

## On the Viscosity of Liquid Hydrocarbon Mixtures

Fausto W. Lima

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sufficient for an investigation of its photographic infrared spectrum. Using an absorbing path of 120 m, two strong  $\parallel$  bands were found at 10308 and 7852A and two very weak bands at 8467 and 7902A. The two strong bands are without doubt the second and third overtones of the  $\equiv\text{C}-\text{H}$  stretching mode ( $3\nu_1$  and  $4\nu_1$ ). The strongest band, at 10308A, is the analog of the  $\text{CH}_3\text{CCH}$  band studied by HPV.

The fine structure of the two bands 10308 and 7852A was clearly resolved in the first and second order, respectively, of a 21-ft grating. By standard methods the following values for the rotational constants  $B$  of  $\text{CD}_3\text{CCH}$  were obtained:

$$B_0 = 0.2456, \quad B_2 = 0.2438, \quad B_4 = 0.2433, \text{ cm}^{-1}.$$

The  $\Delta_2 F''(J)$  values from which  $B_0$  was determined do not show clearly the effect of the rotational constant  $D_J$ . But an approximate value,  $D_J \approx 5 \times 10^{-7} \text{ cm}^{-1}$ , was obtained from the lines of high  $J$  of the  $P$  branch (for which corresponding lines in the  $R$  branch are not resolved and which can, therefore, not be used for the  $\Delta_2 F''(J)$  curve); and this  $D_J$  value was used in determining  $B_0$  from the  $\Delta_2 F''(J)$  values. When the same correction is applied to the values of HPV, a corrected  $B_0$  value of  $\text{CH}_3\text{CCH}$  is obtained:

$$B_0 = 0.2847, \text{ cm}^{-1}.$$

The uncertainty of the  $B$  values is estimated to be  $\pm 0.00020$  for  $\text{CD}_3\text{CCH}$  and  $\pm 0.00040$  for  $\text{CH}_3\text{CCH}$ . The accuracy is somewhat less than customary for photographic infrared work because the unresolved  $K$  structure makes the lines broad.

Using  $I_B = 27.98_{30} \times 10^{-40} / B$ , the moments of inertia in the lowest vibrational level are:

$$\begin{aligned} \text{for } \text{CD}_3\text{CH}, \quad I_B^{[0]} &= 113.91 \times 10^{-40} \text{ g cm}^2, \\ \text{for } \text{CH}_3\text{CCH}, \quad I_B^{[0]} &= 98.27 \times 10^{-40} \text{ g cm}^2. \end{aligned}$$

These two moments of inertia are still not sufficient to determine all the geometrical data. But if the  $\text{C}\equiv\text{C}$  and  $\text{C}-\text{H}$  distance in the acetylene group are assumed to be the same as in  $\text{C}_2\text{H}_2$  (i.e., 1.207 and 1.059A, respectively<sup>5</sup>) and if the  $\text{C}-\text{H}$  distance in the methyl group is assumed to be the same as in methane (1.093A), then the two remaining parameters, the  $\text{C}-\text{C}$  distance and the  $\text{HCH}$  angle, can be determined. The result is

$$r(\text{C}-\text{C}) = 1.461 \pm 0.006\text{A}, \quad \angle\text{HCH} = 108^\circ 6' \pm 1^\circ.$$

During the preparation of these results we obtained, through the courtesy of Professor Gordy, the manuscript of a paper by Trambarulo and Gordy<sup>6</sup> on the microwave spectrum and structure of methyl acetylene. They observed the microwave spectrum for a sufficient number of isotopic species to make it possible to determine all geometric parameters independently of any assumption about bond lengths. Their value for  $I_B^0$  of  $\text{CH}_3\text{CCH}$  is  $98.17_{23} \times 10^{-40} \text{ g cm}^2$ , which agrees well with the (less accurate) value of HPV. They did not obtain the spectrum of  $\text{CD}_3\text{CCH}$  here described. The assumptions made above for the  $\text{C}\equiv\text{C}$  and  $\text{C}-\text{H}$  distances are confirmed by Trambarulo and Gordy within  $\pm 0.003\text{A}$  and the values for  $r(\text{C}-\text{C})$  and  $\angle\text{HCH}$  given above agree with theirs within 1/5 of the uncertainty assigned to our values.

