

Spectra Induced by H⁺ Impact on O₂[†]

R. H. HUGHES AND D. K. W. NG

Physics Department, University of Arkansas, Fayetteville, Arkansas

(Received 10 July 1964)

Spectra induced by 5- to 130-keV H⁺ impact on O₂ have been observed in the visible region. Principal features are O₂⁺, O⁺, and hydrogen Balmer emissions. Absolute cross sections have been determined for excitation of the (0,0), (0,1), (1,0), (2,0), (3,1), and (2,1) bands of the b⁴Σ—a⁴Π first negative system of O₂⁺. Cross sections for populating the v=0, 1, 2, and 3 levels of the b⁴Σ state of O₂⁺ have been estimated. Cross sections for exciting some O_{II} lines have also been determined.

I. APPARATUS

IN the spectral analysis, a JaCo 82-000 500-mm Ebert spectrometer with an EMI 6095B photomultiplier is used. The apparatus has previously been described.¹ The O₂ was obtained from Liquid Carbonics Division of General Dynamics with a specified purity of 99.6%. N₂ appeared in the collision chamber as a contaminant. The N₂ content varied with the condition of the gas supply system. The contaminant did not affect the results within experimental error. A maximum of 1% of N₂ was tolerated.

II. ANALYSIS

Figure 1 shows a spectrogram obtained for 20-keV H⁺ impact. The principal features are seen to be O₂⁺ first negative bands, O⁺ radiation and the hydrogen Balmer emissions. Measurements were made in the 1 μ–5 μ (Hg) pressure range where the emissions were linear with pressure.

Analysis of the O₂⁺ emissions required a more complicated procedure than that for the atomic radiation. The O₂⁺ bands cover relatively large spectral regions and require an integration procedure in order to obtain the photon yield for a given band. Further, some bands overlap, and under insufficient resolution a procedure must be adopted to separate the composite band into its parts.

Figure 2 shows the four principal spectral regions of the O₂⁺ emissions. By knowing the position of the band heads and assuming the contour of the rotational structure, it is possible to synthesize the masked band. Measurement of the area under the composite curve and under the synthesized curve of the masked band allows the determination of the relative contribution of the component bands to the total photon yield in the spectral regions being studied.

Integration of the spectral area was accomplished by a step-wise process. The spectrometer slits were set for a spectral slit width of 25 Å. The photon yield within a 25-Å interval was measured at a particular wave length. The grating was then moved through 25 Å and the photon yield again measured. This procedure required

about five measurements per spectral region. It was determined that the relative rotational structure did not change appreciably with proton energy. The integration was performed at a single energy (20 keV) where the band cross sections were related to the intensity maximum (within a 25-Å interval) of the corresponding spectral region. The excitation function (intensity versus energy) was established for the intensity maxima. These excitation functions were then transformed into the cross-section curves for the various bands shown in Fig. 3.

It is possible to estimate the cross section for populating various vibrational levels in the b⁴Σ state under the assumption that the b⁴Σ—a⁴Π transition is the only mode of decay for the b⁴Σ state. (We have been unable to find any other reported mode.)

We then can write

$$\sigma_{v'v''} = \sigma_{v'} (P_{v'v''} / \sum_{v''} P_{v'v''}),$$

where $\sigma_{v'v''}$ is the cross section for $v' \rightarrow v''$, $\sigma_{v'}$ is the

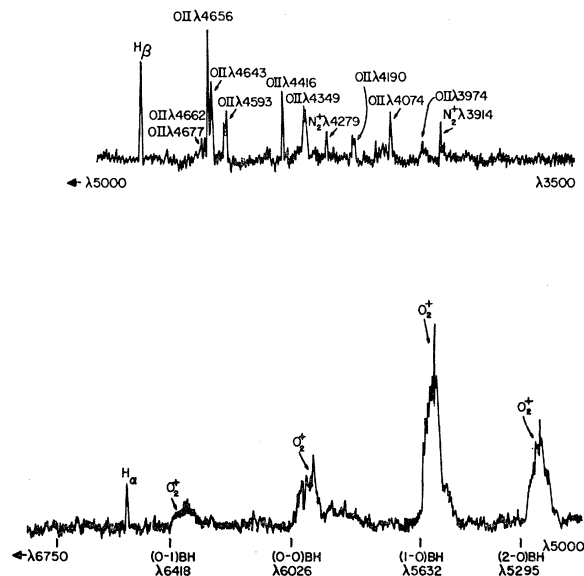


FIG. 1. Spectrum obtained from 20-keV H⁺ impact on O₂. Spectrometer scanned at 250 Å/min with a spectral slit width of 4 Å. Gas pressure was 2.1 μ (Hg) while the beam current was 3.5 μA.

[†] Work supported by the National Science Foundation.

¹ R. H. Hughes, S. Lin, and L. L. Hatfield, Phys. Rev. **130**, 2318 (1963).

