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## Infra-Red Bands of Methylamine and the Phenomenon of Free Rotation

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Two bands in the absorption spectrum of methylamine have been measured in the photographic infra-red. One of the bands shows rotational structure. The bands have been interpreted as involving excitation of the frequencies  $3\nu_{\text{NH}}$  and  $(3\nu_{\text{CH}} + \nu_{\text{CN}})$ . The rotational structure of the latter band suggests that it is a perpendicular-type band, and the precise spacing of the  $Q$  branches suggests that the molecule behaves approximately like a rigid symmetric top. The inference of hindered internal rotation is in agreement with other independent data.

MUCH information about the properties and structure of simple polyatomic molecules has been obtained in recent years from the study of their infra-red spectra. The measurements fall into two classes: on the one hand the examination of the vibration bands in the far infra-red using instruments of low resolving power, and on the other the analysis of overtone or combination bands in the photographic region below 10,000Å where much higher resolving power can be relatively easily applied. Comparatively few molecules have so far been studied in the latter region, since apart from possible experimental difficulties, it is necessary that the molecules shall contain at least one linkage involving a hydrogen atom, in order to bring the frequency absorbed into the accessible region. In addition to this, even with the high resolving power and dispersion of a large grating instrument, it is essential if rotational structure is to be studied, that the moments of inertia shall be relatively small.

It is, nevertheless, desirable to examine as many examples as possible using the high resolving power of the photographic method, since not only may such an analysis lead to a knowledge of the molecular structure, but also to the development of spectral theory, to the understanding of band envelopes, and to the correlation of the spectroscopic data with certain thermodynamic properties of the molecules.

In an examination of the absorption by the vapor of methylamine over the spectral range 7000–11,000Å, we have recently observed two bands of methylamine, one of which has interesting structural features; and since the work must be temporarily suspended, it seems desirable to outline the main results, although it is not at

present possible to give a complete interpretation of them.

In many respects methylamine resembles two other molecules, ethane and methyl alcohol, the infra-red bands of which have been recently studied. Ethane is a symmetric top, and the other two molecules, although in reality asymmetric tops, approximate closely to the symmetric top type. Also all three molecules have an axis about which free rotation, or internal torsion, might well occur. From a consideration of the bands of ethane and from the specific heat data, Howard<sup>1</sup> has suggested that in this molecule free rotation may be completely hindered. Badger and Bauer,<sup>2</sup> on the other hand, have attempted to interpret apparently abnormal rotational structure in the bands of methyl alcohol in terms of the occurrence of some degree of internal torsion. Calculations on the entropy of methyl alcohol, however,<sup>3</sup> suggest that in this molecule too, internal rotation is at least considerably hindered. It will be shown below that there is possible spectral evidence for very restricted rotation in methylamine, and this is interesting in view of similar conclusions reached from considerations of the entropy.<sup>4</sup>

The Raman spectrum of aqueous methylamine has been measured by Dadieu and Kohlrausch,<sup>5</sup> and of the liquid by Venkateswaran and Bhagavantam.<sup>6</sup> A reasonable assignment of frequencies suggests  $\nu_{\text{CH}} \sim 3000$ ,  $\nu_{\text{NH}} \sim 3350$ , and

<sup>1</sup> J. Chem. Phys. **5**, 442, 451 (1937).

<sup>2</sup> J. Chem. Phys. **4**, 469 (1936).

<sup>3</sup> J. Chem. Phys. **5**, 539 (1937).

<sup>4</sup> Aston, Siller and Messerly, J. Am. Chem. Soc. **59**, 1750 (1937); Kistiakowsky and Wilson, J. Am. Chem. Soc. **60**, 494 (1938).

<sup>5</sup> Wien. Akad. **IIA**, **149**, 77 (1930).

<sup>6</sup> Ind. Jour. Phys. **5**, 129 (1930).

