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

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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 $B_0=0.64865\pm0.00005$ 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 ½ 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

$$\begin{aligned}\Delta_2F''&=R(J-1,K)-P(J+1,K)\\&=(4B''-6D_J''-4D_{JK}''K^2)\,(J+\tfrac{1}{2})\\&\qquad-8D_J''(J+\tfrac{1}{2})^3.\quad(1)\end{aligned}$$

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 $5.8\times10^{-6}$ cm$^{-1}$. With this assumed constant, the resulting ground state rotational constants found by least squares

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[1] Figures in brackets indicate the literature references at the end of this paper.

were $B''=0.64865\pm 0.00005$ cm$^{-1}$ and $D''_J=8.4\pm 1.4\times 10^{-7}$ 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 ($D''_J=7\pm 2\times 10^{-7}$ 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 $C^{13}C^{12}H_6$*

| $J_K$ | $^{Q}R_K(J)$ | | $^{Q}P_K(J)$ | |
|---|---|---|---|---|
| | Obs | Calc | Obs | Calc |
| | $cm^{-1}$ | $cm^{-1}$ | $cm^{-1}$ | $cm^{-1}$ |
| $3_0$ | 2754.164 | 2754.141 | ----- | ----- |
| $3_1$ | | 54.163 | ----- | ----- |
| $3_2$ | 54.229 | 54.227 | 2745.290 | 2745.297 |
| $3_3$ | [b] 54.346 | [b] 54.336 | ----- | ----- |
| $4_0$ | 54.362 | 55.331 | ----- | ----- |
| $4_1$ | | 55.353 | ----- | ----- |
| $4_2$ | 55.410 | 55.417 | [b] 43.931 | 43.936 |
| $4_3$ | 55.545 | 55.525 | 44.058 | 44.046 |
| $4_4$ | 55.671 | 55.675 | ----- | ----- |
| $5_0$ | 56.528 | 56.501 | ----- | ----- |
| $5_1$ | | 56.522 | ----- | ----- |
| $5_2$ | 56.589 | 56.585 | 42.550 | 42.553 |
| $5_3$ | 56.719 | 56.691 | 42.652 | 42.662 |
| $5_4$ | 56.838 | 56.840 | 42.825 | 42.814 |
| $5_5$ | [b] 57.072 | 57.061 | ----- | ----- |
| $6_0$ | 57.671 | 57.650 | ----- | ----- |
| $6_1$ | | 57.669 | ----- | ----- |
| $6_2$ | 57.728 | 57.732 | 41.158 | 41.149 |
| $6_3$ | 57.860 | 57.836 | 41.276 | 41.257 |
| $6_4$ | 57.977 | 57.982 | [b] 41.411 | 41.407 |
| $6_5$ | 58.195 | ----- | 41.646 | 41.635 |
| $6_6$ | 58.399 | 58.399 | ----- | ----- |
| $7_0$ | 2758.800 | 2758.775 | 2739.661 | 2739.638 |
| $7_1$ | | 58.795 | | 39.657 |
| $7_2$ | 58.839 | 58.857 | [b] 39.722 | 39.724 |
| $7_3$ | [b] 58.963 | 58.959 | 39.835 | 39.830 |
| $7_4$ | 59.085 | 59.102 | 39.980 | 39.978 |
| $7_5$ | 59.342 | 59.317 | 40.199 | 40.203 |
| $7_6$ | 59.501 | 59.511 | ----- | ----- |
| $8_0$ | 59.898 | 59.882 | 38.209 | 38.193 |
| $8_1$ | | 59.901 | | 38.213 |
| $8_2$ | 59.950 | 59.961 | 38.255 | 38.277 |
| $8_3$ | 60.087 | 60.061 | 38.388 | 38.381 |
| $8_4$ | 60.191 | 60.201 | 38.537 | 38.527 |
| $8_5$ | 60.396 | 60.412 | 38.751 | 38.749 |
| $8_6$ | 60.589 | 60.600 | 38.944 | 38.944 |
| $9_0$ | 60.988 | 60.966 | ----- | ----- |
| $9_1$ | | 60.984 | ----- | ----- |
| $9_2$ | 61.024 | 61.043 | 36.794 | 36.809 |
| $9_3$ | 61.152 | 61.140 | 36.913 | 36.912 |
| $9_4$ | [b] 61.277 | 61.276 | 37.055 | 37.055 |
| $9_5$ | 61.476 | 61.483 | ----- | ----- |
| $9_6$ | 61.664 | 61.666 | 37.468 | 37.463 |
| $10_0$ | 2762.045 | 2762.037 | 2735.269 | 2735.238 |
| $10_1$ | | 62.045 | | 35.258 |
| $10_2$ | 62.079 | 62.103 | 35.315 | 35.320 |
| $10_3$ | 62.203 | 62.197 | 35.433 | 35.420 |
| $10_4$ | 62.322 | 62.330 | 35.560 | 35.560 |
| $10_5$ | 62.534 | 62.531 | 35.757 | 35.773 |
| $10_6$ | 62.721 | 62.708 | 35.948 | 35.959 |
