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### Infra-Red and Raman Spectra of Polyatomic Molecules. III. Ethane

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The Raman and infra-red spectra of ethane have been re-examined. The 993, 2900, and 2955  $\text{cm}^{-1}$  Raman lines are polarized; there were indications of very faint lines appearing at 620 and 820  $\text{cm}^{-1}$ . The strong infra-red peak at 1480  $\text{cm}^{-1}$  is found to be a *single* minimum; the weak band at 1740  $\text{cm}^{-1}$  is confirmed.

The available Raman and infra-red data are evaluated, and possible assignments discussed. It is shown that the observed frequencies do not require a 740  $\text{cm}^{-1}$  fundamental, but are consistent with an "uncertain frequency" of about 1100  $\text{cm}^{-1}$  and a high restricting potential.

RECENT work<sup>1</sup> on the problem of internal rotation in ethane has focussed considerable interest on the vibrational frequencies of this molecule. Although the magnitudes of most of the fundamental frequencies are known sufficiently well for thermodynamic calculations, two widely different values have been proposed for the so-called "uncertain frequency." Heat capacity data,<sup>2</sup> including that at low temperatures, seem unequivocally to indicate a value of about 1100  $\text{cm}^{-1}$  for this frequency; on the other hand, Bartholomé and Karweil<sup>3</sup> have studied the overtone region carefully and find spectral evidence for a value of 740  $\text{cm}^{-1}$ . In connection with this question, we have considered it worth while to re-examine the Raman and infra-red spectra of ethane, and have also considered possible assignments for the observed frequencies.

#### EXPERIMENTAL

The ethane used was especially prepared from pure hydrogen and ethylene. Both materials were obtained from the Ohio Chemical Co.; the hydrogen was rated 99.9 percent, and the ethylene 99.5 percent. Catalytic combination took place on reduced copper oxide at temperatures not exceeding 120°C. The Raman spectrum showed no traces of the strong lines of the probable impurities.

\* National Research Fellow in Chemistry.

<sup>1</sup> G. B. Kistiakowsky and E. B. Wilson, Jr., *J. Am. Chem. Soc.* **60**, 494 (1938); K. S. Pitzer and J. D. Kemp, *ibid.* **60**, 1515 (1938); and references given therein.

<sup>2</sup> W. Hunsmann, *Zeits. f. physik. Chemie* **B39**, 23 (1938); G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, *J. Chem. Phys.* **6**, 407 (1938); E. B. Wilson, Jr., *ibid.* **6**, 408 (1938).

<sup>3</sup> E. Bartholomé and J. Karweil, *Zeits. f. physik. Chemie* **B39**, 1 (1938).

The Raman spectrograph has been previously described;<sup>4</sup> during exposures, the Raman tube containing the liquid ethane was kept at a temperature of about  $-60^{\circ}\text{C}$  by a stream of cold air. Polarization measurements<sup>5</sup> on the four principal lines showed the 993, 2900, and 2955  $\text{cm}^{-1}$  lines to be polarized, and the 1460  $\text{cm}^{-1}$  line, depolarized. Microphotometer records of comparable plates made with polarized and unpolarized light are given in Fig. 1. It will be noted that the 2900  $\text{cm}^{-1}$  line appears to be slightly more polarized than the 2955  $\text{cm}^{-1}$  line.

The Raman spectrum of ethane has been examined several times with instruments of higher dispersion;<sup>6</sup> it does not seem worth while to report our frequencies for the lines previously found, which checked within experimental error.

On several plates, indications were found of two faint lines, difficult to measure, displaced from the Hg 4358A line by about 620 and 820  $\text{cm}^{-1}$ . Professor George Glockler has informed us that these lines had appeared on his plates also,<sup>7</sup> and were measured at 617 and 813  $\text{cm}^{-1}$ . These lines are extremely faint, and moreover the corresponding shifts excited by Hg 4047A were not observed; nevertheless, the appearance of these lines in two independent investigations seems to provide some evidence for their reality.

<sup>4</sup> H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 247 (1938).

<sup>5</sup> J. T. Edsall and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 124 (1938).

<sup>6</sup> P. Daure, *Ann. de physique* **12**, 375 (1929); S. Bhagavantam, *Ind. J. Phys.* **6**, 596 (1931); C. M. Lewis and W. V. Houston, *Phys. Rev.* **44**, 903 (1933); G. Glockler and M. M. Renfrew, *J. Chem. Phys.* **6**, 295 (1938).

