

PHYSICAL REVIEW LETTERS

VOLUME 21

30 DECEMBER 1968

NUMBER 27

MEASUREMENT OF THE SUBMILLIMETER-WAVE ROTATIONAL TRANSITION OF OXYGEN AT 424 kMc/sec*

J. S. McKnight and Walter Gordy

Department of Physics, Duke University, Durham, North Carolina

(Received 18 November 1968)

The submillimeter-wave rotational transition $N=1 \rightarrow 3, J=2 \rightarrow 2$ of oxygen has been measured at a frequency of $424\,763.80 \pm 0.20$ Mc/sec. The millimeter-wave fine-structure frequencies for the $N=1$ and $N=3$ states have been remeasured with high precision. From the results the rotational constant of oxygen $B_0 = 43\,100.589 \pm 0.022$ Mc/sec has been derived.

With high-precision microwave spectroscopy we have measured the $N=1 \rightarrow 3, \Delta J=0$ rotational transition of molecular oxygen in the 0.71-mm-wave region and have derived the precise value of the rotational constant $B_0 = h/8\pi^2 I_0$. The linewidth was approximately 4 Mc/sec. Figure 1 shows one recording of the line. This observation was made with the oxygen at 77°K in a cylindrical cell, 20 ft long and 2.5 in. in diameter, through which the millimeter waves were focused with horns and dielectric lenses. The submillimeter waves were generated and detected with methods¹ developed earlier in this laboratory.



FIG. 1. Recording of the $N=1 \rightarrow 3, \Delta J=0$ rotational line of O_2 at 424 763.80. The linewidth is approximately 4 Mc/sec.

This represents the first measurement of a rotational transition of O_2 with high-resolution microwave spectroscopy and, so far as we are aware, the only such measurement of a rotational transition of a molecule that does not have an electric dipole moment. However, under very low resolution with infrared spectral methods, with pressures above an atmosphere and with a cell of 180-m length, Gebbie, Burroughs, Robb, and Bird² have observed higher frequency rotational transitions of O_2 . The well-known millimeter-wave spectrum of oxygen is not a rotational spectrum but arises from transitions between the fine structure³ of particular rotational states. Many measurements⁴⁻⁸ of this fine structure have been made, from which values of the rotational constant B_0 and the fine-structure constants λ and γ have been derived. This method of derivation of B_0 , which depends on the perturbation of the fine structure by rotation, is not as accurate as the present one by which B_0 is derived in a more direct way from the rotational spectra. We have been able to reduce the limits of error in B_0 by an order of magnitude.

To make the best use of the observed rotational transitions we have remeasured with greater ac-

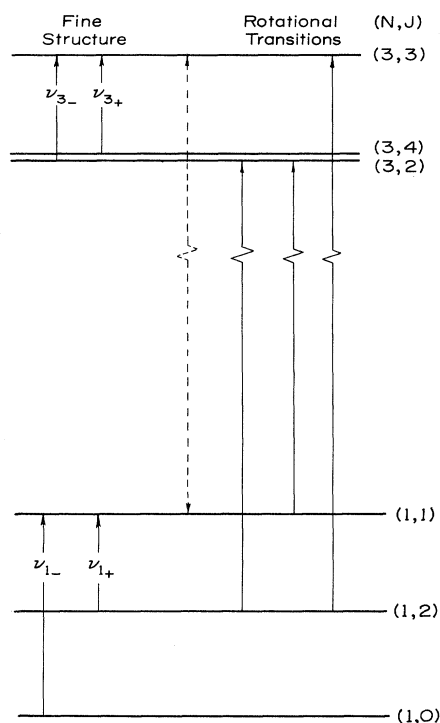


FIG. 2. Energy-level diagram showing observed rotational and fine-structure transitions of O_2 . In this molecule only levels for odd-integral values of the rotational quantum number N occur. The dotted line shows the difference in energy from which the rotational constant B_0 was obtained.

