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## The Infra-Red Absorption Spectrum of Methylamine Vapor

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The infra-red absorption of methylamine vapor has been measured from 2 to  $18\mu$  with a cell of 18 cm length using pressures from 2 to 55 cm. A total of nineteen bands has been observed, nine of which are assigned to fundamental vibrations. The bending vibrations of the two groups give rise to several bands in the region from 6 to  $8\mu$ . This causes considerable overlapping which makes it difficult to locate band centers and to determine band types in this region. Three bands which originate from the C-H vibrations occur at wave-lengths between 3.0 and  $3.6\mu$ . A band due to the N-H parallel valence vibration has been found at  $2.98\mu$ . The most intense band in the spectrum

occurs at  $12.9\mu$ , and arises from a bending vibration of the hydrogen atoms in the amino group. The parallel vibration between the methyl and amino groups gives rise to an intense band at  $9.56\mu$ . This is a parallel band having a sharp and intense zero branch. A band also due to a bending vibration in the amino group was observed at  $16\mu$ , and from the experimental curve it can not be said whether it is parallel or perpendicular; hence definite assignment is not made. The other bands which have been observed have been assigned to overtones and combinations.

### INTRODUCTION

PREVIOUS studies on methylamine have been confined largely to the region less than  $2\mu$ . Kohlrausch<sup>1</sup> has studied the Raman spectrum of aqueous methylamine, and the liquid has been studied by other workers. The assignments for the valence vibrations were  $\nu_{C-H}=3000\text{ cm}^{-1}$ ,  $\nu_{N-H}=3350\text{ cm}^{-1}$ , and  $\nu_{C-N}=1040\text{ cm}^{-1}$ . M. Freymann<sup>2</sup> has studied the region from  $0.8\mu$  to  $1.2\mu$  and found two absorption bands at about 1.042, and  $1.001\mu$ . The more intense band at  $1.042\mu$  was attributed to  $3\nu_{NH}$ . It was thought that a study of the infra-red spectrum to  $20\mu$  would make it possible to discover a large number of the fundamentals, and thus relate the infra-red absorption spectrum to the modes of vibration of the molecule. The spectrum should not vary greatly from that of methyl alcohol, which has been recently studied by Borden and Barker,<sup>3</sup> except for the bands due to absorption by the amino group.

\* This paper is based upon results forming part of the dissertation submitted by A. P. Cleaves to Duke University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. An abstract has been published by the authors in the Bulletin of the American Physical Society (No. 14), April (1939).

<sup>1</sup> K. W. F. Kohlrausch, Monatshefte für Chemie (Wien) **68**, 349 (1936).

<sup>2</sup> M. Freymann, Comptes rendus **202**, 1674 (1936).

<sup>3</sup> A. Borden and E. F. Barker, J. Chem. Phys. **6**, 553 (1938).

### EXPERIMENTAL METHOD

A study has been made of the infra-red absorption of methylamine vapor in the region from  $2-18\mu$  by means of a prism instrument with prisms of fluorite and sylvine; and the regions of more intense absorption have been studied in detail by employing a grating spectrometer of good resolution. The fore prism of the grating spectrometer was of rocksalt. In the region beyond  $16\mu$  the intensity was so low that the grating instrument could not be used. For the region between  $2\mu$  and  $5.5\mu$  a 4812-lines-per-inch grating, having a ruled surface of five inches, was available, while the grating for the region from  $5.5\mu$  to  $13\mu$  was of the same size and had 2060 lines per inch. The effective slit width varied from  $6\text{ cm}^{-1}$  in the  $2\mu$  region to  $1.4\text{ cm}^{-1}$  in the  $13\mu$  region. A Nernst glower was used as the source of radiation, and a thermocouple in conjunction with a Moll thermorelay was used as a detector. The general features of the grating spectrometer were like those of the instrument of Meyer<sup>4</sup> and will not be described. A glass cell of 18 cm length with rocksalt windows was used to contain the gas. Various pressures from 2 to 60 cm were employed in studying the bands in the different regions.

The methylamine vapor was obtained from Kahlbaum, in the form of an anhydrous liquid.

<sup>4</sup> W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).

