

Letters to the Editor

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Microwave Absorption in Compressed Oxygen

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THE microwave absorption in O₂, which is the result of the presence of a permanent magnetic dipole, consists of two parts.¹ The resonant contribution, governed by the selection rules $\Delta J = \pm 1$, $\Delta K = 0$ where J is the quantum number for the total angular momentum and K is that for end-over-end rotation, contains a number of lines which, with one exception, lie in the vicinity of 2 cm⁻¹. Although this absorption has been investigated by a number of workers, the nonresonant, or Debye type, contribution corresponding to $\Delta J = 0$, $\Delta K = 0$ has not been the subject of prior investigation. With the aid of the Van Vleck-Weisskopf

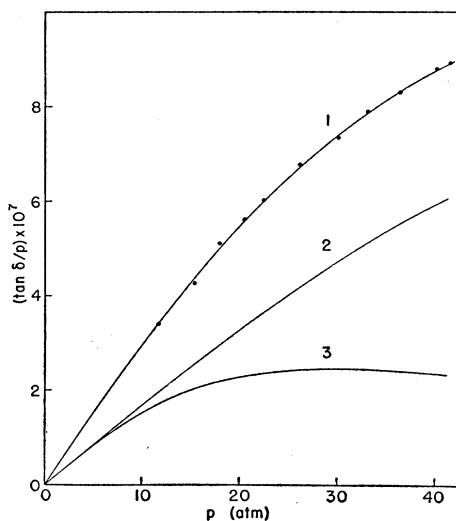


FIG. 1. Data for O₂ at $\nu = 0.778$ cm⁻¹ showing the experimental values of $\tan \delta/p$ (1) and the contribution associated with resonant absorption as derived from the experimental data (2) and from theory (3).

relation² the complete absorption coefficient α (cm⁻¹) is given by

$$\frac{\alpha}{2\pi\nu} = \frac{2\pi N\mu^2}{3kT} \left[\frac{2}{3} \left(\frac{\nu\Delta\nu_d}{\Delta\nu_d^2 + \nu^2} \right) + \sum_{K_{\pm}} \frac{f_{K_{\pm}} |\mu_{K_{\pm}}|^2}{\mu^2} \times \left(\frac{\nu\Delta\nu_{K_{\pm}}}{\Delta\nu_{K_{\pm}}^2 + (\nu - \nu_{K_{\pm}})^2} + \frac{\nu\Delta\nu_{K_{\pm}}}{\Delta\nu_{K_{\pm}}^2 + (\nu + \nu_{K_{\pm}})^2} \right) \right],$$

where $\mu = 0.0262 \times 10^{-18}$ esu, the subscripts K_{\pm} and d refer to the resonant and nonresonant terms, respectively, and the remaining symbols have their usual significance.

Measurements of the absorption were made at 25°C using high- Q resonant cavities at pressures up to 8 atmos for $\nu = 0.0765$ cm⁻¹, and at pressures up to 40 atmos for $\nu = 0.302$ and 0.778 cm⁻¹.

At the lowest frequency, where overlap from the resonant contribution is nearly negligible, the two parameters of the nonresonant term were evaluated. The value of $\tan \delta/p$ (maximum) is $2.9_1 \times 10^{-7}$ atmos⁻¹ and in close agreement with the theoretical value of 2.87×10^{-7} atmos⁻¹. The line breadth parameter $\Delta\nu_d/p$ is 0.017₅ cm⁻¹ atmos⁻¹ and corresponds to an effective collision diameter of 2.6 Å. This value is decidedly smaller than the average value of 4.4 Å effective for resonant absorption³ and also smaller than the kinetic collision diameter of 3.5 Å.

Data obtained at 0.778 cm⁻¹ are shown by curve 1 of Fig. 1. At this frequency substantial contributions arise from both the resonant and the nonresonant terms. Subtraction of the nonresonant part using the above-mentioned parameters gives curve 2. Above 10 atmos this curve lies above that computed for the resonant absorption (curve 3) by summing the contributions of the individual lines using recent data for the line breadth parameters.³ At 40 atmos the value of $\tan \delta/p$ is more than twice that calculated, a discrepancy that is not materially reduced no matter what values are assumed for the resonant and nonresonant line widths. The nature of the discrepancy appears to be analogous to that previously observed for NH₃⁴ and ND₃.⁵ The data can be reconciled with the Van Vleck-Weisskopf line shape only if the resonant frequencies and line breadth parameters are both allowed to decrease with increasing pressure. For example, data at 0.302 cm⁻¹ (not shown) and 0.778 cm⁻¹ require average values of $\Delta\nu_{K_{\pm}}/p$ and $\nu_{K_{\pm}}$ of about 0.025 cm⁻¹ atmos⁻¹ and 0.5 cm⁻¹, respectively, in contrast to the initial values of 0.05 cm⁻¹ atmos⁻¹ and 2.0 cm⁻¹. A detailed report of this work will be published subsequently.

¹ J. H. Van Vleck, *Phys. Rev.* **71**, 413 (1947).

² J. H. Van Vleck and V. F. Weisskopf, *Revs. Modern Phys.* **17**, 227 (1945).

³ J. O. Artman and J. P. Gordon, *Phys. Rev.* **96**, 1237 (1954).

⁴ B. Bleaney and J. H. N. Loubser, *Proc. Phys. Soc. (London)* **A63**, 483 (1950).

⁵ G. Birnbaum and A. A. Maryott, *Phys. Rev.* **92**, 270 (1953).