

# THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 8

MARCH, 1940

NUMBER 3

## The Infra-Red Absorption Spectrum of Methyl Amine

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(Received December 27, 1939)

The parallel type methyl amine band at  $10\mu$  has been resolved. Its center is at  $1045.27\text{ cm}^{-1}$ , and the very regular structure of its *P* and *R* branches indicates a close approximation to axial symmetry. The mean of the two largest moments of inertia is  $37.43 \times 10^{-40}\text{ g}\cdot\text{cm}^2$ . Assuming angles and distances for  $\text{NH}_2$  as in ammonia, and for  $\text{CH}_3$  as in methane, the C-N distance is computed to be  $1.48 \times 10^{-8}\text{ cm}$ . Certain enhanced lines suggest a superposed perpendicular band. The  $13\mu$  band is partially resolved, and assigned to a motion corresponding to  $\nu_3$  in  $\text{NH}_3$ . The bands arising from vibrations characteristic of the amino and methyl groups have been examined but could not be resolved.

OBSERVATIONS upon the infra-red spectrum of methylamine vapor which have recently been published by Cleaves and Plyler<sup>1</sup> include the envelopes of a number of unresolved absorption bands, the frequencies of which have been assigned to various normal modes of vibration of the  $\text{CH}_3\text{NH}_2$  molecule. The same spectrum has been under investigation in this laboratory with a slightly higher dispersion, the results being identical in some respects, but sufficiently different in others to justify further discussion.

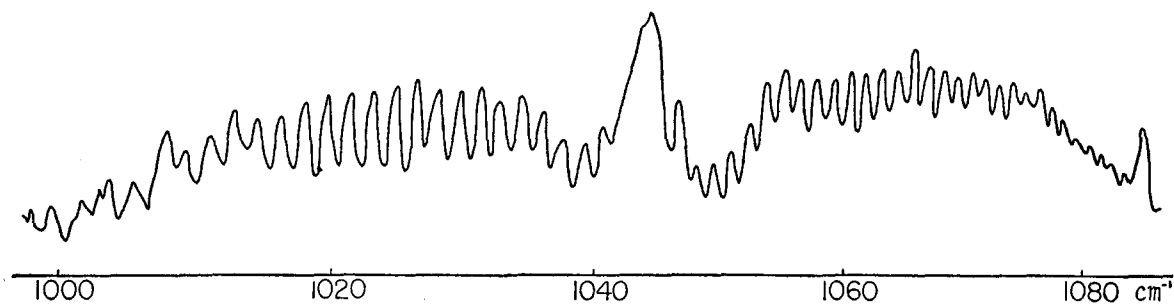
The molecule approximates a rigid rotator which is almost, but not quite, axially symmetrical, and its spectrum is similar in many respects to those of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{F}$ . It may also be thought of as an ammonia derivative in which the methyl group has replaced one of the hydrogen atoms. There is a single plane of symmetry through the CN axis and bisecting the HNH angle. The motions associated with the fifteen vibrational degrees of freedom may be subdivided for convenience into three classes.

Six of them represent the mutual oscillations of the methyl and amino groups; three others are characteristic of the amino group alone, while the remaining six belong primarily to the methyl radical.

### MUTUAL VIBRATIONS OF THE METHYL AND AMINO GROUPS

The molecule may first be considered as consisting of two approximately rigid groups of atoms attached to one another through the C-N bond. Of the six characteristic motions of this structure (rotation and translation excluded) the simplest is the valence oscillation, which is accompanied by a change in electric moment nearly parallel to the CN axis. The corresponding absorption band lies close to  $10\mu$ , and, as represented by Cleaves and Plyler, has a narrow intense zero branch. Under somewhat higher resolution the rotational structure of this band appears, showing the remarkably regular pattern indicated in Fig. 1. The spectral range included in the slit was about  $0.5\text{ cm}^{-1}$ . The zero branch remains quite narrow and unresolved, and the

<sup>1</sup> Cleaves and Plyler, *J. Chem. Phys.* **7**, 563 (1939).

