

On the Pressure Broadening in the Gamma Bands of Nitric Oxide*†

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A quantitative reinvestigation of the pressure broadening in the $\gamma(0,0)$ and $\gamma(1,0)$ bands of nitric oxide has established that the pressure effect is not abnormal as has sometimes been supposed and that the collision diameter of the excited NO molecule is approximately 3.8 Å.

THE γ bands of the ultraviolet absorption spectrum of nitric oxide have been the subject of considerable discussion in the literature.¹⁻⁶ Much of the continued interest has centered in the supposed existence of unusually large pressure effects in the $\gamma(0,0)$ band at $\lambda 2268$ and the $\gamma(1,0)$ band at $\lambda 2159$, and in the possibility suggested by Wulf,¹ that these effects may indicate a pressure-induced predissociation of the molecule.

The bands mentioned above have upper levels lying between the two disputed dissociation limits of the ground state of the NO molecule; and therefore if one could show that a radiationless decomposition occurred from those levels, the lower limit would be the correct one. It should be remarked, however, that although predissociation would provide an explanation for abnormal pressure effects, these effects might be due to other causes and are not sufficient proof that the dissociation limit lies below the levels showing pressure broadening. For example the pressure-induced radiationless transitions might take place into a stable state with a broad, shallow minimum.

Lambrey,² who was the first to note a pressure effect in the nitric oxide bands, found that the optical density (negative decilogarithm of the observed transmission) in the γ bands varies as a function of $(lpP^{0.8})$ where l is the cell path length, p the partial pressure of NO, and P the total pressure. He found no such pressure effect for the $\beta(2,0)$ band at $\lambda 2108$ and concluded that the effect observed in the γ bands must be anomalous. He incorrectly concluded that the optical density in the γ bands is *proportional* to $(lpP^{0.8})$. Other workers³ noted this error, and generally support the conclusion that the optical density is proportional to the *square-root* of

(lpP) . In addition, it has been well substantiated^{3,4} that β and δ bands in the vacuum ultraviolet show the same broadening effects as the γ bands.

Naudé⁵ obtained strong qualitative evidence for a large pressure effect with his photographs of nitric oxide at very long optical paths. He found that lines separated by 1 Å appeared sharp initially, but that on addition of 440 mm nitrogen, "every rotational line is broadened so much that the absorption becomes complete." On the other hand, Gaydon and Fairbairn⁶ obtained spectra of nitric oxide at a much shorter optical path which fail to show any significant change in line width on the addition of one atmosphere of nitrogen. They point out that at the long optical path used by Naudé, significant changes in the appearance of the spectrum may arise from the contributions of the wings of the lines, without necessary alteration in the line breadth. In fact, however, a rough calculation shows that it is impossible to reconcile the photographs of Gaydon and Fairbairn with those of Naudé even on this basis.

This communication summarizes some further quantitative measurements which we have made recently in an attempt to determine the collision diameter for the NO molecule.

Carefully purified nitric oxide was examined with a Cary ultraviolet recording spectrophotometer, Model 11M, which gives direct tracings of optical density *versus* wavelength. The optical density was measured for cells from 2.4 to 11.5 cm in length, filled with nitric oxide at pressures from 1 to 100 mm Hg, and nitrogen added at pressures from 0 to 500 mm Hg. For the two bands which were studied, [$\gamma(0,0)$ and $\gamma(1,0)$] it was found that at total pressures above 10 to 15 mm and partial pressures of NO above 8 to 10 mm, the optical density follows roughly the expression $d=C(lpP)^{\frac{1}{2}}$, where C is a constant. If one defines the optical absorbing path by $x=lp$, then $d=C(xP)^{\frac{1}{2}}$. Our values of optical density are in reasonable quantitative agreement with those obtained by Marmo⁴ in those cases where comparison can be made.

To interpret the observed pressure effect in terms of a line width parameter, it is necessary to take into account the limited resolution of the spectrometer (the slit used in our experiments includes 30 or more lines when it is centered on the intensity maximum of the band). The problem essentially is to compute the

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¹ O. R. Wulf, *Phys. Rev.* **46**, 316 (1934).

² M. Lambrey, *Compt. rend.* **189**, 574-575 (1929); **190**, 261-263 (1930); *Ann. phys.* **14**, 95-183 (1930).

³ J. Mayence, *Ann. phys.* **7**, 453-505 (1952).

⁴ R. F. Marmo, Ph.D. dissertation, Harvard (1952).

⁵ S. M. Naudé, *Phys. Rev.* **36**, 333-346 (1930).

⁶ A. G. Gaydon and A. R. Fairbairn, *Proc. Phys. Soc. (London)* **A67**, 474-476 (1954).