It must be emphasized that both Trambarulo and Gordy's and our bond distances and angles depend on the assumption that the effect of zero-point vibrational motion can be neglected. To be free of this assumption, one will have to determine all the rotational constants  $\alpha$ . Our data allow only the determination of  $\alpha_1$  which is found to be  $0.00060 \text{ cm}^{-1}$ .

Further work on the infrared spectra of  $\text{CD}_3\text{CCH}$ ,  $\text{CD}_3\text{CCD}$ , and  $\text{CH}_3\text{CCH}$ , both in the region of the fundamentals and the overtones, is in progress.

<sup>1</sup> Herzberg, Patat, and Verleger, *J. Chem. Phys.* **41**, 123 (1937), in future referred to as HPV.

<sup>2</sup> R. M. Badger and S. H. Bauer, *J. Chem. Phys.* **5**, 599 (1937).

<sup>3</sup> Pauling, Springall, and Palmer, *J. Am. Chem. Soc.* **61**, 2922 (1939).

<sup>4</sup> L. C. Leitch and R. Renaud (to be published).

<sup>5</sup> See G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand and Company, Inc., New York, 1945).

<sup>6</sup> R. Trambarulo and W. Gordy, *J. Chem. Phys.* **18**, 1613 (1950).

## Infrared Absorption Spectrum of $\text{H}_2\text{C}=\text{CHD}$

C. COURTOY, M. DE HEMPTINNE, AND M. V. MIGEOTTE  
Institut de Physique, Parc d'Arenberg, Louvain, France  
November 22, 1950

IN preceding works<sup>1</sup> it has not been possible to assign all the fundamental frequencies of  $\text{H}_2\text{C}=\text{CHD}$ . We have hoped that the study of the rotational fine structure of the unassigned experimental frequencies lower than  $1200 \text{ cm}^{-1}$  using the grating spectrograph of the Institut d'Astrophysique de l'Université de Liège<sup>2</sup> might solve the question definitely.

Although we are not yet able to present the complete solution, we think that the results of our measurements may be of some use.

The infrared spectrum shows:

(1) At  $1121 \text{ cm}^{-1}$  an absorption band of medium intensity and of the parallel type. The corresponding line in the Raman spectrum is strong and polarized; this makes the assignment of the line very difficult.

(2) At  $1000.44 \text{ cm}^{-1}$  a strong absorption band of perpendicular type. The  $Q$  bands may be found using a formula based on the model proposed by W. S. Gallaway and E. F. Barker for ethylene:

$$\nu = 1000.44 + 3.13K'^2 - 3.2K''^2 - 0.0005K'^4 + 0.0003K''^4.$$

(3) At  $943.68 \text{ cm}^{-1}$ , a strong absorption band of a perpendicular type, the  $Q$  bands being very accurately given by the formula:

$$\nu = 943.68 + 3.12K'^2 - 3.2K''^2 - 0.0003(K'^4 - K''^4).$$

(4) At  $807.88 \text{ cm}^{-1}$  a strong perpendicular band, the  $Q$  band being given by

$$\nu = 807.88 + 3.25K'^2 - 3.2K''^2 + 0.0003K''^4.$$

A second, but weaker, maximum appears at  $809.68 \text{ cm}^{-1}$ ; it is possible that two bands superpose in this region, but we were unable to find a reasonable formula taking all the lines into account.

(5) Around  $765.02 \text{ cm}^{-1}$  a somewhat complicated absorption spectrum.

<sup>1</sup> M. de Hemptinne, 7ième conseil de Chimie Solvay, p. 161 (1948). M. de Hemptinne and C. Courtoy, *Ann. Soc. Sci. Série I* **63**, 98 (1949). W. S. Gallaway and E. F. Barker, *J. Chem. Phys.* **7**, 96 (1942). <sup>2</sup> M. Migeotte, *Mem. soc. roy. sci. Liège*, Tome I, Fasc. 3 (1945).

## On the Viscosity of Liquid Hydrocarbon Mixtures

FAUSTO W. LIMA  
Escola Politécnica, Department of Chemistry, University of São Paulo,  
São Paulo, Brazil  
October 23, 1950

TREVOY and Drickamer<sup>1</sup> presented data on the viscosity of binary mixtures of normal paraffins, benzene, and 2,4 dimethyl pentane in 50 mole percent concentration. It was shown that Roegiers and Roegiers' formula<sup>2</sup> best correlated the viscosity data on those mixtures and that the use of the mentioned formula to calculated viscosities of the mixtures yielded values subject to an average error of about 5 percent and a maximum error of 14 percent.