curacy the fine-structure transitions within the $N=1$ and $N=3$ rotational levels. This could be done with ease because the sensitivity of our spectrometer permitted observation of the lines on a cathode-ray oscilloscope. From combination of the results we obtain a direct evaluation of the frequency of separation of the $N=1, J=1$ and the $N=3, J=3$ levels. Since the energy expression for the $N=J$ levels, represented by

$$E(N=J) = B_0 N(N+1) + D_0 N^2(N+1)^2 + H_0 N^3(N+1)^3, \quad (1)$$

does not involve the fine-structure constants, we need to know only the centrifugal distortion constants D_0 and H_0 in order to obtain B_0 from our measurements. These distortion constants have been measured by Babcock and Herzberg⁹ with uv spectroscopy from transitions involving very high rotational states for which the stretching effects are large. Their values,

$$\begin{aligned} D_0 &= (-4.913 \pm 0.020) \times 10^{-6} \text{ cm}^{-1} \\ &= -0.1472 \pm 0.0006 \text{ Mc/sec}, \\ |H_0| &= 0.3 \times 10^{-9} \text{ cm}^{-1} = 0.00009 \text{ Mc/sec}, \quad (2) \end{aligned}$$

Table I. Measured frequencies.

Rotational transitions $N, J \rightarrow N', J'$	Frequency	Fine-structure frequencies
$1, 1 \rightarrow 3, 2$	$368\,499.02 \pm 0.21$	$1_- \quad 118\,750.343 \pm 0.01$
$1, 2 \rightarrow 3, 2$	$424\,763.80 \pm 0.20$	$1_+ \quad 56\,264.778 \pm 0.01$
$1, 2 \rightarrow 3, 3$	$487\,250.05 \pm 0.21$	$3_- \quad 62\,486.255 \pm 0.01$
		$3_+ \quad 58\,446.600 \pm 0.01$

are sufficiently accurate for evaluation of the relatively small centrifugal stretching effects on the lowest rotational transition $N=1 \rightarrow 3$ so that B_0 can be obtained with great accuracy from our measurements. Similar values of the stretching constants, -0.1470 ± 0.001 Mc/sec and 0 ± 10^{-5} Mc/sec, have been obtained from microwave measurement of the fine structure⁷ of high- N levels.

From Eq. (1) the difference in the (1, 1) and (3, 3) energy levels is

$$[E(3, 3) - E(1, 1)]/h = 10B_0 + 140D_0 + 1720H_0. \quad (3)$$

Also, from Fig. 2 the dotted line shows

$$[E(3, 3) - E(1, 1)]/h = \nu(1, 2 \rightarrow 3, 2) - \nu_{1+} + \nu_{3-}. \quad (4)$$

Combining Eqs. (3) and (4) and substituting the frequencies given in Table I with D_0 and H_0 from Eq. (2), we obtain

$$B_0 = 43\,100.589 \pm 0.022 \text{ Mc/sec}.$$

This value of B_0 is in good agreement with the most recent value derived from the fine structure by West and Mizushima,⁸ $43\,100.3$ Mc/sec, but not in very good agreement with the older uv value, $143\,777 \text{ cm}^{-1} = 43\,103.3$ Mc/sec by Babcock and Herzberg.⁹

From Fig. 2 we see that the rotational transitions (1, 1) \rightarrow (3, 2) and (1, 2) \rightarrow (3, 3) are also permitted between $N=1$ and $N=3$. The corresponding transitional frequencies are evaluated from the relation

$$\begin{aligned} \nu(1, 1 \rightarrow 3, 2) &= \nu(1, 2 \rightarrow 3, 2) - \nu_{1+} \\ &= 368\,499.02 \text{ Mc/sec} \end{aligned}$$

$$\begin{aligned} \nu(1, 2 \rightarrow 3, 3) &= \nu(1, 2 \rightarrow 3, 2) + \nu_{3+} \\ &= 487\,250.05 \text{ Mc/sec}. \end{aligned}$$

These values of $\nu(1, 1 \rightarrow 3, 2)$ and $\nu(1, 2 \rightarrow 3, 3)$ can be regarded as experimental values since the sum on the right involves only measured frequencies.

*Work supported by the U. S. Air Force Office of

Scientific Research, Grant No. AF-AFOSR-66-0493A.

¹W. C. King and W. Gordy, *Phys. Rev.* **93**, 407 (1954).

²H. A. Gebbie, W. J. Burroughs, J. A. Robb, and G. R. Bird, *Nature (London)* **212**, 66 (1966).