<sup>7</sup> We are indebted to Professor Glockler for sending us these data; he had not reported them because on his plates, as on ours, these shifts excited by the Hg 4047A line did not appear.

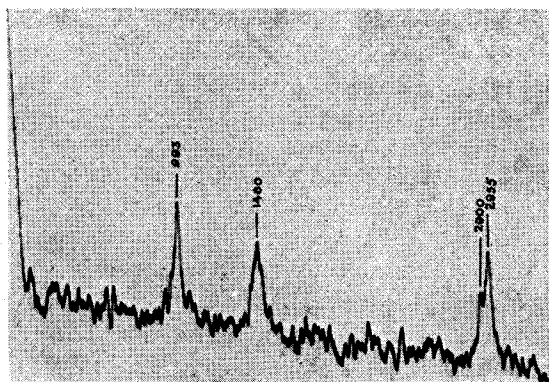


FIG. 1 (a). Microphotometer records of plates made with polarized light, showing the shifts at 993 (*P*), 1460 (*D*), 2900 (*P*), and 2955 (*P*)  $\text{cm}^{-1}$ . To conform with Table I the lines are labeled with the corresponding gas-phase frequencies instead of the actual liquid-phase frequencies.

The infra-red absorption of gaseous ethane was studied with the spectrometer previously described;<sup>8</sup> a fluorite prism was used for the region from 3 to  $9\mu$ , and a rocksalt prism from 9 to  $15\mu$ . Transmission curves of the absorption regions beyond  $5\mu$  are given in Fig. 2.

The infra-red spectrum has been studied by several investigators.<sup>9</sup> The band at  $827\text{ cm}^{-1}$  is well established. The  $1740\text{ cm}^{-1}$  band was reported by Benedict, Morikawa, Barnes and Taylor as lying at  $1770\text{ cm}^{-1}$ ; we believe our value of the frequency to be more reliable than theirs, since they used a rocksalt prism, which gives lower resolution.

Our results for the  $7\mu$  region are of particular interest. This region was examined under high resolution by Levin and Meyer; their measurements show a peak at  $1379\text{ cm}^{-1}$ , a region of weak absorption between  $1390$  and  $1430\text{ cm}^{-1}$ , and a strong band with center about  $1480\text{ cm}^{-1}$  which shows regular rotational spacing from  $1442$  to  $1515\text{ cm}^{-1}$ , and gives every appearance of a single band of the perpendicular type. Bartholomé and Sachsse, using a fluorite prism, found a single weak minimum at  $1365\text{ cm}^{-1}$ , and found the strong peak to be double, with minima at

<sup>8</sup> H. Gershonowitz and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 197 (1938).

<sup>9</sup> A. Levin and C. F. Meyer, *J. Opt. Soc. Am.* **16**, 137 (1928); E. Bartholomé and H. Sachsse, *Zeits. f. physik. Chemie* **B30**, 40 (1935); W. S. Benedict, K. Morikawa, R. B. Barnes, and H. S. Taylor, *J. Chem. Phys.* **5**, 1 (1937); E. Bartholomé and J. Karweil, *Zeits. f. physik. Chemie* **B39**, 1 (1938).

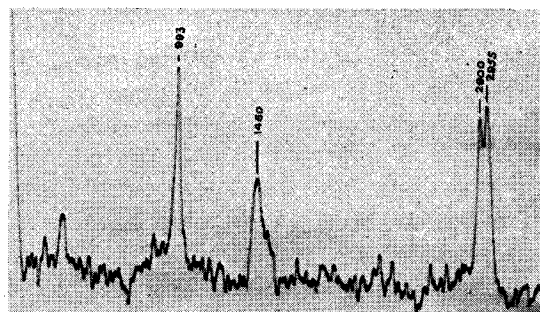


FIG. 1 (b). Microphotometer records of plates made with unpolarized light, showing the shifts at 993 (*P*), 1460 (*D*), 2900 (*P*), and 2955 (*P*)  $\text{cm}^{-1}$ . To conform with Table I the lines are labeled with the corresponding gas-phase frequencies instead of the actual liquid-phase frequencies.

$1465$  and  $1495\text{ cm}^{-1}$ . Our curve (Fig. 2) shows a *single* strong minimum at  $1477\text{ cm}^{-1}$ , and two weaker minima at  $1380$  and  $1414\text{ cm}^{-1}$ . The resolution of our spectrometer in this region is more than adequate; in studies of cyclopropane, two minima at  $1425$  and  $1445\text{ cm}^{-1}$  are clearly resolved. It is difficult to explain the double minimum found by Bartholomé and Sachsse; it is possible that they did not properly correct for the strong atmospheric water bands which overlie this region. Considering our own data and those of Levin and Meyer, we believe that the evidence is strongly in favor of a single strong band at  $1480\text{ cm}^{-1}$ , with weaker bands at  $1380$  and  $1415\text{ cm}^{-1}$ , as shown in our curve.