Recently Lima<sup>3</sup> showed that the application of Souders' Viscosity Constant<sup>4</sup> to mixtures would give the following relation between the viscosity of the mixture  $\eta$  and the viscosities of pure components

$$\log \log \eta = (x_1 I_1 + x_2 I_2)(d - k) / (x_1 M_1 + x_2 M_2), \quad (1)$$

where  $x_i$  ( $i=1, 2$ ) is the mole fraction of component  $i$ ,  $M_i$  its molecular weight,  $I_i$  its Souders Viscosity Constants,<sup>4</sup>  $d$  the density of the mixture in  $\text{g/cc}$ , and  $k$  is a constant. The value of  $k$  depends only on the type of mixture and not on concentration or temperature, and so it can be determined by the knowledge of the viscosity of the mixture at one concentration and temperature and be used for other concentrations and temperatures. For the values determined by Trevoy and Drickamer,  $x_1 = x_2 = 0.5$ , and so

$$\log \log \eta = (I_1 + I_2)(d - k) / (M_1 + M_2). \quad (2)$$

TABLE I.<sup>a</sup> Observed and calculated viscosities of 50 mole percent liquid mixtures.

| Mixtures                                     | T°K   | k     | $\eta_{\text{calc}}$ | $\eta_{\text{obs}}^b$ | $\Delta\eta/\eta\%$ |
|--|-------|-------|----------------------|-----------------------|---------------------|
| Ph- $\pi$ C <sub>7</sub>                     | 298.0 | 2.928 | ...                  | 4.167                 | ...                 |
|  | 318.0 |       | 3.38                 | 3.407                 | -0.9                |
|  | 335.8 |       | 2.87                 | 2.850                 | +0.6                |
| Ph- $\pi$ C <sub>10</sub>                    | 298.0 | 2.935 | ...                  | 6.712                 | ...                 |
|  | 318.0 |       | 5.18                 | 5.262                 | -1.5                |
|  | 335.8 |       | 4.26                 | 4.272                 | -0.3                |
| Ph- $\pi$ C <sub>12</sub>                    | 298.0 | 2.921 | ...                  | 9.053                 | ...                 |
|  | 318.0 |       | 6.73                 | 6.904                 | -2.6                |
|  | 335.8 |       | 5.34                 | 5.494                 | -2.81               |
| Ph- $\pi$ C <sub>14</sub>                    | 298.0 | 2.920 | ...                  | 12.394                | ...                 |
|  | 318.0 |       | 9.15                 | 9.217                 | -0.7                |
|  | 335.8 |       | 7.00                 | 7.175                 | -2.4                |
| Ph- $\pi$ C <sub>16</sub>                    | 298.0 | 2.925 | ...                  | 16.502                | ...                 |
|  | 318.0 |       | 11.9                 | 11.919                | +0.1                |
|  | 335.0 |       | 8.79                 | 9.081                 | -3.2                |
|  | 298.0 |       | 16.5                 | 16.515                | -0.1                |
|  | 318.0 |       | 11.9                 | 11.928                | 0.0                 |
|  | 335.8 |       | 8.79                 | 9.100                 | -3.3                |
| Ph- $\pi$ C <sub>18</sub>                    | 298.0 | 2.916 | ...                  | 21.226                | ...                 |
|  | 318.0 |       | 15.3                 | 15.012                | +2.2                |
|  | 335.8 |       | 11.0                 | 11.284                | -2.1                |
| $\pi$ C <sub>7</sub> - $\pi$ C <sub>12</sub> | 298.0 | 2.888 | ...                  | 7.873                 | ...                 |
|  | 318.0 |       | 6.00                 | 6.058                 | -1.8                |
|  | 335.8 |       | 4.74                 | 4.859                 | -2.4                |
|  | 298.0 |       | 7.87                 | 7.868                 | +0.1                |
|  | 318.0 |       | 6.00                 | 6.054                 | -1.7                |
| $\pi$ C <sub>7</sub> - $\pi$ C <sub>14</sub> | 298.0 | 2.887 | ...                  | 10.314                | ...                 |
|  | 318.0 |       | 7.50                 | 7.754                 | -3.3                |
|  | 335.8 |       | 5.90                 | 6.149                 | -4.1                |
|  | 298.0 |       | ...                  | 13.766                | ...                 |
|  | 318.0 |       | 9.90                 | 10.046                | -1.5                |
| $\pi$ C <sub>7</sub> - $\pi$ C <sub>16</sub> | 298.0 | 2.885 | ...                  | 13.766                | ...                 |
|  | 318.0 |       | 9.90                 | 10.046                | -1.5                |
|  | 335.8 |       | 7.64                 | 7.765                 | -1.6                |
|  | 298.0 |       | ...                  | 17.300                | ...                 |
|  | 318.0 |       | 12.6                 | 12.412                | +1.2                |
| $\pi$ C <sub>7</sub> - $\pi$ C <sub>18</sub> | 298.0 | 2.879 | ...                  | 17.300                | ...                 |
|  | 318.0 |       | 12.6                 | 12.412                | +1.2                |
|  | 335.8 |       | 9.49                 | 9.416                 | +0.8                |
|  | 298.0 |       | ...                  | 7.489                 | ...                 |
|  | 318.0 |       | 5.71                 | 5.809                 | -1.6                |
| $i$ C <sub>7</sub> - $\pi$ C <sub>12</sub>   | 298.0 | 2.882 | ...                  | 7.489                 | ...                 |
|  | 318.0 |       | 5.71                 | 5.809                 | -1.6                |
|  | 335.8 |       | 4.58                 | 4.682                 | -2.2                |
|  | 298.0 |       | ...                  | 13.144                | ...                 |
|  | 318.0 |       | 9.30                 | 9.631                 | -3.5                |
| $i$ C <sub>7</sub> - $\pi$ C <sub>14</sub>   | 298.0 | 2.885 | ...                  | 13.144                | ...                 |
|  | 318.0 |       | 9.30                 | 9.631                 | -3.5                |
|  | 335.8 |       | 7.23                 | 7.510                 | -3.8                |
|  | 298.0 |       | ...                  | 3.825                 | ...                 |
|  | 318.0 |       | 3.17                 | 3.140                 | +1.0                |
| Ph- $i$ C <sub>7</sub>                       | 298.0 | 2.935 | ...                  | 3.825                 | ...                 |
|  | 318.0 |       | 3.17                 | 3.140                 | +1.0                |
|  | 335.8 |       | 2.72                 | 2.641                 | +3.0                |