$\nu_{\text{CN}} \sim 1040$ . The only measurements on the infra-red spectrum appear to be those of R. and M. Freymann,<sup>7</sup> extending over the range 0.8–1.2 $\mu$ , but using low resolution and an aqueous solution. The essential feature found was that two bands occur, at 10,420Å and 10,102Å or *ca.* 9600 and 9990  $\text{cm}^{-1}$ . The band at 9600  $\text{cm}^{-1}$ , which is by far the most intense, was attributed to the excitation of  $3\nu_{\text{NH}}$  i.e., a second overtone of the N–H fundamental. When it is remembered that in solution the bands may have become somewhat displaced to lower frequencies, this assignment seems fully justified.

### EXPERIMENTAL

The spectrograph used was a three-meter concave grating with Eagle mounting. The grating had approximately 15,500 lines to the inch and its effective width was about three inches. The spectra were studied in the first order, the dispersion being 5.8Å per mm.

The methylamine was a Kahlbaum product supplied as pure, but found to contain a considerable quantity of dissolved ammonia. Repeated fractionation removed the latter perhaps completely, but in any case to such an extent that no absorption attributable to ammonia could be detected.

The absorption tube was in general a steel pipe 8 cm in diameter and 5.5 meters in length, having a side arm connected to manometer, to glass tubes containing the methylamine, and via taps to an oil pump. In some experiments an additional tube 7.5 meters in length was used in series with the above, so as to obtain a total column length of 13 meters, but in the latter case the exposure times were very considerably lengthened. The ends of the absorption tubes were closed by glass plates cemented on with suitable wax. The continuous source was a tungsten arc lamp. Higher order spectra were eliminated by means of the Ilford Infra-red or Wratten 88 filters. The plates used were Agfa 850, 950 and 1050, Kodak I R, I P, and I Q, and Ilford Infra-red, and all were hypersensitized before use. The exposures varied from 4 to 30 hours according to the type of plate used. Considerable difficulty was experienced with the Agfa 1050 and Kodak Q plates working

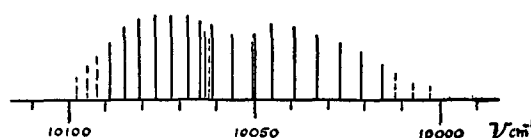


FIG. 1.

at wave-lengths longer than 10,000Å, since delivery was inconvenient and the plates seemed to have lost most of their sensitivity in transit.

Pressures of methylamine up to one atmosphere were used. Unfortunately with the higher pressures which were necessary for the detection of the bands so far found, there appeared to be a considerable pressure broadening effect.

### RESULTS

The two bands found lie at wave-lengths *ca.* 10,300Å and 9940Å and are best described separately.

*Band A* with center at 10,300Å or 9700  $\text{cm}^{-1}$  is relatively intense, and can be observed with pressures of less than an atmosphere in columns of two meters. It has not been possible to detect any rotational structure in this band, nor even a contour suggesting *P*, *Q* and *R* branches. The band is some 100–150  $\text{cm}^{-1}$  broad depending upon the pressure used.

*Band B* which is represented diagrammatically in Fig. 1, consists of a group of roughly equidistant lines centered around *ca.* 9940Å i.e., 10,060  $\text{cm}^{-1}$ . The appearance of this band is surprisingly simple, but this simplicity is almost certainly misleading. For the most part, the lines, which are broad, are separated from each other by 4–6Å i.e., a mean separation of about 5Å which corresponds to about 5  $\text{cm}^{-1}$ . The spacing of the lines is, however, clearly not regular, and there is a close group of about three lines in the center which at first sight appears to divide the band into two parts. The band is far less easily detected than band *A* above and requires a column of fifteen feet at atmospheric pressure for development.

### DISCUSSION

The two bands found at 10,060  $\text{cm}^{-1}$  (band *B*) and 9700  $\text{cm}^{-1}$  (band *A*) with methylamine vapor agree well with those reported by Frey-

<sup>7</sup> Comptes rendus 202, 1674 (1936).

mann at  $9990\text{ cm}^{-1}$  and  $9600\text{ cm}^{-1}$  for the aqueous solution. Band *A* can with reasonable certainty be attributed to the excitation of  $3\nu_{\text{NH}}$  and band *B* is probably to be interpreted by the combination ( $3\nu_{\text{CH}} + \nu_{\text{CN}}$ ). On the basis of the generally accepted values for the fundamentals quoted above there is good agreement.