Our results above  $2000\text{ cm}^{-1}$  are consistent with the grating measurements of Bartholomé and Karweil in this region, except for one very large discrepancy. Their curves show a band at  $2303\text{ cm}^{-1}$ , while we find this band at  $2353\text{ cm}^{-1}$ , as shown in Fig. 2. While our resolution was con-

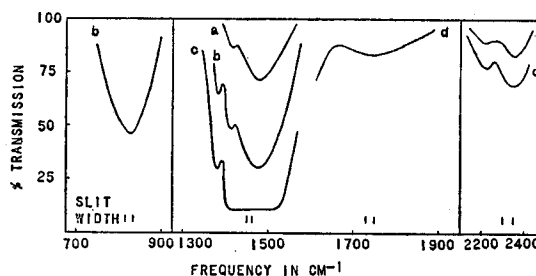


FIG. 2. Infra-red transmission of ethane gas. Path length, 30 cm; pressures, (a) 60 mm, (b) 125 mm, (c) 355 mm, (d) 760 mm.

siderably less than that of Bartholomé and Karweil, this difference of  $50\text{ cm}^{-1}$  lies far outside the experimental error.

### DISCUSSION

After a study of the various investigations referred to above, we have arrived at the observed frequencies given in Table I as being the most complete and reliable list available at present. The Raman frequencies are principally the gas-phase values of Lewis and Houston; we have rejected the weak  $1344\text{ cm}^{-1}$  line, which is almost certainly due to ethylene present as an impurity, and have added the  $620$  and  $820\text{ cm}^{-1}$  lines discussed above, the  $1463$  and  $2963\text{ cm}^{-1}$  shifts observed in the liquid by Glockler and Renfrew, and the  $975\text{ cm}^{-1}$  shift found by Bhagavantam. Of the infra-red frequencies, those lying below

$2000\text{ cm}^{-1}$  have been discussed above. The higher frequencies are taken from Bartholomé and Karweil; we have preferred to regard their peak at  $2230\text{ cm}^{-1}$  as a single perpendicular band rather than as two bands  $15\text{ cm}^{-1}$  apart. With regard to the discrepancy mentioned above, we have included their value of  $2303\text{ cm}^{-1}$  as well as our own value,  $2350\text{ cm}^{-1}$ .

Glockler and Renfrew<sup>10</sup> have recently suggested that the  $813$  and  $1463\text{ cm}^{-1}$  Raman lines found in liquid ethane may be the infra-red fundamentals at  $827$  and  $1480\text{ cm}^{-1}$ , appearing in the Raman effect through a breakdown of the selection rules due to intermolecular forces active in the liquid. These frequencies would actually be permitted in the Raman effect if the selection

<sup>10</sup> G. Glockler and M. M. Renfrew, J. Chem. Phys. **6**, 409 (1938).