<sup>a</sup> T = temperature °K; k = constant, Eq. (1);  $\eta_{\text{calc}}$  = calculated viscosity in millipoise;  $\eta_{\text{obs}}$  = observed viscosity in millipoise;  $\Delta\eta/\eta$  = deviation in percent.

<sup>b</sup> Taken from Trevoy and Drickamer (reference 1).

Equation (2) was applied to the data of Trevoy and Drickamer,<sup>1</sup> giving an average error of 1.8 percent and a maximum error of 4.1 percent. The values of the constant k were calculated with the data at 298.0°K for every mixture. Values of  $I_z$  were taken from Souders<sup>4</sup> work for every component of the mixtures. No results are shown for  $\eta$  at 298.0°K, since the deviation would be zero, obviously. The results are shown in Table I.

<sup>1</sup> D. G. Trevoy and H. G. Drickamer, J. Chem. Phys. 17, 582 (1949).

<sup>2</sup> M. Roegiers and K. Roegiers, *The Viscosity of Normal Fluids* (Société des Huiles de Cavel e Roegiers (Electron Oil Works) Conpure 197, Ghent, 1945).

<sup>3</sup> F. W. Lima, "On the viscosity of binary liquid mixtures," Thesis, University of Wisconsin, 1950; *Ann. Acad. Bras. Cienc.*, to be published.

<sup>4</sup> M. Souders, Jr., J. Am. Chem. Soc. 60, 154 (1938).

## Vibration-Rotation Spectrum and Structure of Monochlorosilane

ANDRÉ MONFILS

University of Liège, Liège, Belgium  
November 10, 1950

UP to the present, a great deal of work in infrared spectroscopy has been devoted to molecules having  $C_{3v}$  symmetry, with special emphasis on the  $CH_3X$  ( $X$  = halogen) compounds.<sup>1</sup>

In contrast to the many studies of organic compounds, silicon compounds of the same symmetry have received little attention; and, in particular, the  $SiH_3X$  molecules have not been investigated in spite of their considerable importance. The purpose of this note is to report briefly on some results which we have obtained for  $SiH_3Cl$ .

