

## LETTERS TO THE EDITOR

*Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the*

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### The Pressure Broadening in the Gamma-Bands of Nitric Oxide

The  $\gamma$ -bands of nitric oxide are known to show strong pressure broadening either under the increase of the nitric oxide pressure itself or that of foreign gases. So far as the writer is aware the effect was discovered by Lambrey<sup>1</sup> who observed that the apparent absorption increased approximately as the square (the value of the exponent found by Lambrey was 1.81) of the pressure of NO. Naudé<sup>2</sup> made a careful study of this effect which was described in the paper in which he reported the discovery of the nitrogen isotope N<sup>15</sup>. He showed that it was a pressure broadening of the individual lines of the  $\gamma$ -bands, and published a picture of the effect. It is very pronounced even under low dispersion; we have had to take account of it in this laboratory for some time in absorption spectra work on the nitrogen oxides.

Such a very pronounced pressure broadening leads one to suspect that some process other than mere collision is leading to the rapid shortening of the lifetime of the excited state as the number of molecular collisions increases. In the halogen molecules iodine and bromine<sup>3</sup> such an effect has already been observed. It has been shown, moreover, that this is in all probability due to a predissociation of the halogen molecule caused by collisions inducing predissociation normally forbidden by selection rules<sup>4</sup> from the excited <sup>3</sup>I state of the halogen molecule which gives rise to the band absorption in the visible, into the continuous energies beyond dissociation of the lower lying triplet level. Optical transitions to this latter in absorption are very weak. They were studied by W. C. Brown.<sup>5</sup>

It therefore seems natural to inquire whether a similar effect in nitric oxide can account for this strong pressure broadening.<sup>6</sup> The recent work which has led to a lowering of the heat of dissociation of nitrogen has, of course, necessitated also a lowering of the heat of dissociation of nitric oxide. In a recent Letter to the Editor, Professor Mulliken<sup>7</sup> has concluded that we may probably now accept as rounded values 7.3 volts for N<sub>2</sub> and 5.25 volts for NO. References will be found there to the several pieces of work bearing upon this. But the upper electronic level of the  $\gamma$ -bands lies at 5.45 volts, thus above the energy of dissociation of the NO molecule. The rotational states of the vibrational levels built on this electronic level could, therefore, quite reasonably be broadened by collision, if there existed in NO a third level, dissociating into normal atoms, into which the induced predissociation might occur. Professor

Mulliken has called my attention to the predicted low-lying <sup>4</sup>I level<sup>8</sup> in NO, dissociating into normal atoms. Predissociation from the states of the <sup>2</sup> $\Sigma$  level of the  $\gamma$ -bands into this level would be possible, were it not for selection rules<sup>4</sup> prohibiting it. Both multiplicity and angular momentum change in this case and these changes are normally forbidden. But as in the iodine and bromine molecules, collisions could effect a weakening of the selection rules and thereby cause a pressure broadening of the  $\gamma$ -bands. It seems probable that this is the explanation of this example of remarkably strong pressure broadening.

It is interesting that no such effect was found by Lambrey<sup>1</sup> in the  $\beta$ -bands of NO. The approximate position of the <sup>4</sup>I level as predicted by Professor Mulliken in the figure on page 51 of reference 8 will be seen to be such as to permit transitions in conformity with the Franck-Condon principle into it from the <sup>2</sup> $\Sigma$  level of the  $\gamma$ -bands, but not from the <sup>2</sup>I level of the  $\beta$ -bands.

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<sup>1</sup> Lambrey, *Comptes Rendus* **189**, 574 (1929); **190**, 261, 670 (1930); *Annales de physique* **14**, 95 (1930).

<sup>2</sup> Naudé, *Phys. Rev.* **36**, 333 (1930).

<sup>3</sup> Loomis and Fuller, *Phys. Rev.* **39**, 180 (1932); Turner, *Phys. Rev.* **41**, 627 (1932); Kondratjew and Polak, *Zeits. f. Physik* **76**, 386 (1932).

<sup>4</sup> Kronig, *Zeits. f. Physik* **62**, 300 (1930).

<sup>5</sup> Brown, *Phys. Rev.* **38**, 1179 (1931); **38**, 1187 (1931).

<sup>6</sup> Kondratjew and Polak, *Phys. Zeits. d. Sow.* **4**, 764 (1933), suggested an explanation of this effect based on an "inner predissociation" of the molecule at a time when the heat of dissociation of NO still seemed to be appreciably higher than the upper electronic level of the  $\gamma$ -bands.

<sup>7</sup> Mulliken, *Phys. Rev.* **46**, 144 (1934).

<sup>8</sup> Mulliken, *Rev. Mod. Phys.* **4**, 1 (1932).

### Curved Quartz Crystal X-Ray Spectrograph

About a year ago we constructed in this laboratory a curved crystal focussing x-ray spectrograph of the transmission type described by Cauchois.<sup>1</sup> The instrument was originally designed for use with mica but we have been unable to obtain samples of mica sufficiently flat to give spectra of the desired sharpness. At the time of the original construction DuMond suggested that quartz would probably serve well as a crystal for this type of an instrument because of its elastic properties and small grating constant. The suggestion was repeated by Carlsson<sup>2</sup> who, however, makes no mention of having attempted to use quartz in this way.