TABLE I. Observed frequencies of ethane, with a possible assignment.\*

| FREQ. $\text{cm}^{-1}$ | INT'Y.;<br>TYPE | ASS.   | CALC.<br>FREQ.  | SYMMETRY          |                      |
|------------------------|-----------------|--|---|-------------------|----------------------|
|                        |                 |  |   | $D_{3h}$          | $D_{3d}$             |
| <i>Infra-Red:</i>      |                 |  |   |                   |                      |
| 827                    | $\perp$ s       | Fund.  | (827)   | $E'$              | $E_u$                |
| 1380                   | $\parallel$ w   | Fund.  | (1380)  | $A_2''$           | $A_{2u}$             |
| 1414                   | $\perp$ w       | $1120+300$   | 1420  | $E'$              | $E_u$                |
| 1480                   | $\perp$ s       | Fund.  | (1480)  | $E'$              | $E_u$                |
| 1740                   | ? w             | $1460+300$   | 1760  | $E'$              | $E_u$                |
| 2230                   | ? $\perp$ w     | $\left\{ \begin{array}{l} 1120^2 \\ 1375+827 \end{array} \right.$            | 2240  | $A_1'+A_2'+E'$    | —                    |
|                        |                 | $827+1480$   | 2202  | —                 | $E_u$                |
| 2303                   | ? $\parallel$ w | $827+1460$   | 2307  | $A_1'+A_2'+E'$    | —                    |
| 2350                   | ? $\parallel$ w | 993+1380   | 2287  | —                 | $A_{1u}+A_{2u}+E_u$  |
| 2660                   | $\perp$ w       | 2970-300   | 2373  | $A_2''$           | $A_{2u}$             |
| 2755                   | $\parallel$ m   | 1380+1375  | 2670  | $E''$             | $E_u$                |
| 2895                   | $\parallel$ m   | Fund.  | 2755  | $A_2''$           | $A_{2u}$             |
| 2955                   | s               | $\left\{ \begin{array}{l} 1480+1460 \\ 993+827+1120 \end{array} \right.$     | 2926  | $A_2''$           | $A_{2u}$             |
| 3007                   | $\parallel$ m   |  | 2940  | $A_1''+A_2''+E''$ | $A_{1u}+A_{2u}+E_u$  |
| 2950-3000              | $\perp$ w       | Fund.  | 2940  | $A_1''+A_2''+E''$ | $A_{1u}+A_{2u}+E_u$  |
| 3100-3150              | $\perp$ w       | $827^2+1480$   | 2980  | $E'$              | $E_u$                |
| 3186                   | $\parallel$ w   | $\left\{ \begin{array}{l} 1460^2+300 \\ 1120+1480+300^2 \end{array} \right.$ | 3134  | $A_1'+A_2'+2E'$   | $A_{1u}+A_{2u}+2E_u$ |
| 3223                   | $\parallel$ w   |  | 3220  | $A_1''+A_2''+E''$ | $A_{1u}+A_{2u}+E_u$  |
|                        |                 |  | 3200  | $A_1''+A_2''+E''$ | $A_{1u}+A_{2u}+E_u$  |
| <i>Raman:</i>          |                 |  |   |                   |                      |
| (620)?                 | v. w.           | $300^2$  | 600   | $A_1'$            | $A_{1g}$             |
| (813)                  | v. w.           | Fund.  | (827)   | $E'$              | $E_u$                |
| 975                    | w               | $C^{12}-C^{13}$ Fund.  | —   | $A_1'$            | $A_{1g}$             |
| 993                    | s, P            | Fund.  | (993)   | $A_1'$            | $A_{1g}$             |
| (1463)                 | m, D            | Fund.  | $\left\{ \begin{array}{l} (1460) \\ 1480 \end{array} \right.$ | $E''$             | $E_g$                |
| 2744                   | w               | $\left\{ \begin{array}{l} 1375^2 \\ 1380^2 \end{array} \right.$              | 1480  | $E'$              | $E_u$                |
| 2778                   | w               |  | 2750  | $A_1'$            | $A_{1g}$             |
| 2900                   | s, P            | $\left\{ \begin{array}{l} 1380^2 \\ \text{Fund.} \end{array} \right.$        | 2760  | $A_1'$            | $A_{1g}$             |
| 2955                   | s, P            | $\left\{ \begin{array}{l} 1460^2 \\ 1480+1460 \end{array} \right.$           | 2927  | $A_1'$            | $A_{1g}$             |
|                        |                 |  | 2920  | $A_1'$            | $A_{1g}$             |
| 2940                   | w               | $\left\{ \begin{array}{l} 1480+1460 \\ 1480^2 \end{array} \right.$           | 2940  | $A_1''+A_2''+E''$ | —                    |
| (2963)                 | w               | Fund.  | 2960  | —                 | $A_{1g}+A_{2g}+E_g$  |
|                        |                 |  | 2970  | $E''$             | $E_g$                |

\* Liquid-phase frequencies in parentheses: s=strong, m=medium, w=weak, v.w.=very weak, P=polarized, D=depolarized.

† Breakdown of  $D_{3d}$  selection rules.

rules appropriate to the  $D_{3h}$  configuration apply to ethane.<sup>11</sup>

If the  $620\text{ cm}^{-1}$  line is real, there is the interesting possibility that it is the first overtone of the internal torsional motion associated with a high potential barrier. The selection rules permit the appearance of this overtone in the Raman effect. Professor E. B. Wilson, Jr., has calculated certain levels of this motion;<sup>12</sup> for a restricting potential of  $3000\text{ cal./mole}$  magnitude and the usually assumed cosine shape, the two lowest excited levels lie at about  $300$  and  $565\text{ cm}^{-1}$ . While this value for the overtone is too low to fit the  $620\text{ cm}^{-1}$  Raman line, it is quite possible that the actual potential barrier has a different shape which would give a somewhat higher second excited level when adjusted to fit the thermodynamic data, an idea which is confirmed by a study of a square potential barrier. Another possible assignment for the  $620\text{ cm}^{-1}$  line would be the difference tone  $1463-813$  (liquid-phase frequencies); this calculated value lies  $30\text{ cm}^{-1}$  too high.