³M. Tinkham and M. W. P. Strandberg, *Phys. Rev.* **97**, 937 (1955).

⁴J. H. Burkhalter, R. S. Anderson, W. V. Smith, and W. Gordy, *Phys. Rev.* **79**, 651 (1950).

⁵S. L. Miller and C. H. Townes, *Phys. Rev.* **90**, 537

(1953).

⁶M. Mizushima and R. M. Hill, *Phys. Rev.* **93**, 745 (1954).

⁷R. W. Zimmerman and M. Mizushima, *Phys. Rev.* **121**, 152 (1961).

⁸B. G. West and M. Mizushima, *Phys. Rev.* **143**, 31 (1966).

⁹H. D. Babcock and L. Herzberg, *Astrophys. J.* **108**, 167 (1948).

DETECTION OF VIBRATIONALLY EXCITED N₂ BY SUPERELASTIC ELECTRON IMPACT*

P. D. Burrow and Paul Davidovits

Mason Laboratory, Yale University, New Haven, Connecticut

(Received 26 November 1968)

We have observed electrons scattered superelastically from nitrogen molecules vibrationally excited by quenching collisions with optically excited rubidium atoms. Analysis of the energy gained by the electrons shows that in more than 10 % of the quenching collisions the highest energetically allowed vibrational state of N₂, $v=5$, is populated. The relative superelastic cross section for collisions between molecules in this state and electrons is measured and compared with that predicted by detailed balance.

In a superelastic collision, an electron colliding with an excited atom or molecule gains kinetic energy and leaves the atom or molecule in a lower energy state. This process has been studied with excited mercury¹ and more recently in excited rubidium.² In the present experiment, superelastic electrons are observed from collisions with vibrationally excited N₂ molecules in their ground electronic state. This technique should prove useful in the study of collisional processes involving vibrationally excited molecules, in particular homonuclear molecules, which are difficult to detect because of the absence of infrared emission.

In this experiment, vibrationally excited N₂ is produced by the quenching of optically excited Rb vapor. Rubidium resonance radiation is incident on a collision chamber containing Rb vapor and N₂. A fraction of the excited Rb(²P_{1/2, 3/2}) atoms produced by photon absorption collide with N₂ and are quenched with high efficiency.³ As a result of the quenching, vibrationally excited N₂ is produced. A low-energy electron beam is passed through the collision chamber, and those electrons making superelastic collisions are analyzed. Preliminary information is obtained on the transfer of Rb electronic energy into vibrational energy of N₂.

The apparatus, which is shown in Fig. 1, has been previously described¹ and only a brief discussion is given here. Plates S₁ through S₅ form an electron gun which may be operated in the re-

tarding-potential-difference mode.⁴ Typical electron beam currents of 5×10^{-8} A with a resolution of 0.2 eV at half-maximum are used. The electron beam is collimated by a uniform axial magnetic field of 180 G. A retarding voltage may be applied to electrode S₇, to analyze the energy of the electrons. The electron current transmitted past the retarding plate is collected at EC and measured with a vibrating-reed electrometer.

The collision chamber is surrounded by a concentric quartz cylinder which admits Rb resonance radiation at 7800 and 7948 Å from three low-pressure Osram arc lamps positioned around the cylinder. The lamps are modified to include

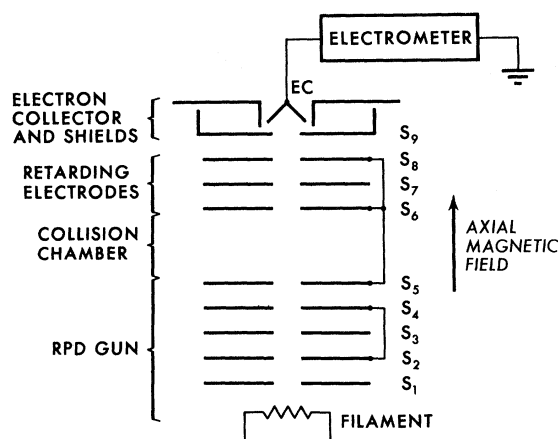


FIG. 1. Schematic diagram of the electron gun.