FIG. 1. The band at  $10\mu$ .

individual lines composing the wings show no observable splitting. This indicates that axial symmetry is closely approximated. Table I presents the positions of the observed lines, in wave numbers, reduced to vacuum.

An unusual feature of this band is the enhancement in intensity of certain lines, particularly of  $+1$ , although  $+7$ ,  $+15$  and others stand out above the envelope, and a strong narrow line appears at  $1085\text{ cm}^{-1}$ , at the high frequency end of the band. This suggests that a weak perpendicular type band with relatively wide spacing is superposed upon the principal absorption. Further observations with different amounts of gas may reveal more detail.

A second mode of motion associated with the CN axis is the torsional oscillation. Cleaves and Plyler assign to it the frequency  $620\text{ cm}^{-1}$ , and report a band envelope resembling that of a parallel vibration, with an intense though rather wide central maximum. Our observations seem hardly compatible with this. While an irregular pattern of rather weak absorption extends from  $500$  to  $700\text{ cm}^{-1}$ , we have observed no region of particularly high intensity, and no characteristic band structure. It is of course possible that this absorption represents the fundamental band due to torsional oscillation, but we are inclined to believe that the frequency is too high\* to be so interpreted, and that instead one or more difference bands are involved.

A pair of perpendicular vibrations are expected in which the C—N bond is deformed either in the plane of symmetry or normal to this plane. These are perhaps represented by rather weak bands at

\* This supposition is supported by observations of Randall and Lawson, as yet unpublished, but kindly communicated to us. They find a region of rather strong absorption in the neighborhood of  $270\text{ cm}^{-1}$ .

about  $1130\text{ cm}^{-1}$  and  $1150\text{ cm}^{-1}$ . Here the structure is quite complicated, with no very intense lines, and is not sufficiently resolved to permit an analysis.

The other two vibrations characteristic of a molecule considered as a pair of approximately rigid groups are torsional oscillations in which the hydrogens belonging to  $\text{NH}_2$  move, either in the same sense or in opposite senses, along lines perpendicular to the N—H bond and parallel to the plane of symmetry. Thinking of the structure as a substituted ammonia, the first of these corresponds to the symmetrical  $\text{NH}_3$  vibration  $\nu_3$ , which gives rise to a pair of bands near  $10\mu$ , the doubling being a consequence of the two minimum potential function. This interesting characteristic must persist in methyl amine, though somewhat modified by the fact that whenever the N atom passes through the H—H— $\text{CH}_3$  plane from one equilibrium position to the other, the methyl group must rotate through an angle of  $60^\circ$  about its own symmetry axis. The resulting absorption band extends from about  $710\text{ cm}^{-1}$  to about  $850\text{ cm}^{-1}$ , its central portion having the structure indicated in Fig. 2.

TABLE I. Observed wave numbers, reduced to vacuum, for lines in the  $10\mu$  band.  $J$  for the lower rotation state.

P BRANCH	$J$	R BRANCH	P BRANCH	$J$	R BRANCH
—	0	1046.44	1026.23	11	1061.52
—	1	1047.86	1024.56	12	1062.77
1040.50	2	1049.30	1022.90	13	1064.08
1038.96	3	1050.71	1021.19	14	1065.39
1037.42	4	1052.11	1019.54	15	1066.70
1035.89	5	1053.45	1017.84	16	1067.90
1034.31	6	1054.85	1016.10	17	1069.10
1032.67	7	1056.21	1014.35	18	1070.24
1031.03	8	1057.56	1012.56	19	1071.38
1029.47	9	1058.86	1010.82	20	1072.59
1027.84	10	1060.22	1009.06	21	1073.73

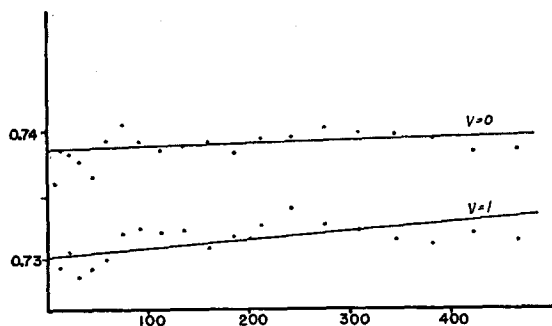
FIG. 2. A part of the  $13\mu$  band.

