LETTERS TO THE EDITOR

The Pressure Broadening in the Gamma-Bands of Nitric Oxide

The γ-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[1] 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[2] made a careful study of this effect which was described in the paper in which he reported the discovery of the nitrogen isotope N^{15}. He showed that it was a pressure broadening of the individual lines of the γ-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[3] 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[4] from the excited $^3\Pi$ 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.[5]

It therefore seems natural to inquire whether a similar effect in nitric oxide can account for this strong pressure broadening.[6] 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[7] has concluded that we may probably now accept as rounded values 7.3 volts for N_2 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 γ-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 $^4\Pi$ level[8] in NO, dissociating into normal atoms. Predissociation from the states of the $^2\Sigma$ level of the γ-bands into this level would be possible, were it not for selection rules[4] 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 γ-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[1] in the β-bands of NO. The approximate position of the $^4\Pi$ 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 $^2\Sigma$ level of the γ-bands, but not from the $^2\Pi$ level of the β-bands.

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    July 10, 1934.

[1] Lambrey, Comptes Rendus 189, 574 (1929); 190, 261, 670 (1930); Annales de physique 14, 95 (1930).
[2] Naudé, Phys. Rev. 36, 333 (1930).
[3] Loomis and Fuller, Phys. Rev. 39, 180 (1932); Turner, Phys. Rev. 41, 627 (1932); Kondratjew and Polak, Zeits. f. Physik 76, 386 (1932).
[4] Kronig, Zeits. f. Physik 62, 300 (1930).
[5] Brown, Phys. Rev. 38, 1179 (1931); 38, 1187 (1931).
[6] 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 γ-bands.
[7] Mulliken, Phys. Rev. 46, 144 (1934).
[8] 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.[1] 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[2] who, however, makes no mention of having attempted to use quartz in this way.
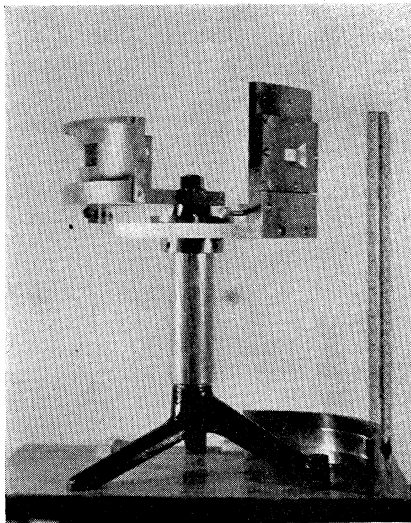
FIG. 1.

Very recently we have cut a slab of quartz parallel to the optic axis, ground it to a thickness of 0.21 mm and given it a radius of curvature of approximately 20 cm. Before bending, the quartz slab was plane and parallel to within 0.01 mm. The curvature was impressed upon this thin sheet of quartz by imprisoning it between two heavy metallic lamina machined to the required radius. The x-rays pass through an aperture (2 cm × 1 cm) cut in this crystal holder.

In addition to the crystal holder the spectrograph (Fig. 1) consists of a film holder and graduated circle which turn on the same vertical axis as the crystal holder. The film holder also consists of two heavy metallic lamina machined to one-half the radius of curvature of the crystal holder in accordance with the focussing condition outlined by Cauchois.[3] The circle is graduated in half degrees and with the help of verniers the positions of the crystal and film holders can be read to one minute of arc.