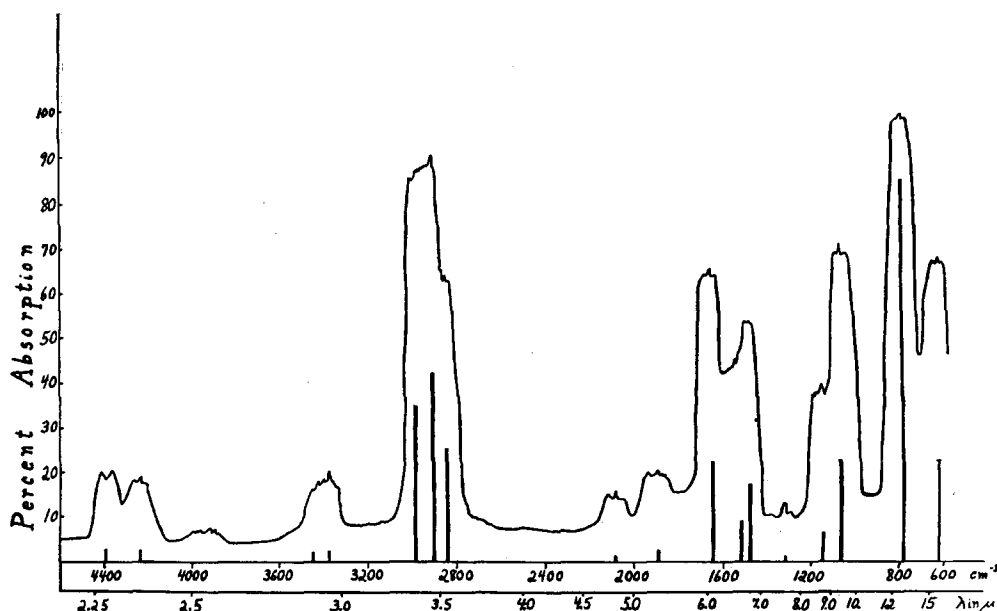


FIG. 1. Infra-red absorption by methylamine vapor from  $2.2\mu$  to  $18\mu$  at pressures from 2 to 55 cm in an 18-cm cell. The vertical lines indicate the relative intensities of the bands.

It was then triply distilled and silica gel was used as a drying agent. After each condensation any remaining volatile material was pumped away. The most likely impurity would be ammonia, but as no band was observed at  $950\text{ cm}^{-1}$ , which is a strong  $\text{NH}_3$  absorption region, it was concluded that this impurity was not present in appreciable amounts.

## RESULTS

The region of general absorption by methylamine vapor from  $2.2$  to  $18\mu$  are shown in Fig. 1. The region from  $1.8$  to  $2.2\mu$  was also surveyed and several weak bands were observed. Since these bands arise from harmonics or combinations and fall in a region where a grating of good resolution was not available, these bands were not studied in detail. The vertical lines under these bands represent the absorption reduced to a pressure of 3 cm in the cell. In the actual drawing the absorption in the weaker bands has been exaggerated. The band at  $12.9\mu$  is the most intense one in the entire spectrum. In Fig. 1 is shown a total of 19 bands. The two very weak bands at about  $4000\text{ cm}^{-1}$  are due to combinations, and the stronger bands at about  $4200$  and  $4400\text{ cm}^{-1}$  are also due to combinations. The details as to the assignment of the modes of

vibration will appear in the discussion. Also the structure of these bands obtained by a detailed study is shown in Figs. 2–8. In Table I is given the frequency, wave-length, effective slit width, pressure of gas, and the assigned mode of vibration of each band.

TABLE I. The positions of the observed bands, pressures, effective slit widths, and assignments of vibrations.