There is a rather strong central region around  $780\text{ cm}^{-1}$ , obviously consisting of many lines, and flanked on either side by a fairly sharp maximum suggesting a  $Q$  branch. The positions of these maxima are  $763\text{ cm}^{-1}$  and  $795\text{ cm}^{-1}$ . The change in electric moment will include both parallel and perpendicular components.

The corresponding unsymmetrical oscillation introduces an angular momentum which must be compensated by a tilting of the methyl group. Thus the change in electric moment is principally in a direction normal to the symmetry plane of the molecule. This nondegenerate perpendicular vibration corresponds to the  $6\mu$  band,  $\nu_4$ , of  $\text{NH}_3$ . It has not been identified in the spectrum, but may possibly lie in the  $10\mu$  region, or even as far out as  $16\mu$ .

#### VIBRATIONS CHARACTERISTIC OF $\text{NH}_2$

The symmetrical valence oscillation of the amino group should have both perpendicular and parallel components. The latter, though relatively less intense, is unmistakable because of its sharp  $Q$  branch, and the frequency may thus be determined. Our observations are so nearly identical with those presented by Cleaves and Plyler,\* that it is not necessary to reproduce the curves. The zero branch is plainly indicated at  $3360\text{ cm}^{-1}$ . The absorption pattern is not symmetrical with respect to this ordinate, however, but is much more intense on the high frequency side. Its appearance suggests a superposed per-

FIG. 3.  $\Delta_2 F/2(2J+1)$  vs.  $(J+\frac{1}{2})^2$ .

\* Reference 1, Fig. 6.

pendicular band at about  $3410\text{ cm}^{-1}$  due to the unsymmetrical valence oscillation.

The symmetrical deformation oscillation of the  $\text{NH}_2$  group, which includes both perpendicular and parallel components, is represented by a band at  $1625\text{ cm}^{-1}$ . Our observations show no more detail than those of Cleaves and Plyler, as represented in Fig. 4 of their report.

#### VIBRATIONS OF THE METHYL RADICAL

The symmetrical and unsymmetrical valence oscillations in  $\text{CH}_3$  yield superposed bands in the neighborhood of  $3.5\mu$ . A well-defined zero branch appears at  $2820\text{ cm}^{-1}$ , with a somewhat similar maximum at  $2964\text{ cm}^{-1}$ . These are also observed in Raman scattering as strong sharp lines.<sup>2</sup> Whether or not they are related through resonance with  $2\delta_{\text{CH}}$  is not clear, but the question of resonance in this case is complicated by the lack of true axial symmetry or complete degeneracy. The center of the strong perpendicular type band appears to be around  $2930\text{ cm}^{-1}$ .

The symmetrical and unsymmetrical deformation vibrations produce bands in the neighborhood of  $7\mu$ , which we find very poorly resolved. There seems to be a weak zero branch at  $1385\text{ cm}^{-1}$ , and a broad complex absorption with its center near  $1470\text{ cm}^{-1}$ .

#### MOLECULAR MOMENTS OF INERTIA

When the molecule is considered as a symmetrical rotator the term values may be written

$$W/hc = G(v) + F(J, K, v),$$

where

$$F(J, K, v) = X_1^v J(J+1) + X_{01}^v K^2 + X_2^v J^2(J+1)^2 + X_{02}^v K^4.$$

The mean of the two larger and nearly equal moments of inertia for the ground state is equal to  $h/8\pi^2 c X_1^0$ , which may be evaluated by the usual combination relations.

$$\begin{aligned} \Delta_2 F^0 &= R(J+1) - P(J-1) \\ &= 2(2J+1) \left\{ (X_1^0 + \frac{3}{2} X_2^0) + 2X_2^0 (J + \frac{1}{2})^2 \right\}. \end{aligned}$$

<sup>2</sup> Kirby-Smith and Bonner, J. Chem. Phys. 7, 880 (1939).