| $11_0$ | 63.082 | 63.069 | 33.756 | 33.731 |
| $11_1$ | | 63.086 | | 33.749 |
| $11_2$ | 63.150 | 63.141 | 33.802 | 33.810 |
| $11_3$ | 63.236 | 63.233 | [b] 33.908 | 33.907 |
| $11_4$ | [b] 63.356 | 63.361 | 34.044 | 34.043 |
| $11_5$ | 63.540 | 63.556 | 34.241 | 34.253 |
| $11_6$ | 63.717 | 63.728 | 34.440 | 34.433 |
| $12_0$ | 64.104 | 64.089 | 32.230 | 32.201 |
| $12_1$ | | 64.105 | | 32.218 |
| $12_2$ | 64.143 | 64.158 | 32.270 | 32.278 |
| $12_3$ | [b] 64.253 | 64.247 | [b] 32.369 | 32.373 |
| $12_4$ | [b] 64.368 | 64.370 | 32.509 | 32.505 |
| $12_5$ | 64.558 | 64.560 | 32.696 | 32.710 |
| $12_6$ | 64.715 | 64.723 | 32.890 | 32.883 |
| $13_0$ | 65.111 | 65.087 | 30.679 | 30.649 |
| $13_1$ | | 65.103 | | 30.667 |
| $13_2$ | 65.150 | 65.154 | 30.719 | 30.725 |
| $13_3$ | [b] 65.231 | 65.238 | 30.834 | 30.816 |
| $13_4$ | [b] 65.358 | 65.357 | 30.937 | 30.945 |
| $13_5$ | 65.529 | 65.540 | 31.150 | 31.144 |
| $13_6$ | 65.700 | 65.696 | 31.310 | 31.311 |
| $14_0$ | ----- | ----- | 2729.112 | 2729.077 |
| $14_1$ | | | | 29.095 |
| $14_2$ | ----- | ----- | 29.142 | 29.151 |
| $14_3$ | 2766.237 | 2766.208 | 29.239 | 29.239 |
| $14_4$ | [b] 66.319 | 66.321 | 29.363 | 29.363 |
| $14_5$ | 66.508 | 66.497 | 29.542 | 29.556 |
| $14_6$ | 66.638 | 66.645 | ----- | ----- |
| $15_2$ | 67.070 | 67.079 | 27.548 | 27.556 |
| $15_3$ | ----- | ----- | [b] 27.618 | 27.641 |
| $15_4$ | [b] 67.259 | 67.263 | 27.755 | 27.759 |
| $15_5$ | 67.444 | 67.431 | 27.952 | 27.947 |
| $15_6$ | 67.591 | 67.571 | 28.097 | 28.098 |
| $16_0$ | 67.976 | 67.952 | 25.894 | 25.872 |
| $16_1$ | | 67.964 | | 25.888 |
| $16_2$ | 68.010 | 68.009 | 25.935 | 25.940 |
| $16_3$ | ----- | ----- | 26.030 | 26.021 |
| $16_4$ | ----- | ----- | 26.137 | 26.134 |
| $16_5$ | 68.330 | 68.342 | ----- | ----- |
| $16_6$ | 68.468 | 68.473 | ----- | ----- |
| $17_0$ | ----- | ----- | 24.268 | 24.238 |
| $17_1$ | | | | 24.252 |
| $17_2$ | ----- | ----- | 24.298 | 24.302 |
| $17_3$ | 68.990 | 68.985 | 24.385 | 24.379 |
| $17_4$ | ----- | ----- | 24.487 | 24.487 |
| $17_5$ | 69.236 | 69.234 | ----- | ----- |
| $17_6$ | 69.356 | 69.352 | ----- | ----- |
| $18_2$ | ----- | ----- | 22.649 | 22.644 |
| $18_3$ | ----- | ----- | 22.707 | 22.716 |
| $18_4$ | ----- | ----- | 22.818 | 22.818 |
| $19_3$ | ----- | ----- | 2721.030 | 2721.032 |
| $19_4$ | ----- | ----- | 21.129 | 21.127 |
| $20_2$ | ----- | ----- | 19.270 | 19.264 |
| $20_3$ | ----- | ----- | 19.348 | 19.327 |

[b] Blended line.

TABLE 2. *Rotational constants of* $C^{13}C^{12}H_6$ *derived from the combination band,* $\nu_2+\nu_6$ *in* $\mathrm{cm}^{-1}$[a]

| | |
|---|---|
| $\nu_0$ | $2749.164 \pm 0.002$ |
| $B''$ | $0.64865 \pm 0.00005$ |
| $D_J''$ | $8.4 \pm 1.4 \times 10^{-7}$ |
| $D_{JK}''$ | $5.8 \times 10^{-6}$ (assumed) |
| $B'-B''$ | $-0.01062 \pm 0.00001$ |
| $D_{JK}'-D_{JK}''$ | $3.12 \pm 0.07 \times 10^{-5}$ |
| $D_J'-D_J''$ | $\sim 0$ |
| $D_K'-D_K''$ | $\sim 0$ |
| $(A'-B')-(A''-B'')=0.0226 \pm 0.0005$ | |

[a] Uncertainties cited are probable errors.

## 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

$$\Delta I_0 = \mu r_s^2 \tag{3}$$

where $\Delta I_0$ 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 $\Delta m$ 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.

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## 5. References

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