| WAVE NUMBERS | MICRONS $\mu$ | PRESSURE CM HG | EFFECTIVE SLIT CM <sup>-1</sup> | ASSIGNMENT*   |
|--------------|---------------|----------------|---------------------------------|---|
| 4385         | 2.278         | 40             | 6                               | $\{\nu_{\text{CH}} \perp + \delta_{\text{CH}} \parallel\}$                      |
| 4226         | 2.370         | 40             | 6                               | $\{3\delta_{\text{CH}} \perp^{(2)}\}$   |
| 3470R        |               |                |                                 | $\{\nu_{\text{CH}} \parallel + \delta_{\text{CH}} \parallel\}$                  |
| 3425         | 3.080         | 55             | 5                               | $\{\nu_{\text{CH}} \parallel + \delta_{\text{CH}} \perp^{(2)}\}$                |
| 3360         | 2.976         | 55             | 5                               | $\nu_{\text{NH}} \perp$   |
| 2968         | 3.370         | 3              | 5                               | Probably combinations   |
| 2895         | 3.45          | 3              | 5                               | $\nu_{\text{CH}} \perp$   |
| 2819         | 3.55          | 3              | 5                               | $2\delta_{\text{CH}} \perp^{(2)}$   |
| 2072         | 4.83          | 50             | 4                               | $\nu_{\text{CH}} \parallel$   |
| 1814         | 5.52          | 40             | 4                               | $2\nu_{\text{CN}} \parallel$  |
| 1625         | 6.15          | 4              | 3.5                             | $\delta_{\text{NH}} \parallel^{(1)} + \nu_{\text{CN}} \parallel$                |
| 1516         | 6.60          | 10             | 3                               | $\delta_{\text{NH}} \perp^{(2)}$  |
| 1460         | 6.85          | 7              | 3                               | $2\delta_{\text{NH}} \parallel^{(1)}$   |
| 1426         | 7.02          | 7              | 3                               | $\delta_{\text{CH}} \perp^{(2)}$  |
| (1312)?      | 7.62          | 45             | 3                               | $\delta_{\text{CH}} \parallel$  |
| 1127         | 8.88          | 20             | 2.5                             | $\delta_{\text{CH}} \perp^{(1)}$  |
| 1045         | 9.56          | 4              | 2.0                             | $\delta_{\text{NH}} \parallel^{(2)}?$   |
| 783          | 12.92         | 2              | 1.4                             | $\nu_{\text{CN}} \parallel$   |
| 630          | 16            | 20             | 8                               | $\delta_{\text{NH}} \parallel^{(1)}$  |
|              |               |                |                                 | $\delta_{\text{NH}} \perp^{(1)} \text{ or } \delta_{\text{NH}} \parallel^{(2)}$ |

\* Different vibrations of the same type are denoted by superscripts on the right side.

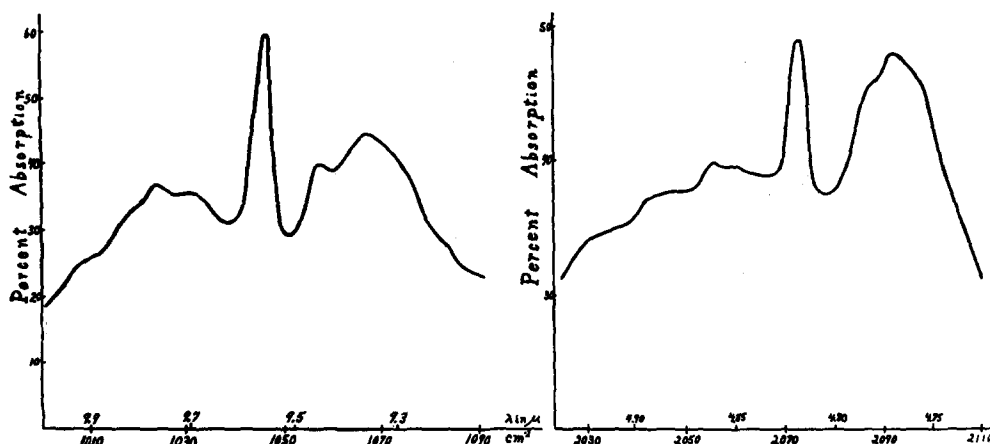


FIG. 2. The  $\nu_{\text{CN}}$  vibration at  $1045 \text{ cm}^{-1}$  and its first harmonic  $2\nu_{\text{CN}}$  at  $2072 \text{ cm}^{-1}$ .

### DISCUSSION OF RESULTS

The form of the methylamine molecule is known from stereochemical data, from electron diffraction<sup>5</sup> measurements, from Raman<sup>1</sup> and photographic infra-red<sup>6,7</sup> spectra of gaseous and liquid methylamine and of its solutions and from corresponding data on similar molecules. From all these data there is evidence that the methyl group angles are approximately tetrahedral, that the C-H distances are of the same magnitude as in methane ( $1.1 \times 10^{-8} \text{ cm}$ ), that the C-N-H angles are about  $108^\circ$  and that  $r_{\text{CN}} = 1.47 \text{ \AA}$  and  $r_{\text{NH}} = 1.02 \text{ \AA}$ . The molecule is in reality an asymmetrical top, but the asymmetry is only slight as in methyl alcohol<sup>3</sup> so that it can (approximately) be treated as a symmetric top with a symmetry axis lying along the C-N bond. The only symmetry element which is preserved when considering the molecule as an asymmetric top, is a plane through the figure axis (C-N) and through one of the H atoms. The moment of inertia about the figure axis is approximately  $C = 8 \times 10^{-40} \text{ g cm}^2$ , and the average value of the two larger moments of inertia  $A$  and  $B$ , which are very similar, is about  $38 \times 10^{-40}$ .<sup>6</sup>

The methylamine molecule possesses 15 fundamental vibrations. Since it is an asymmetric top all of these vibrations are allowed and so should occur in the infra-red, but some vibrations, such as perpendicular ones in  $\text{CH}_3$ , may retain their

degeneracy, so that less than 15 frequencies may be observed. Of the nineteen bands found in the near infra-red in the present research eleven have been assigned to the fundamental modes of motion, two of these tentatively. The difference in these numbers arises from the fact that three of the assigned frequencies are likely to be doubly degenerate, and the 15th fundamental frequency has been observed only in the Raman spectrum.<sup>8</sup> The remaining eight bands have been assigned to overtones and combinations.