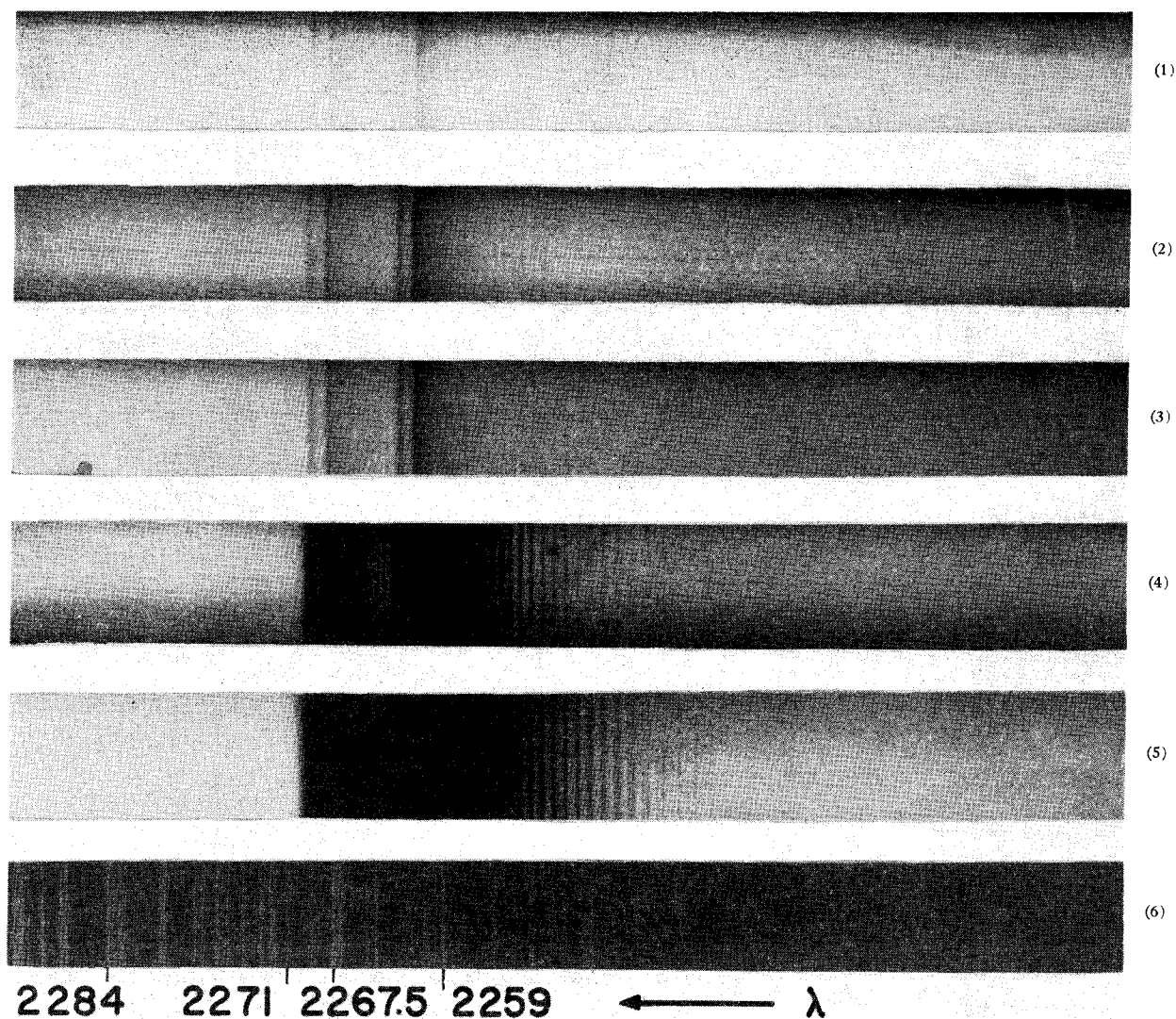


FIG. 1. Nitric oxide, $\gamma(0,0)$ band. Quartz Littrow spectrograph, slit width 0.010 mm. Hydrogen discharge was used as source. Key: (1) Cell length 10.0 cm, nitric oxide pressure 3.3 mm Hg. (2) Cell length 10.0 cm, nitric oxide partial pressure 3.3 mm, nitrogen pressure 675 mm Hg. (3) Cell length 0.053 cm, nitric oxide pressure 603 mm Hg. (4) Cell length 40.0 cm, nitric oxide pressure 47.5 mm Hg. (5) Cell length 40.0 cm, nitric oxide partial pressure 47.5 mm, nitrogen pressure 511 mm Hg. (6) Fe arc comparison. (4) and (5) show appearance of spectra under conditions similar to those in the experiments of Naudé.