Infrared spectra of  $SiH_3Cl$  vapor were recorded with a Perkin-Elmer model 12C spectrometer in the region  $650\text{ cm}^{-1}$  to  $2200\text{ cm}^{-1}$  and with the prism-grating spectrometer described elsewhere by M. V. Migeotte.<sup>2</sup> The spectra were obtained at pressures ranging from 5 to 0.3 mm Hg, by means of gas cells having optical thicknesses of 17 and 10 cm. The following fundamental frequencies ( $\text{cm}^{-1}$ ) were found:

770 952 1090 2150 2195.

Only three of the bands have been observed at high dispersion (952, 2150, 2195) and for them the origins have been located with accuracy. For the remaining two the figures given correspond to the middle of the band.

If the molecule is assumed to have a  $C_{3v}$  symmetry, it follows that the six normal modes are divided into three totally symmetric and three doubly degenerate vibrations, giving rise respectively to parallel and perpendicular bands. The bands observed at 952 and  $2150\text{ cm}^{-1}$  are perpendicular, whereas the band at  $2195\text{ cm}^{-1}$  is parallel. The only possibility left for the bands at 770 and  $1090\text{ cm}^{-1}$ , taking into account their contours and magnitudes, is to identify them as respectively perpendicular and parallel. The following assignment of the bands to the normal modes is given (Dennison's notation):

$\nu_1 = 2195$                        $\nu_2 = 2150$   
 $\nu_3 = 1090$                        $\nu_4 = 952$   
 $\nu_5 \approx 460$                        $\nu_6 = 770$ .

The question as to what is the value of  $\nu_5$ , which has not been observed, is solved by analogy with the value measured in similar compounds.<sup>3</sup> For the  $\nu_5$  frequency, corresponding to the  $SiCl$  vibration, a value of  $460\text{ cm}^{-1}$  is proposed.

The structure of the bands at 2150 and  $952\text{ cm}^{-1}$  indicates the presence of a threefold symmetry axis, every third Q branch being enhanced. The infrared evidence is therefore in favor of a  $C_{3v}$  symmetry, in agreement with the microwave results.<sup>4</sup> The spacing between the zero branch lines is reduced to  $5.48\text{ cm}^{-1}$  for the  $2150\text{ cm}^{-1}$  band and to  $6.18\text{ cm}^{-1}$  for the other if one takes into account a slight convergence observed for the latter band. The variation in the spacings is due to a coupling between the rotation and the internal angular momentum of vibrational origin. One is struck by the appearance of a rather regular fine structure between the Q branches of the  $952\text{ cm}^{-1}$  band. This must be due to the lines of the P and R branches, which nearly exactly overlap one another. The average spacing between these lines in the best parts of the band is  $0.449\text{ cm}^{-1}$ . From this result we can therefore deduce  $I_A = 124.52 \times 10^{-40}\text{ g-cm}^2$ , where  $I_A$  is the moment of inertia about an axis perpendicular to the symmetry axis of the molecule. This result compares favorably with the microwave data,<sup>4</sup> which give  $I_A = 125.6815 \times 10^{-40}\text{ g-cm}^2$ . Since the perpendicular band at  $770\text{ cm}^{-1}$  has not yet been resolved, it is not possible to draw any precise conclusion about  $I_c$ , the other moment of inertia.

However, if we assume the spacing between the Q branches to be  $4.1\text{ cm}^{-1}$ , by analogy with what occurs in  $CH_3Cl$ ,<sup>5</sup> we can deduce  $I_c = 9.7 \times 10^{-40}\text{ g-cm}^2$  for  $SiH_3Cl$ , instead of  $9.33 \times 10^{-40}\text{ g-cm}^2$  obtained by Trindal, Straley, and Nielsen for  $SiH_4$ .<sup>6</sup> Future measurements on  $\nu_6$ , which are now planned, will allow us to determine  $I_c$  with much greater accuracy. A detailed account of this work will appear in the near future.

We are particularly indebted to Dr. Jules Duchesne, who suggested the problem, for his constant interest and many helpful discussions. Our thanks are also due to Professor L. D'Or for advice in connection with the preparation of  $SiH_3Cl$ , and to Dr. M. V. Migeotte for much help during the course of the spectroscopic experiments.