### THE C-N VIBRATION

One of the strongest bands in the spectrum appears at  $9.57 \mu$  corresponding to a frequency of  $1045 \text{ cm}^{-1}$ . It has the shape of a parallel band (see Fig. 2), and corresponds to the parallel vibration between the methyl and amino groups. It has very nearly the same frequency as that found for the  $\text{CH}_3\text{-OH}$  vibration in  $\text{CH}_3\text{OH}$  at  $1034 \text{ cm}^{-1}$  and corresponds closely to  $1048 \text{ cm}^{-1}$  for  $\text{CH}_3\text{-F}$ . This is due to similarity of the masses of fluorine and the amino group. The band at  $1045 \text{ cm}^{-1}$  has very recently been simultaneously reported by Owens and Barker,<sup>9</sup> who, with an instrument with greater resolving power in this region than that used in this work, were able to obtain the fine structure of this band.

The  $1045 \text{ cm}^{-1}$  band has its first harmonic at  $4.83 \mu$  or  $2072 \text{ cm}^{-1}$  giving an anharmonicity of

<sup>5</sup> L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).

<sup>6</sup> H. W. Thompson and H. A. Skinner, J. Chem. Phys. **6**, 775 (1938).

<sup>7</sup> M. & R. Freymann, J. de phys. et rad. **4**, 476 (1936).

<sup>8</sup> J. S. Kirby-Smith and L. G. Bonner, Bull. Phys. Soc. April (1939).

<sup>9</sup> R. G. Owens and E. F. Barker, Bull. Am. Phys. Soc. **14**, April (1939).

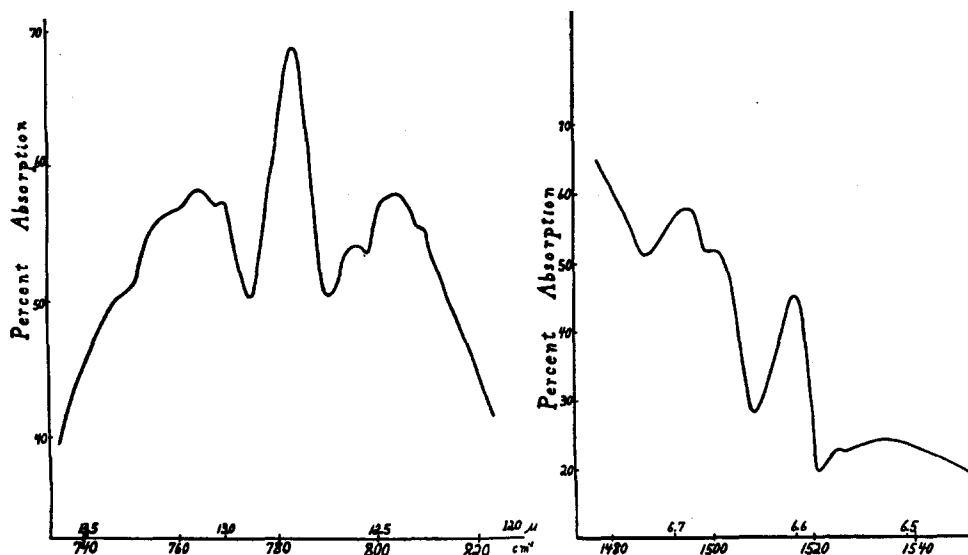


FIG. 3. The  $\delta_{\text{NH}}||^{(1)}$  vibration at  $783 \text{ cm}^{-1}$  and its first harmonic  $2\delta_{\text{NH}}||^{(1)}$  at  $1516 \text{ cm}^{-1}$ .

$9 \text{ cm}^{-1}$ . This small value is reasonable for this type of vibration. The harmonic is shown in Fig. 2 and resembles very much the overtone at  $2054 \text{ cm}^{-1}$  of the  $1034$  band in methyl alcohol.