The interpretation of the rotational structure of the two bands is less obvious. It is at once clear that considerably more spectral data, and also the relevant theory, will be required before it is possible to deduce the molecular structure from spectroscopic data alone. Therefore we must rather begin by assuming a plausible structure for the molecule and attempt to interpret the band structures found.

In methylamine the methyl group angles are roughly tetrahedral, and the C—N—H angles are close to  $105^\circ$ . The bond lengths have the probable values  $r_{\text{CH}} = 1.08\text{ \AA}$ ,  $r_{\text{CN}} = 1.47\text{ \AA}$ ,  $r_{\text{NH}} = 1.02\text{ \AA}$ . The possibility of free rotation about the C—N axis makes it impossible to specify the exact relative orientation of the two end groups. The molecule is in reality an asymmetric top, but like methyl alcohol<sup>8</sup> approaches closely to the type of symmetric top, with symmetry axis along the C—N bond. The moments of inertia about this axis of the  $\text{CH}_3$  and  $\text{NH}_2$  groups are respectively about  $5.4 \times 10^{-40}$  and  $3 \times 10^{-40}\text{ g cm}^2$ , so that if regarded as rotating as a whole about the C—N axis, the moment is  $I_x = 8.4 \times 10^{-40}$ . The moments  $I_y$  and  $I_z$  will each be about  $38 \times 10^{-40}$ .

The rotational energy of a symmetric top is given by

$$E_{\text{rot}} = \frac{h}{8\pi^2} \left\{ \frac{J(J+1)}{I_y} - K^2 \left[ \frac{1}{I_x} - \frac{1}{I_y} \right] \right\},$$

in which  $|K| \leq J$  and  $J = 0, 1, 2, \dots$

Two types of band may be distinguished according to the direction of change of the electric moment with respect to the symmetry axis. For the "parallel" bands ( $\Delta J = 0, \pm 1, \Delta K = 0$ ) there will be a single *P*, *Q* and *R* branch structure, the spacing in each of the *P* and *R* branches being  $h/4\pi^2 I_y$ . The "perpendicular" bands ( $\Delta J = 0, \pm 1, \Delta K = \pm 1$ ) will consist of a superposition of subbands each with *P*, *Q* and *R* branches of unequal

intensity, so that the *Q* branches usually stand out against a more or less unresolved background. The separation of the *Q* branches will be given by

$$(h/4\pi^2) \{1/I_x - 1/I_y\}.$$

Many polyatomic molecule vibrations, however, involve a change in the component of the electric moment both parallel and perpendicular to the symmetry axis, and in such cases there will be a superposition of the two types of band. Such a superposition may occur in the case of methyl alcohol, and might also occur in the excitation of vibrations in the  $\text{NH}_2$  group in methylamine.

Unfortunately in methylamine there is an additional complication, the possibility of free rotation about the C—N axis. The effect of internal torsion on the rotational energy levels of molecules has been studied by several workers. For our present purpose we may use the result of Nielsen,<sup>9</sup> who showed that for a symmetric torsional oscillator,

$$E_{\text{rot}} = \frac{h}{8\pi^2} \left[ \frac{J(J+1)}{I_y} - \frac{(K_1 + K_2)^2}{I_y} + \frac{K_1^2}{I_x'} + \frac{K_2^2}{I_x''} \right],$$

in which  $J = 0, 1, 2, \dots$

$K_1$  and  $K_2$  have values  $0, \pm 1, \pm 2$ , subject to the rule  $J \geq (K_1 + K_2)$ .  $I_x'$  and  $I_x''$  are the moments of inertia of the end groups about the symmetry axis, and  $I_y$  is the moment of the entire molecule about an axis perpendicular to the symmetry axis.

