

## LETTERS TO THE EDITOR

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#### The Photographic Absorption Spectrum of Gaseous Ammonia

The absorption spectrum of the ammonia molecule, which is of the symmetrical top type, has been investigated by many authors. The four bands in the photographic region, 10,230A, 7920A, 6470A and 5490A,<sup>1</sup> have generally been considered to be harmonics of the fundamental band at  $3\mu(\nu_1)$ . Because of the complexity of the structure, only partial analyses of these bands have been made. A higher resolution has been attained in the present work, but a satisfactory analysis has not yet been completed. Nevertheless a brief preliminary report will be given in the following.

The 10,230A band appears in the present work to consist of two separate bands which can be distinguished by their intensity in absorption and which slightly overlap at 10,150A. The one of longer wave-length is the stronger and its center is approximately at 10,230A, while the center of the weaker band appears to be at 9900A. In the former, there are several groups of strong lines on the high frequency side with intervals of about  $10\text{ cm}^{-1}$ , half the spacing of the parallel type band. This suggests similarity to the perpendicular type band such as  $1.97\mu$ , studied by Stinchcomb and Barker.<sup>2</sup> The structure of the weaker band is relatively simpler.

In the 6470A band, a group of strong lines which are nearly equally spaced in the center of the band suggests the  $Q$  branch of a perpendicular type band, while there are also other groups of lines resembling  $P$  and  $R$  branches. Its appearance is similar to that expected for a perpendicular type band derived from rotation energy levels

$$E_r/hc = BJ(J+1) + \beta BK^2,$$

where  $B=9.92$ ,  $\beta B=1.4\text{ cm}^{-1}$  ( $1.4$ =half the average spacing of the lines in the  $Q$  group). There are, however, several discrepancies. For instance, the spacing of the lines due to changes of  $K$  with fixed  $J$ -values are smaller in the  $R$  branch and are larger in the  $P$  branch than those in the  $Q$  branch.

Recently Adel<sup>3</sup> proposed that the 6470A band is the fourth harmonic of the parallel type band,  $\nu_1$ , with a doubling similar to the  $10\mu$  band. But the structure of the band does not agree with this type, even with different values of  $B$  and  $\beta$  in the normal and excited states. As already mentioned, the structure looks much more like that of a perpendicular type band, although it has not yet been possible to make it fit this type entirely.

In order to account for perpendicular type bands in the photographic region, the following possibilities may be considered. The first possibility is that, if the  $1.97\mu$  band is considered, as was done by Barker,<sup>2</sup> to be one of the

fundamentals of the perpendicular type,  $\nu_2$ , then the 10,230A band or else the 9900A band may be the first and the 6470A band the second harmonic of this fundamental. The second possibility is that, if  $\nu_2$  is in the neighborhood of  $3300\text{ cm}^{-1}$  as suggested by Amaldi and Placzek,<sup>4</sup> then the four bands will be harmonics of this perpendicular type fundamental band. Although this 3300 frequency has been found only in the Raman spectrum of liquid ammonia, it should be noted that Howard<sup>5</sup> recently showed by calculations based on the valence force potential function that one of the perpendicular type fundamentals is probably approximately at  $3450\text{ cm}^{-1}$ , which is very close to  $\nu_1$ .

It has been shown<sup>6</sup> that the harmonics of perpendicular type bands in general include a set of several parallel and perpendicular type bands, so that their structure should be rather complex.

I wish to express my appreciation to Professor R. S. Mulliken for the proposal of the problem and for constant inspiration and valuable advice throughout the investigation.

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<sup>1</sup> P. Lueg and Hedfeld, *Zeits. f. Physik* **75**, 599 (1932); H. J. Unger, *Phys. Rev.* **43**, 123 (1933); R. M. Badger and R. Mecke, *Zeits. f. physik. Chemie* **B5**, 333 (1929); R. M. Badger, *Phys. Rev.* **35**, 1038 (1930).

<sup>2</sup> G. A. Stinchcomb and E. F. Barker, *Phys. Rev.* **33**, 305 (1929).

<sup>3</sup> A. Adel, *Phys. Rev.* **48**, 103 (1935).

<sup>4</sup> E. Amaldi and G. Placzek, *Zeits. f. Physik* **81**, 259 (1933); P. Daure, *Ann. de Physique* **12**, 375 (1929); R. G. Dickinson, R. T. Dillon and F. Rasetti, *Phys. Rev.* **34**, 582 (1929).

<sup>5</sup> J. B. Howard, *J. Chem. Phys.* **3**, 207 (1935).

<sup>6</sup> Cf. L. Tisza, *Zeits. f. Physik* **82**, 48 (1933).

#### Fine Structure in the K X-Ray Edge of Gallium

Previous investigations have shown no extended fine structure in the  $K$  x-ray absorption edge of Ga. In view of Hanawalt's work<sup>1</sup> on the fine structure in the  $K$  edge of Fe as a function of temperature, it was thought that a structure might exist in the Ga edge at temperatures sufficiently below the melting point,  $30^\circ\text{C}$ . Accordingly, absorption spectra in the vicinity of the Ga  $K$  edge were investigated at low temperatures, and a preliminary report of the results is given herewith.

The Ga absorber was a rolled foil 0.001 inch thick, supported on stiff paper. The source of x-rays was a tungsten target, water-cooled, metal tube run at 38 kv and 24 ma. A Société Gènevoise double crystal spectrometer was used as a single crystal instrument, observations being made by the ionization method. Blank runs were taken to ensure