#### THE AMINO VIBRATIONS

The band at  $12.92\mu$  corresponding to a frequency of  $783 \text{ cm}^{-1}$  is the most intense in the entire spectrum. The low frequency suggests a bending vibration. Since it is of the parallel type, the change of the electric moment must lie in the direction of the C—N axis. A vibration which has this characteristic and which should have a low frequency, is one in which the H atoms in the

$\text{NH}_2$  group move perpendicular to the N—H bonds and almost parallel to the figure axis of the molecule on account of the C—N—H angle. The hydrogens in this vibration move jointly in a group. Although the corresponding band has not been found in the infra-red spectrum of  $\text{CH}_3\text{OH}$ , we would like to make this assignment.

The harmonic of the  $783 \text{ cm}^{-1}$  band is the parallel band located at  $1516 \text{ cm}^{-1}$  having an anharmonicity of  $25 \text{ cm}^{-1}$  which is a reasonable value. The band is reproduced also in Fig. 3. The strong absorption in the *P* branch region is caused by overlapping absorption of the  $1450 \text{ cm}^{-1}$  region.

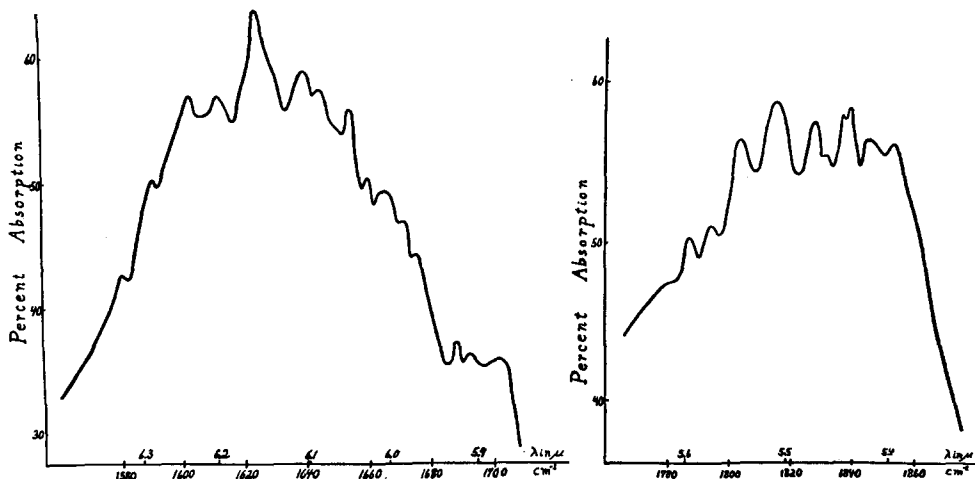


FIG. 4. The  $\delta_{\text{NH}}\perp^{(2)}$  vibration at  $1625 \text{ cm}^{-1}$  and the combination band  $\delta_{\text{NH}}||^{(1)} + \nu_{\text{CN}}||$  at  $1814 \text{ cm}^{-1}$ .

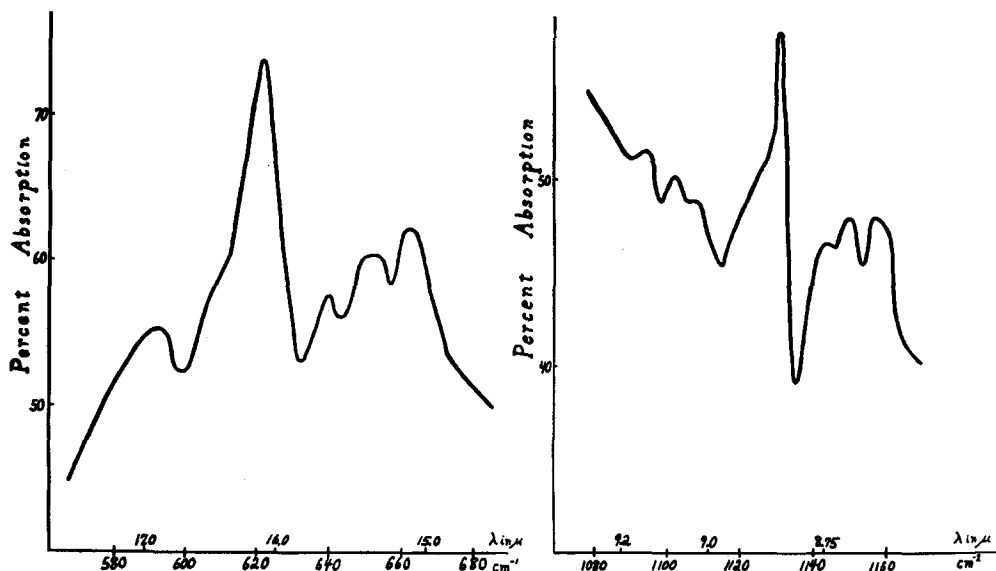


FIG. 5. The absorption in the  $620\text{ cm}^{-1}$  region and the  $1127\text{ cm}^{-1}$  band.

