencies from the $K=5$ substate omitted. The constants obtained from this treatment are listed in table 2. The spectrum calculated from these constants is compared with the observed spectrum in table 1. For the $K=5$ substate, the observed origin was used instead of that calculated from eq (2).

TABLE 1. *Comparison between observed and calculated spectrum of $\nu_2+\nu_6$ of $C^{13}C^{12}H_6$*

J_K	$^QR_K(J)$ Obs	$^QR_K(J)$ Calc	$^QP_K(J)$ Obs	$^QP_K(J)$ Calc	J_K	$^QR_K(J)$ Obs	$^QR_K(J)$ Calc	$^QP_K(J)$ Obs	$^QP_K(J)$ Calc
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}		cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
3_0	} 2754.164	{ 2754.141	....	....	11_0	63.236	63.243	ᵇ33.908	33.907
3_1		54.103			11_1	ᵇ63.356	63.361	34.044	34.043
3_2	54.229	54.227	2745.290	2745.297	11_2	63.549	53.546	34.241	34.253
3_3	ᵇ54.346	ᵇ54.335			11_3	63.717	63.728	34.449	34.483
4_0	} 54.362	{ 55.334			12_0	} 64.104	{ 64.089	32.230	{ 32.201
4_1		55.383			12_1		64.106		32.218
4_2	55.410	55.417	ᵇ43.931	43.938	12_2	64.143	64.158	32.270	32.278
4_3	55.545	55.625	44.098	44.046	12_3	ᵇ64.253	64.247	ᵇ32.389	32.373
4_4	55.671	55.675			12_4	ᵇ64.368	64.370	32.509	32.505
5_0	} 56.528	{ 56.601			12_5	64.559	64.580	32.696	32.710
5_1		56.622			12_6	64.715	64.723	32.890	32.883
5_2	56.689	56.685	42.600	42.653	13_0	} 65.111	{ 65.087	30.679	{ 30.649
5_3	56.712	56.691	42.662	42.662	13_1		65.108		30.667
5_4	56.835	56.840	42.826	42.814	13_2	65.150	65.154	30.719	30.725
5_5	ᵇ57.072	57.061			13_3	ᵇ65.231	65.238	30.834	30.816
6_0	} 57.571	{ 57.660			13_4	ᵇ65.355	65.357	30.937	30.945
6_1		57.689			13_5	65.529	65.540	31.150	31.144
6_2	57.728	57.732	41.198	41.149	13_6	65.700	65.696	31.310	31.311
6_3	57.880	57.836	41.276	41.257	14_0	}	{	2729.112	{ 2729.077
6_4	57.977	57.982	ᵇ41.411	41.407	14_1				29.096
6_5	58.195	....	41.646	41.635	14_2			29.142	29.151
6_6	58.399	58.399			14_3	2765.237	2766.908	29.239	29.239
7_0	} 2758.800	{ 2758.776	2739.681	{ 2739.638	14_4	ᵇ66.319	66.321	29.363	29.363
7_1		58.795		39.657	14_5	66.508	66.497	29.542	29.556
7_2	58.839	58.857	ᵇ39.722	39.724	14_6	66.638	66.645	....	....
7_3	ᵇ58.963	58.959	39.895	39.880	15_2	67.070	67.079	27.548	27.556
7_4	59.086	59.102	39.980	39.978	15_3			ᵇ27.616	27.641
7_5	59.342	59.317	40.199	40.208	15_4	ᵇ67.259	67.263	27.755	27.759
7_6	59.501	59.511			15_5	67.444	67.431	27.952	27.947
8_0	} 59.898	{ 59.882	38.209	{ 38.193	15_6	67.591	67.571	28.097	28.096
8_1		59.901		38.213	16_0	} 67.976	{ 67.952	25.894	{ 25.872
8_2	59.950	59.961	38.255	38.277	16_1		67.964		25.888
8_3	60.087	60.001	38.388	38.381	16_2	68.010	68.009	25.935	25.940
8_4	60.191	60.201	38.537	38.527	16_3			26.030	26.021
8_5	60.396	60.412	38.751	38.749	16_4			26.137	26.134
8_6	60.589	60.600	38.944	38.944	16_5	68.350	68.342		
9_0	} 60.966	{ 60.966	....	....	16_6	68.468	68.473		
9_1		60.984			17_0	}	{	24.268	{ 24.238
9_2	61.024	61.043	36.794	36.809	17_1				24.252
9_3	61.162	61.140	36.913	36.912	17_2			24.298	24.302
9_4	ᵇ61.277	61.276	37.055	37.055	17_3	68.990	68.985	24.365	24.379
9_5	61.476	61.483			17_4			24.457	24.457
9_6	61.664	61.686	37.468	37.463	17_5	69.236	69.234		
10_0	} 2762.045	{ 2762.037	2735.289	{ 2735.238	17_6	69.356	69.352		
10_1		62.045	35.265	35.265	18_2			22.649	22.644
10_2	62.079	62.103	35.315	35.320	18_3			22.707	22.715
10_3	62.203	62.197	35.433	35.420	18_4			22.818	22.819
10_4	62.322	62.330	35.560	35.560					
10_5	62.534	62.531	35.757	35.773	19_2			2721.030	2721.032
10_6	62.721	62.708	35.949	35.969	19_3			21.129	21.127
11_0	} 63.062	{ 63.069	33.755	{ 33.731	20_2			19.270	19.264
11_1		63.086		33.749	20_3			19.346	19.327
11_2	63.150	63.141	33.802	33.810					

ᵇ Blended line.

4. Results

For a symmetric top molecule, the "r_s" distance of an atom on the symmetry axis from the center of gravity is given by the relation

$$\Delta I_0 = \mu r_s^2 \qquad (3)$$

where ΔI_0 is the change of the moment of inertia upon substitution, $\mu = m\Delta m/(M+2m)$, M is the mass of the original molecule, and Δm is the change of mass upon substitution. Using the B_0 value obtained earlier for ethane and the value found for the C^{13} substituted ethane above, a "r_s" value of 1.527 ± 0.004 A for the C—C distance is calculated. The uncertainty cited is probable error.

This value supports Lide's estimate that the "r_s" value for ethane lies in the range 1.525–1.530 A [6] and is in good, albeit somewhat fortuitous, agreement with the value 1.526 A found for the C—C bond lengths in propane and isobutane.

5. References

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