With molybdenum radiation excited under 40 kv and 15 m.a., a fluorescent spectrum of zirconium (Fig. 2) was obtained in two and a half hours. The secondary radiator was large enough to illuminate the entire crystal aperture for the first and second orders of ZrK. The first order $K\alpha$ doublet is visibly resolved.
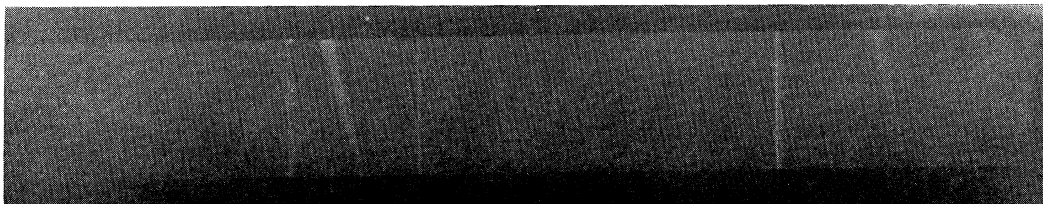
The crystal planes which are effective in the reflection of the x-rays are those perpendicular to the optic axis. For these planes the second order reflection is stronger than the first because of the alternate spacing of oxygen and silicon atoms. Thus the effective grating constant, already small, is further reduced. The reflecting planes are approximately perpendicular to the surface of the crystal lamina and hence converge to a point near the center of curvature of the crystal.

The quartz crystal shows promise of being far superior to mica for this purpose. The luminosity of the instrument claimed by Cauchois for mica seems to be retained. In addition because of the good crystalline quality of quartz the spectra are sharp and clear which was not the case with the mica we used. Furthermore, because of the small grating constant of quartz the dispersion and resolution of the spectrograph have been greatly enhanced.

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July 25, 1934.

[1] Y. Cauchois, J. de phys. et le rad. 4, 61 (1933).
[2] E. Carlsson, Zeits. f. Physik 84, 806 (1933).
[3] Y. Cauchois, J. de phys. et le rad. 4, 320 (1932).

The Magnetic Moment of Caesium Determined from the Hyperfine Structure of the $6p\ ^2P_{\frac{1}{2}}$ State

The hyperfine structure of the line $\lambda 8761.35$ $(6d\ ^2D_{3/2} - 6p\ ^2P_{1/2})$ in the arc spectrum of caesium has been investigated with a Fabry-Perot interferometer. This line shows two components which arise from the $P_{1/2}$ state, the splitting of the $D_{3/2}$ state being too small to observe. The separation obtained, corrected for mutual influence of the components is 0.035 ± 0.001 cm^{-1}. On allowing a ratio of 0.0278 between the interval factors of the $D_{3/2}$ and the $P_{1/2}$ states the separation of the $P_{1/2}$ state becomes 0.037 ±0.001 cm^{-1}. By using this separation and applying Goudsmit's formulas a g value of 0.70 is obtained for caesium.

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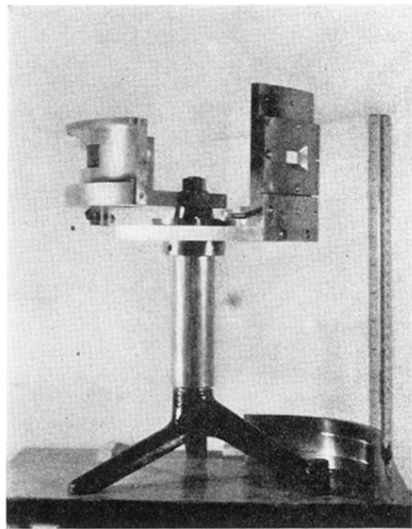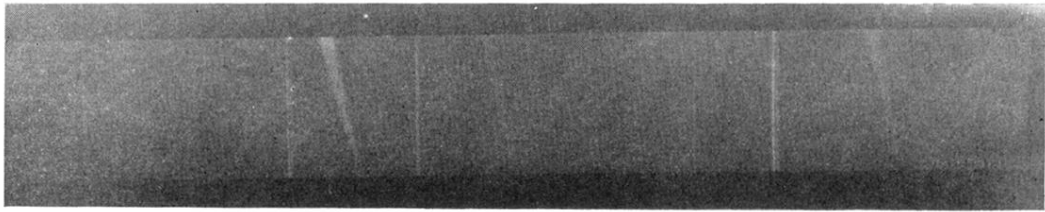University Heights,
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FIG. 2.

FIG. 1.

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