There is a probability that the combination frequency of  $783\text{ cm}^{-1}$  and  $1045$  which should occur rather strongly can be correlated with the band at  $5.52\mu$  or  $1814\text{ cm}^{-1}$ .

Another bending vibration should arise from a motion of the two H atoms moving towards each other perpendicular to the N—H bonds as in the  $\delta_{\parallel}$  ( $1595\text{ cm}^{-1}$ ) vibration of  $\text{H}_2\text{O}$ . However, while this vibration results in a change in electric moment parallel to the figure axis in  $\text{H}_2\text{O}$ , it gives in the case of methylamine a strong

component perpendicular to the C—N axis because of the angle C—N—H. Looking for a band in this region it seems that the band at  $1625\text{ cm}^{-1}$  would give the best fit in frequency. It is presented in Fig. 4 and certainly resembles a parallel type band more than a perpendicular one. However, there is serious overlapping in this region which may arise due to combinations of  $1045$  and  $630\text{ cm}^{-1}$ .

Two other types of motion in the  $\text{NH}_2$  group consist of the hindered rotation and a bending

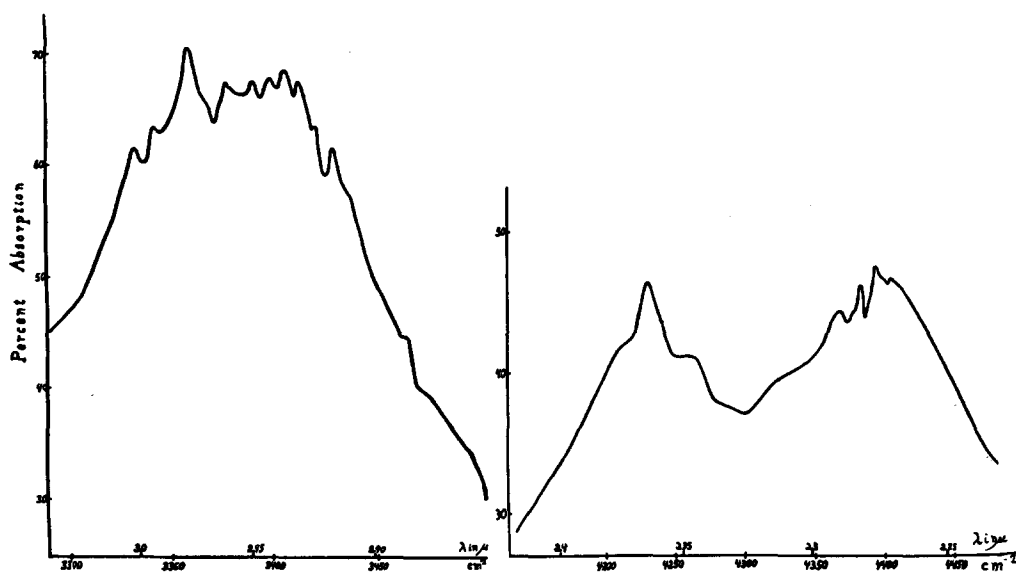


FIG. 6. The  $\nu_{\text{NH}}$  vibration at  $3360\text{ cm}^{-1}$  and combination bands at higher frequencies.