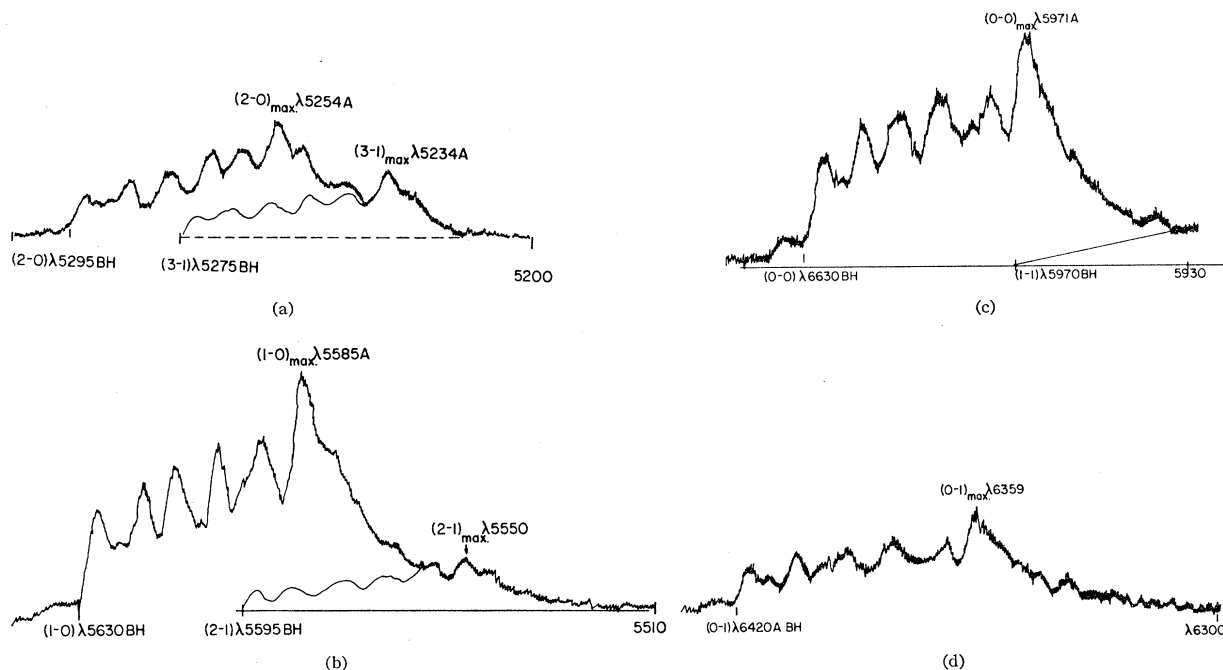


FIG. 2. O₂⁺ first negative bands scanned at 20 Å/min (a) (2,0) and (3,1) bands, spectral slit 3.2 Å; (b) (1,0) and (2,1) bands, slit 3.2 Å; and (c) (0,0) band, slit 4 Å; and (d) (0,1) band, slit 4 Å.

cross section for populating the v' state, $P_{v'v''}$ is the $v' \rightarrow v''$ transition probability, and $(\sum_{v''} P_{v'v''})^{-1}$ is the mean life of the $b^4\Sigma$ state. Under the assumption that the Franck-Condon principle holds,

$$\sigma_{v'v''} = \sigma_{v'} (\nu_{v'v''}^3 q_{v'v''} / \sum_{v''} \nu_{v'v''}^3 q_{v'v''}),$$

where $\nu_{v'v''}$ is the transition frequency and $q_{v'v''}$ is the Franck-Condon factor. The Franck-Condon factors have been calculated for this electronic transition by

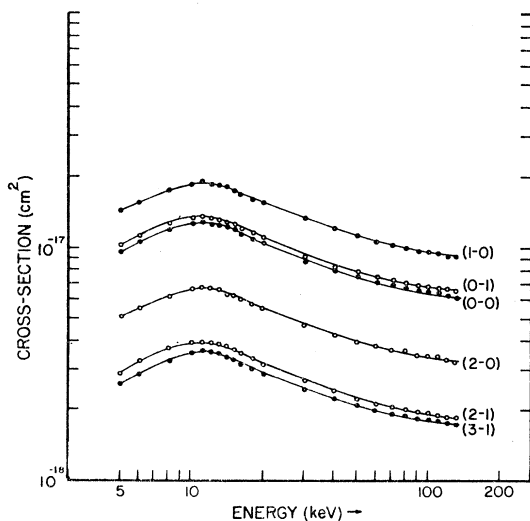


FIG. 3. O₂⁺ first negative band cross sections.

