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Citation: *The Journal of Chemical Physics* **6**, 902 (1938); doi: 10.1063/1.1750186

View online: <http://dx.doi.org/10.1063/1.1750186>

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## A Note on the Raman Spectra of Nitrogen\*

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(Received October 30, 1938)

**F**OLLOWING the successful concentration of the  $N^{15}$  isotope in this laboratory,<sup>1</sup> plates were taken of the Raman spectra of ordinary nitrogen to see if the method could be used to determine the alternating intensity ratio of  $N_2^{15}$ . Although excellent rotational Raman spectra were obtained, it was found that a clear-cut determination of the  $N^{15}$  nuclear spin could not be made in this way because of the greatly increased number of lines that would result from the mixture of three isotopic molecules. However, as the only published values for the ground state rotational transitions of nitrogen are those of Rasetti,<sup>2</sup> it seemed worth while to record the frequency and intensity values obtained.

The Raman tube and mercury arcs used were those described by Teal and MacWood.<sup>3</sup> A Hilger E-1 quartz prism spectrograph, which was

maintained at constant pressure and temperature, and contained mercury vapor to absorb the exciting line Hg,  $\lambda 2537$ , was used to make the exposures. A stream of carbon dioxide was passed between the reflector and Raman tube to prevent the formation of ozone. The slit width was 0.03 mm, and the nitrogen pressure four atmospheres. A strong exposure could be obtained in 20 hours on a rapid plate (Eastman Ortho-Press), but in order to get better resolution a 100-hour exposure was made on a process plate.

The rotation spectrum is shown in Fig. 1, and a microphotometer tracing obtained from it in Fig. 2. The intensity relation for a rotation Raman transition of this type is given by Placzek and Teller<sup>4</sup> as:

$$I = I_0^0 \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)} (2J+1) g_j e^{-(E_{rot.}/kT)} Q,$$

where  $I_0^0$  is the total intensity of the O—O band,  $g_j$  the nuclear spin factor, and  $Q$  the state summation. Intensities could not be measured directly as the plate was not calibrated for this purpose. However, as the darkenings for most of the lines fall on the linear portion of the sensitivity curve, darkenings have been plotted against log intensity (theoretical) with the result shown in Fig. 3. Points for lines too close to Hg  $\lambda 2537$  for intensity measurement, or too faint to lie on the

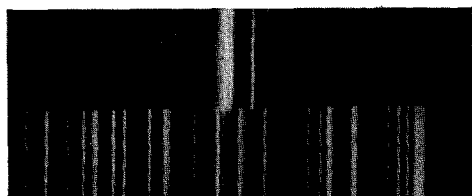


FIG. 1. O—O nitrogen rotation band.

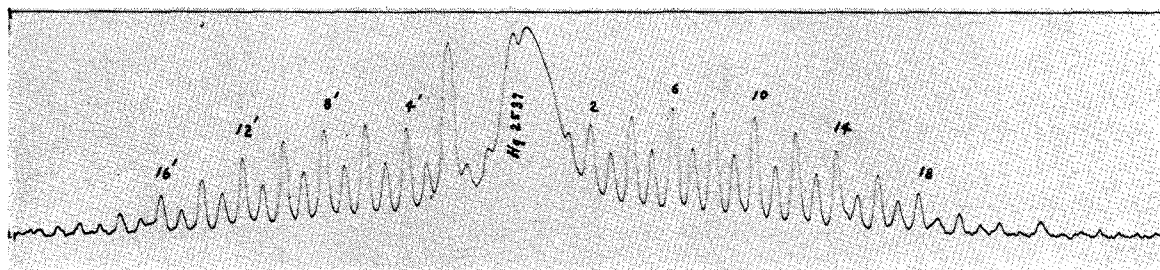


FIG. 2. Microphotometer tracing of nitrogen O—O band.

\* Placzek and Teller, *Zeits. f. Physik* **81**, 209 (1933).

\* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

<sup>1</sup> Thode and Urey, *J. Chem. Phys.*, to be published.

<sup>2</sup> Rasetti, *Proc. Nat. Acad. Sci.* **15**, 515 (1929); *Phys. Rev.* **34**, 367 (1929).

<sup>3</sup> Teal and MacWood, *J. Chem. Phys.* **3**, 760 (1935).