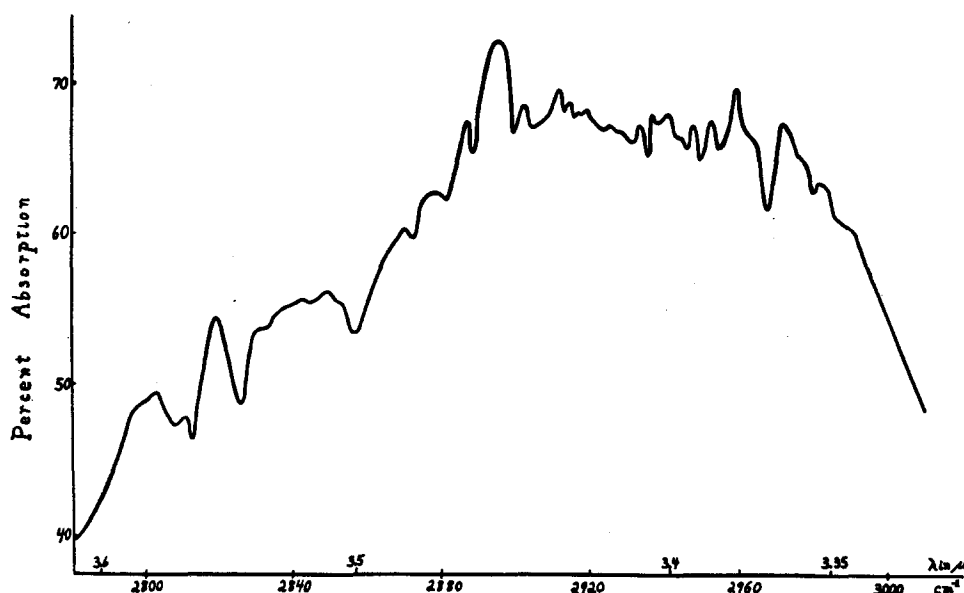


FIG. 7. The  $\nu_{\text{CH}}||$  vibration at  $2819\text{ cm}^{-1}$ , the  $\nu_{\text{CH}}\perp$  vibration at  $2968\text{ cm}^{-1}$ , also the harmonic  $2\delta_{\text{CH}}\perp^{(2)}$  at  $2895\text{ cm}^{-1}$ .

vibration which consists of an oscillation of the hydrogen atoms perpendicular to the N—H bonds, a sort of twisting motion, giving a change of the electric moment with its major component parallel to the figure axis. The motion is similar to the one for the  $783\text{ cm}^{-1}$  frequency with the only difference that the two hydrogen atoms are now moving in opposite directions. The frequencies of the two bands associated with these vibrations would no doubt be low. Unfortunately the low frequency region was studied only with a sylvine prism, and the results could not be carried beyond the region of  $18\mu$ . An absorption band was observed which extended from  $680\text{ cm}^{-1}$  to  $570\text{ cm}^{-1}$ . The graph shown in Fig. 5 indicates a parallel type of band. When measured at high pressures the band developed a second rather narrow branch not as intense as the main branch, and spaced about  $20\text{ cm}^{-1}$  toward higher wave numbers from it; so that from the experimental data it cannot be clearly stated whether this is a parallel or a perpendicular band. The parallel band at  $1127\text{ cm}^{-1}$  is shown in Fig. 5. If this were a fundamental, it would have to be associated with the N—H twisting vibration described above, however, we are aware that our investigation has been limited in the low frequency region.

The region of the N—H valence vibration

shows an unexpected feature. While there is no doubt that the band at  $3360\text{ cm}^{-1}$  must be associated with the vibration  $\nu_{\text{NH}}||$  there is no evidence for the perpendicular vibration which from Raman measurements<sup>8</sup> in gaseous methylamine is fixed at  $3470\text{ cm}^{-1}$ . Since  $\nu_{\text{NH}}||$  is very strong in the Raman effect and  $\nu_{\text{NH}}\perp$  is very weak, one would expect a strong infra-red band corresponding to the frequency of the latter vibration. It can be seen from Fig. 6 that no strong absorption occurs at the expected position. Instead there is a weaker band at  $3425\text{ cm}^{-1}$ , but it is possible that the whole region from  $3390$  to  $3430\text{ cm}^{-1}$  consists of overlapping absorption of different combination bands. So far no explanation can be given as to why the perpendicular N—H valence vibration is missing, but we should like to mention that the same is true for  $\text{NH}_3$  where this vibration is calculated from overtones and combinations.

#### THE C—H VIBRATIONS

The valence vibrations along the CH bonds give rise to two bands at  $3.55\mu$  and  $3.37\mu$  corresponding to the parallel vibration of the three hydrogens,  $\nu_{\text{CH}}||$  ( $2819\text{ cm}^{-1}$ ). The results are shown in Fig. 7. There is indication of some resolution in the latter band's *P* and *R* branches. It is a doubly degenerate vibration as in methyl