Fig. 3 shows  $\Delta_2 F/2(2J+1)$  plotted against  $(J+\frac{1}{2})^2$ , the upper line corresponding to  $v=0$ , and the lower one to  $v=1$ . While the points scatter considerably, due in part to the superposition of one or more weak bands, they approximate straight lines with the constants

$$X_1^0 = 0.7385 \text{ cm}^{-1} \quad \text{and} \quad X_2^0 = 12 \times 10^{-7}, \\ X_1^1 = 0.7300 \text{ cm}^{-1} \quad \text{and} \quad X_2^1 = 36 \times 10^{-7}.$$

The moment of inertia in the ground state is, therefore,  $37.43 \times 10^{-40}$  g cm<sup>2</sup>, and the corresponding C-N distance is  $1.48 \times 10^{-8}$  cm, assuming angles and distances for NH<sub>2</sub> as in ammonia, and for CH<sub>3</sub> as in methane.

The band center is at 1045.27 cm<sup>-1</sup>. Its position is obtained by extrapolating to  $J=0$  the midpoints between successive pairs of lines chosen

from the *P* and *R* branches. These midpoints are well represented by the equation

$$\bar{\nu} = \nu_v + (X_1^1 - X_1^0)J^2 = 1045.27 - 0.0085J^2.$$

The smallest moment of inertia would be obtained at once from the spacing between *Q* branches in any nondegenerate perpendicular band. If the enhanced lines in the 10 $\mu$  region constitute such a band, with a mean spacing of about 6.2 cm<sup>-1</sup>, the value of *C* is about  $7.2 \times 10^{-40}$  g·cm<sup>2</sup>. This can hardly be considered as well established, however.

The examination of methyl amine was suggested to us by Professor J. G. Aston, of Pennsylvania State College, and it is a pleasure to acknowledge our indebtedness to him for a supply of ammonia-free material.

## Spectral Transmission of Glucose Glass in the Near Infra-Red

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(Received November 13, 1939)

The transmission of samples of glucose glass varying in thermal history was previously investigated. This work covered the visible part of the spectrum. Transmission data in the near infra-red are presented now as far as could be obtained photographically (12,000Å). No limit of absorption was found at long wave-lengths as far as tested. The possible use of organic glass for investigations in the near infra-red is discussed.

### I. THE METHOD

**T**HIS paper is a continuation of my paper.<sup>1</sup> Two series of glucose glasses have been tested prepared by somewhat different methods, see paper I. The series include samples GG 1, 2; and 3, 5, 6, 8, 9, respectively. (Glasses GG 4 and 7 were now omitted because of increased crystallization.) The samples range from clear to dark brown in color. The Hilger grating spectrograph of paper I was adapted for work in the near infra-red. The first order was used, the overlapping ultraviolet of the second order being eliminated by means of a No. 88 Wratten filter. A neutral wedge equal in length to the length of the slit was inserted in front of the slit as discussed in paper I. The width of the slit varied from 0.1 to 0.3 mm.

<sup>1</sup> Willi M. Cohn, "A Spectral Investigation of Glucose Glass," *J. Chem. Phys.* 6, 65-67 (1938). (Cited as "paper I.")

Wedge spectra were obtained on Eastman plates, emulsions K, P, M, and Z using sensitivities I or 144. Plates of series M and Z were hypersensitized by means of ammonia. A reference spectrum of an incandescent lamp operated at a constant voltage, together with spectra of one or two glass samples were taken on a plate. The photometric reduction was carried out as discussed in paper I.

### II. THE RESULTS

Transmission values  $D_\lambda$  as a function of the wave-length are presented in Table I. These data include results of both former and present investigations. We further computed the "relative transmission" of the samples by arbitrarily setting the transmission at  $\lambda 6000$  equal to 1.0. This permits an easier comparison of the two groups of samples. Fig. 1 shows the relative transmission as a function of the wave-length.