integral

$$\int_{-\infty}^{\infty} \rho(\nu - \nu_0) [1 - e^{-X f_t(\nu)}] d\nu,$$

where X is an optical path factor and $f_t(\nu)$ is the true absorption coefficient, obtained by summing contributions from all the individual rotational lines; $\rho(\nu - \nu_0)$ is a weighting function which represents the effect of the slits and prisms and goes rapidly to zero for values of $|\nu - \nu_0|$ larger than a characteristic width. The weighting function used in our calculations was a Gaussian curve with half-width equal to the slit width. The band lines were assumed to have identical contours and half-widths, with spacings and relative intensities calculated from the rotational constants and the Hönl-London

formulas,⁷ respectively. The doublet splitting in the ground state of NO is so large (120 cm^{-1}) that it essentially separates each band into two sub-bands; since in our calculation the frequency setting of the slit was chosen near the band head at $\lambda 2268$, only one sub-band had to be considered. Spin doubling from the upper state and the Λ -type doubling were neglected. Calculations were made only for a single value of ν_0 (chosen at or near the intensity maximum of the band), and for various values of the optical path factor and the line-width parameter. Two sets of calculations were made, first assuming the lines to have pure Lorentz contour, and later assuming a Doppler contour with Lorentz

⁷ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, 1950), p. 205.

contributions.⁸ The first calculations give the asymptotic behavior of the optical density at high pressures, since in that case the contour becomes almost purely Lorentzian in form. However, in the range of pressures and optical paths where the pressure effect is first observed, the assumption of pure Lorentz contour is incorrect, and the less naive model of a combined Doppler-Lorentz contour is necessary to produce the experimentally observed behavior. Unfortunately, due to mathematical difficulties the calculations based on the second model could not be carried much beyond the point where Lorentz broadening begins to become significant, but by interpolation between the two sets of calculations it was possible quantitatively to predict "curves of growth," which portray the calculated optical density as a function of the pressure-broadened line width parameter for constant values of the optical path factor.

These curves reproduce the observed behavior of the optical density as a function of total pressure for constant optical path of nitric oxide. Curves of growth for different optical path factors have the same general shape, but are displaced relative to one another along the abscissa axis as well as the ordinate axis; consequently, an unambiguous matching of theoretical and experimental curves is not possible without more information. A knowledge of the absolute intensity of the $\gamma(0,0)$ band provides the necessary information, since it yields a correlation between the theoretical optical path factors X and the experimental optical paths x . The absolute intensities of some of the γ bands have been measured recently by Weber and Penner.⁹ Using their data it is possible to obtain a determination of line width and hence a collision diameter. The value obtained is 3.8 Å. No estimate of error was made, but probable limits are ± 1 Å.

Since measurements of optical collision diameters in the infrared spectra of NO and CO, and in the broadening of the microwave spectrum of ammonia by NO, CO, and N₂ lead to values of the same order of magnitude, it may be concluded that the pressure broadening in the γ bands is not unusually strong.

Because this conclusion appears to be at variance

with those reached by Naudé, his observations, as well as those of Gaydon and Fairbairn, were repeated using a Bausch & Lomb quartz Littrow spectrograph with a hydrogen discharge as source. Figure 1 shows the photographs obtained. The photographs for the conditions of Gaydon and Fairbairn are very similar to those they obtained. In the experiment repeating the conditions used by Naudé, the optical path of NO was the same as he employed, but the partial pressure of NO was twice as large; this would tend to accentuate the broadening effects. It can be seen in the figure that *the fine structure is not removed even by the addition of 511 mm of nitrogen*, in strong contradiction to Naudé's photograph. There is therefore no remaining evidence for an unusually strong pressure broadening.

It has often been supposed as a rule-of-thumb that the onset of observable pressure effects occurs when the Lorentz half-width becomes comparable with the Doppler half-width. This is indeed the case if the optical path is sufficiently small; but as Gaydon and Fairbairn have pointed out, with greater optical paths the contributions of the line wings become more important and the rule is not valid. The importance of the wings of the γ bands is evident from the calculations. The fact that the $\beta(2,0)$ band at $\lambda 2108$ does not seem to show the pressure effect exhibited by the γ bands arises simply from its very much lower intensity; the effect is the same as though it were being viewed through a much shorter optical path, where the wing contributions are of negligible importance.

The simple theory of Lorentz collision broadening has thus provided an adequate explanation of the pressure broadening effects in the γ bands of nitric oxide, by the application of a detailed analysis to the band structure. While the square-root dependence of the optical density upon total pressure is a general feature of Lorentz collision broadening in spectra with unresolved fine structure, the specific correlation of the line-width parameter with the pressure depends upon the details of the band structure and the resolving instrument. Caution is therefore necessary in the qualitative interpretation of pressure effects in molecular spectra.

ACKNOWLEDGMENTS

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⁸ S. S. Penner and R. W. Kavanagh, *J. Opt. Soc. Am.* **43**, 385-388 (1953).

⁹ D. Weber and S. S. Penner, *J. Chem. Phys.* **26**, 860 (1957).