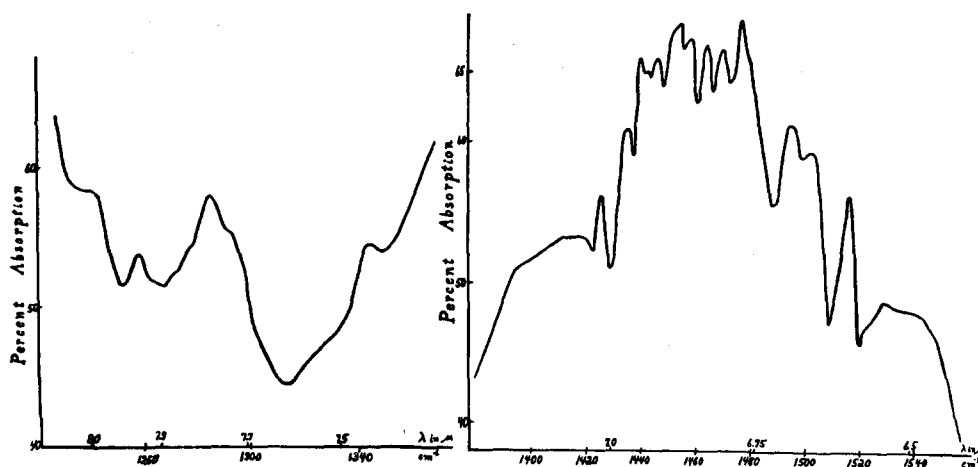


FIG. 8. The  $\delta_{\text{CH}}||$  vibration at  $1426\text{ cm}^{-1}$ , the  $\delta_{\text{CH}}\perp^{(2)}$  vibration at  $1460\text{ cm}^{-1}$ , the  $2\delta_{\text{NH}}||^{(1)}$  harmonic at  $1516\text{ cm}^{-1}$ , and the  $\delta_{\text{CH}}\perp^{(1)}$  vibration at  $1312\text{ cm}^{-1}$ .

alcohol, the degeneracy probably not being removed on account of the very small deviation of the molecule from being a symmetric top.

As is characteristic for the methyl group in many compounds, particularly the methyl halides, another strong band appears in the same region, that is in  $\text{CH}_3\text{NH}_2$  at  $3.45\mu$  or  $2895\text{ cm}^{-1}$ . In these mentioned cases this band has been interpreted as being an overtone of the higher frequency perpendicular  $\text{CH}_3$  bending vibration intensified by an interaction with  $\nu_{\text{CH}}||$ . The same explanation can be applied here.

The fundamental vibration  $1460\text{ cm}^{-1}$   $\delta_{\text{CH}}\perp^{(2)}$  involved in the last discussed band is the most intense band in the  $7\mu$  region, partially resolved, and shown in Fig. 8. It is somewhat similar in contour to the trace of the perpendicular band at  $9940\text{Å}$  which is reported in the photographic region.<sup>6</sup> By analogy with this band the center is chosen at  $6.85\mu$  or  $1460\text{ cm}^{-1}$ , a value which makes the suggested interaction seem reasonable. In the Raman effect<sup>8</sup> a broad line has been observed at  $1460\text{ cm}^{-1}$  possibly due to the superposition of two lines. A weaker parallel band found at  $7.02\mu$  ( $1426\text{ cm}^{-1}$ ) may be assigned to the parallel deformation vibration,  $\delta_{\text{CH}}||$ . The corresponding bands in methyl alcohol have been located at  $1477$  and  $1455\text{ cm}^{-1}$ . The other perpendicular  $\text{CH}_3$  bending vibration has been assigned in  $\text{CH}_3\text{OH}$  to a band at  $1340\text{ cm}^{-1}$ . There is no definitely perpendicular band in that region that could be assigned unambiguously to

this vibration unless one considers the remote possibility of associating the minimum at  $1312\text{ cm}^{-1}$  with the center of a band.

It seems reasonable to mention the perpendicular band at  $2.278\mu$  ( $4385\text{ cm}^{-1}$ ) and the parallel band at  $2.37\mu$  ( $4226\text{ cm}^{-1}$ ), shown in Fig. 6, in connection with the C—H frequencies. No unambiguous explanation can be given for these bands since several combinations seem possible. The following pairs would account for the bands in question:  $2968 + 1426$  ( $\nu_{\text{CH}}\perp + \delta_{\text{CH}}||$ ),  $2820 + 1426$  ( $\nu_{\text{CH}}|| + \delta_{\text{CH}}||$ ) and  $3 \times 1460 = 4380$  ( $3\delta_{\text{CH}}\perp^{(2)}$ ) and

$$2820 + 1460 = 4280 (\nu_{\text{CH}}|| + \delta_{\text{CH}}\perp^{(2)}).$$

The second pair corresponds to a suggestion by Adel and Barker,<sup>10</sup> based upon the interaction between the levels involved.

In conclusion, it should be emphasized that a good agreement of the assigned frequencies with the possible modes of vibration has been reached. On account of the overlapping of some bands not all frequencies could be identified with the same certainty. The writers wish to express their appreciation to Dr. H. Sponer of Duke University for many helpful suggestions in the interpretation of the results. The research was supported in part by a grant to her from the Duke University Research Fund.

<sup>10</sup> A. Adel and E. F. Barker, J. Chem. Phys. 2, 627 (1934).