Since a study of the infra-red and Raman spectra of heavy ethane,  $\text{C}_2\text{D}_6$ , is now in progress in this laboratory, it seems best to postpone any final vibrational analysis until data for the two isotopic molecules may be considered together. However, it may be well to point out that the overtone region, studied by Bartholomé and Karweil, does not afford conclusive evidence on the magnitude of the "uncertain frequency." These authors account for their observed frequencies with the use of a  $740\text{ cm}^{-1}$  fundamental and the selection rules appropriate to the  $D_{3h}$  configuration. The double minimum,  $1465$  and  $1495\text{ cm}^{-1}$ , reported by Bartholomé and Sachsse, would suggest a  $740\text{ cm}^{-1}$  fundamental; as discussed above, however, the evidence seems to be in favor of a *single* peak at  $1480\text{ cm}^{-1}$ . When we accept this single peak, it is possible to account for the observed frequencies without the use of a  $740\text{ cm}^{-1}$  frequency. To illustrate this, we give in

TABLE II. A possible set of fundamental frequencies for ethane.

| (SYMMETRY SYMBOLS ARE GIVEN FOR POINT GROUPS $D_{3h}$ , <sup>11</sup> $D_{3d}$ , AND $D_{3d}$ , IN THAT ORDER.) |        |                      |        |
|---|--------|----------------------|--------|
| $A_1, A_1', A_{1g};$  | 993    | $E, E', E_u;$        | 827    |
|   | (1375) |                      | 1480   |
|   | 2927   |                      | 2980   |
| $\bar{A}_2, A_2'', A_{2u};$   | 1380   | $\bar{E}, E'', E_g;$ | (1120) |
|   | 2926   |                      | 1460   |
| $\bar{A}_1, A_1'', A_{1u};$   | (300)  |                      | 2970   |

Table I possible assignments of the observed frequencies, using the fundamentals listed in Table II. These fundamentals are consistent with the existence of a  $3000\text{ cal./mole}$  restricting potential, an "uncertain frequency" of about  $1100\text{ cm}^{-1}$ , and an internal torsional oscillation of about  $300\text{ cm}^{-1}$ . We have given assignments satisfying the selection rules for both the  $D_{3h}$  and the  $D_{3d}$  equilibrium configurations; the  $D_{3h}$  assignment is slightly more satisfactory in the three cases where different assignments are required. It is to be emphasized that this assignment is not to be regarded as a final one, but is given merely to show that the observed overtones do not require a  $740\text{ cm}^{-1}$  fundamental.

In concluding, we should like to express our gratitude to Professor E. B. Wilson, Jr., who suggested this project and has constantly contributed to its progress.\*

\* *Note added in proof:* Since this paper was submitted, two papers of the same series as that of Bartholomé and Karweil<sup>3</sup> have been received, one by Goubeau and Karweil (Zeits. f. physik. Chemie **B40**, 376 (1938)) on the Raman effect, and one by Karweil and Schäfer (ibid., **B40**, 382) on the assignment.

The Raman work of Goubeau and Karweil shows four shifts differing significantly from previous work— $786$ ,  $1335$ ,  $1491$ , and  $2791\text{ cm}^{-1}$ . The values  $786$  and  $2791\text{ cm}^{-1}$  deviate from the measurements of Glockler and Renfrew further than one would expect. The evidence that the  $1335\text{ cm}^{-1}$  line arises from ethane seems insufficient. The  $1491\text{ cm}^{-1}$  line may well be the second degenerate fundamental of this magnitude (see Table I).

The analysis now given by Karweil and Schäfer, which differs from the former analysis of Bartholomé and Karweil, is based on essentially the same set of fundamentals as ours. However, we feel that the available evidence is insufficient to exclude the  $D_{3d}$  equilibrium configuration, contrary to the conclusion of Karweil and Schäfer.

<sup>11</sup> J. B. Howard, J. Chem. Phys. **5**, 442 (1937).

<sup>12</sup> E. B. Wilson, Jr., J. Chem. Phys. **6**, 408 (1938).