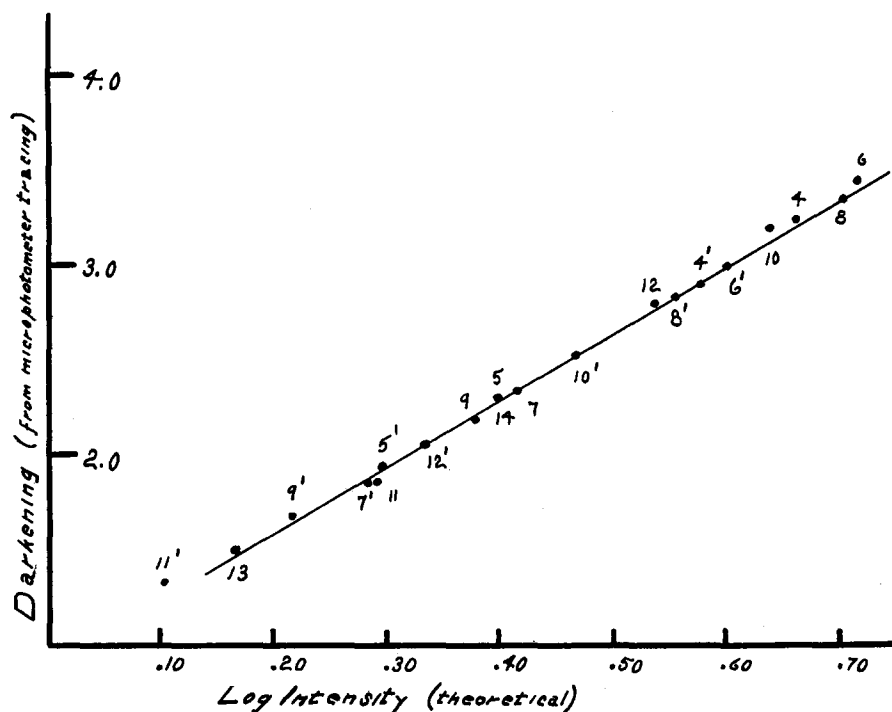


FIG. 3. The figures on the curve give initial  $J$  values for Stokes and Anti-Stokes lines. Primed values refer to Anti-Stokes lines.

linear part of the curve, have been omitted. This would seem to give a good experimental test of the equation of Placzek and Teller. Regardless of the plate characteristics it is seen that the transitions from  $J=5$  and 14, which have the same theoretical intensity, give the same darkening. Measured and calculated intensities for hydrogen have been compared by Raman and Bhagavantam.<sup>5</sup>

The spectrograph has a dispersion of 2.7 Å/mm in the region near  $\lambda 2537$ . Rotational frequency shifts first obtained showed differences between corresponding Stokes and Anti-Stokes lines too large to be accounted for by an error in plate measurement. This was traced to errors as large as 0.02 Å in the values given for the iron arc wavelengths in this region. The final calibration was made using the iron lines of wave-length 2519.628, 2530.694, and 2542.887 Å, given by Meggers and Humphreys<sup>6</sup> to 0.0005 Å, and the results corrected to vacuum. The frequency of Hg  $\lambda 2537$  was taken as  $39412.76 \text{ cm}^{-1}$ , this being

an average value for symmetrically displaced Stokes and Anti-Stokes lines. The values of  $B_0$

TABLE I.

$(J)$	THIS PAPER		RASETTI		CALCULATED $\text{cm}^{-1}$
	STOKES $\text{cm}^{-1}$	ANTI-STOKES $\text{cm}^{-1}$	STOKES $\text{cm}^{-1}$	ANTI-STOKES $\text{cm}^{-1}$	
2	27.8				27.9
3	35.8	35.8			35.8
4	43.7	43.6		44.0	43.8
5	51.7	51.7			51.7
6	59.7	59.8	60.0	59.9	59.7
7	67.7	67.7			67.6
8	75.7	75.6	76.0	76.5	75.6
9	83.7	83.5			83.5
10	91.5	91.3	92.1	91.8	91.5
11	99.3	99.5			99.4
12	107.2	107.3	108.2		107.4
13	115.4	115.6			115.3
14	123.2	123.3	124.2		123.3
15	131.2	131.6			131.2
16	139.1	139.3			139.1
17	146.7	—			147.1
18	154.8	155.0			155.0

$$B_0 = 1.980 \pm 0.002 \text{ cm}^{-1}, \text{ (this paper)}$$

$$B_0 = 1.992 \pm 0.005 \text{ cm}^{-1}, \text{ (Rasetti)}$$

$$0-1 \text{ vibration frequency} = 2328.3 \text{ cm}^{-1}, \text{ (this paper)}$$

$$0-1 \text{ vibration frequency} = 2330.7 \text{ cm}^{-1}, \text{ (Rasetti)}$$

(Calculated values contain a first-order correction term with  $D_e = 5.8 \times 10^{-6} \text{ cm}^{-1}$ .)

<sup>5</sup> Raman and Bhagavantam, Ind. J. Phys. 6, 353 (1931).  
<sup>6</sup> Meggers and Humphreys, Bur. Standards J. Research 18, 543 (1937).

were obtained after adding to each frequency a correction term  $= D_e(4J+6)(3J^2+3J+3)$ , the value of  $D_e$  being obtained theoretically<sup>7</sup> from the vibration frequency as  $5.8 \times 10^{-6} \text{ cm}^{-1}$ . This correction, while somewhat uncertain, amounts

<sup>7</sup> Jevons, Report on Band Spectra of Diatomic Molecules, The Physical Society, (1932) p. 27.

to only  $0.17 \text{ cm}^{-1}$  at  $J=18$ . Measured and calculated values of the rotation frequencies are given in Table I.  $B_0$  was obtained using the value  $0.018 \text{ cm}^{-1}$  for  $\alpha$ , as given by Jevons.<sup>8</sup> The value for the 0-1 vibration frequency was found to be  $2328.3 \text{ cm}^{-1}$ .

<sup>8</sup> See reference 7, p. 284.

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### Correction: On the Paramagnetic Conversion of Parahydrogen and Orthodeuterium in the Presence of Nitrous Oxide (The Magnetic Moment of the Deuteron)

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*Department of Physical Chemistry, The Hebrew University, Jerusalem*  
(J. Chem. Phys. **6**, 260 (1938))

THE title of the article referred to above should have read  
"Nitric Oxide" instead of "Nitrous Oxide."