This expression refers in reality to a molecule (like ethane) having two end groups free to rotate with respect to each other, and with a coincident symmetry axis. As Badger and Bauer have shown, for a vibration in which the change in moment is parallel to the symmetry axis,  $\Delta J = 0, \pm 1, \Delta K_1 = \Delta K_2 = 0$  giving a band with *P*, *Q* and *R* branches as for the normal rigid symmetric top, the spacing being unaffected. For a perpendicular band, assuming the vibration to be largely localized in one of the end groups,  $\Delta J = 0, \pm 1, \Delta K_2 = 0$  but  $\Delta K_1 = \pm 1$  giving subbands the separation of whose centers is given by

$$(h/4\pi^2) \{1/I_x' - 1/I_y\},$$

in which  $I_x'$  is the moment about the symmetry

<sup>8</sup> J. Chem. Phys. **4**, 469 (1936).

<sup>9</sup> Phys. Rev. **40**, 445 (1932).

axis of the group in which the vibration is localized. The  $Q$  branches will each be flanked with  $P$  and  $R$  branches having the same spacing as those in the parallel bands.

Finally as in the case of a rigid rotator, if the vibration under consideration leads to a change in the electric moment both parallel and perpendicular to the symmetry axis, we may expect to find a superposition of the different types of band.

Turning now to the specific case of methylamine, it is most convenient first to discuss the band at 9940A. At first sight this band may be thought to have in a modified form the simple structure of a parallel band with a crowding of lines in the center giving in some measure the appearance of a  $Q$  branch. This cannot be so. Assuming as a first approximation that the molecule is a rigid symmetric top having the moments of inertia estimated above, the separation of the lines in the  $P$  and  $R$  branches would be  $1.45\text{ cm}^{-1}$ . With such a separation the lines would hardly have been resolved in the present measurements. The separation observed was *ca.*  $5\text{ cm}^{-1}$ . The occurrence of free rotation could not affect the spacing of a parallel band. If, however, the lines are regarded as  $Q$  branches of a perpendicular-type band, their spacing for a rigid top should be *ca.*  $5\text{ cm}^{-1}$ , a value surprisingly close to that found. Despite the various approximations in the above argument, and not forgetting the irregularities in the spacings, it is reasonable therefore to interpret the band as being essentially a normal perpendicular-type band. If completely free rotation were occurring the  $Q$  branch separation, assuming the vibration to be largely localized in the methyl group and the  $\text{NH}_2$  group as fairly rigid, would be about  $10\text{ cm}^{-1}$ . Hence we

should infer that the internal rotation must be almost completely hindered.

The irregularities in the band structure do not seem such as to vitiate this conclusion. The central group of lines together with the fact that the separation of the lines to one side of the band center is about  $4\text{ cm}^{-1}$  and to the other side about  $6\text{ cm}^{-1}$  may suggest that the band really falls into two parts, but the broad general interpretation still seems the most probable.

Band  $A$  at 10,300A was interpreted as arising from the excitation of  $3\nu_{\text{NH}}$ . Now a vibration of the  $\text{NH}_2$  radical might involve a change in the electric moment with components both parallel and perpendicular to the symmetry axis (the  $\text{C}-\text{N}$  axis). Hence we might find a superposition of bands of both types. This may be the reason for the unresolved nature of the band, and further measurements using higher resolving power and longer columns with lower pressures are clearly desirable.

The suggestion of hindered rotation in methylamine is a matter worthy of further consideration. Kemp and Pitzer<sup>10</sup> have recently shown that the entropy of ethane calculated from specific heat data is lower than that calculated from other molecular data (e.g. vibration frequencies), and have suggested that the discrepancy arises from a hindrance of internal rotation. Howard has also shown that the spectroscopic data with ethane lead to a similar conclusion. Aston, Siller and Messerly<sup>11</sup> have made similar calculations of the entropy of methylamine and found a similar discrepancy, which has been interpreted in the same manner. The spectroscopic result is not, therefore, at variance with the conclusions of other independent methods.

<sup>10</sup> J. Chem. Phys. **4**, 749 (1936).

<sup>11</sup> J. Am. Chem. Soc. **59**, 1750 (1937).