Jarman *et al.*² Using the frequencies calculated by using the band-head wavelengths, the proper branching ratios were determined. The sum over v'' was carried out to a sufficiently high v'' . The estimated cross sections for populating the $v=0, 1, 2,$ and 3 levels of the $b^4\Sigma$ state are shown in Fig. 4. The $v=0$ curve was established by

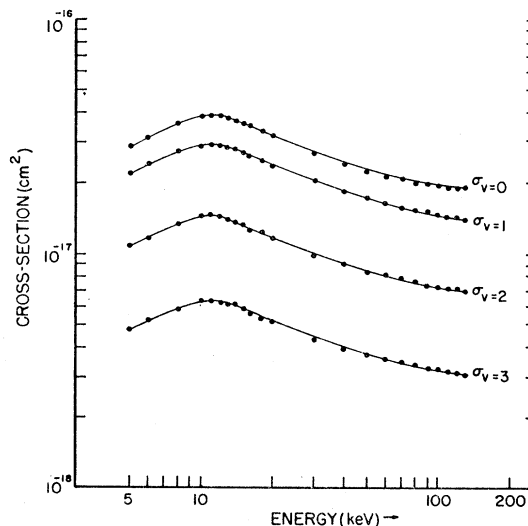


FIG. 4. Estimated cross sections for populating the $v=0, 1, 2,$ and 3 vibrational levels of the $b^4\Sigma$ state of O₂⁺.

² W. R. Jarman, P. A. Fraser, and R. W. Nicholls, *Astrophys. J.* **122**, 55 (1955).

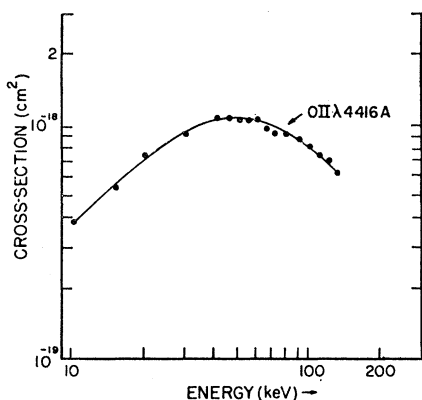


FIG. 5. Cross sections for exciting the $3s\ ^2P_{3/2,1/2} - 3p\ ^2D_{5/2,3/2}$ ($\lambda\lambda 4415\ \text{\AA}$, $4417\ \text{\AA}$) transitions in O^+ .

taking the average of the $v=0$ determinations from the (0,0) and (0,1) data. The two values were the same to within 5%. This is an indication of the accuracy of the

relative values of the calculated Franck-Condon factors. Cross sections were measured for the $O_{II}\lambda 4416\text{-}\text{\AA}$ lines ($3s\ ^2P_{3/2} - 3p\ ^2D_{5/2}$, $\lambda 4415\ \text{\AA}$ and $3s\ ^2P_{1/2} - 3p\ ^2D_{3/2}$, $\lambda 4417\ \text{\AA}$). The two components were not resolved. These measurements are shown in Fig. 5.

We took some relative measurements of other O_{II} emissions at 20 and 100 keV at reduced slit widths so that the measurements were on completely resolved lines. Relative to the $\lambda 4416\text{-}\text{\AA}$ lines, the cross sections for the $3s\ ^4P_{5/2} - 3p\ ^4D_{7/2}$ ($\lambda 4649\ \text{\AA}$), $3s\ ^4P_{3/2} - 3p\ ^4D_{1/2}$ ($\lambda 4674\ \text{\AA}$), and $3s\ ^4P_{3/2} - 3p\ ^4D_{3/2}$ ($\lambda 4662\ \text{\AA}$) transitions are 1.7, 0.2₆, and 0.3₅, respectively.

Cross-section measurements were made on the H_α and H_β emissions. We postpone the reporting of these radiations until we have developed the technique for experimentally treating the radiation from fast hydrogen atoms. However, these emissions are about the same as those reported³ for H^+ on N_2 .

³ J. L. Philpot and R. H. Hughes, *Phys. Rev.* **133**, A107 (1964).

Molecular-Beam Magnetic-Resonance Studies of the Nitrogen Molecule*

SUNNEY I. CHAN,† MILTON R. BAKER,‡ AND NORMAN F. RAMSEY

Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts

(Received 30 June 1964)

The radio-frequency spectra corresponding to the reorientations of the N^{15} nuclear moment and the molecular rotational magnetic moment have been studied in N_2^{15} by the molecular-beam magnetic-resonance method. A magnetic-resonance molecular-beam apparatus with an electron-bombardment detector was used for the experiments. In order to study these small moments, very narrow multiple slits were employed. The intensity of the molecular beam was maintained at the normal level through the use of multiple beams. From an analysis of the N^{15} resonance, the magnitude of the spin-rotational constant for the N^{15} nucleus was determined to be 22 ± 1 kc/sec. This result can be shown to be consistent with available nitrogen chemical-shift data when the sign of the spin-rotational constant is positive. The magnitude of the rotational magnetic moment was found to be 0.2593 ± 0.0005 nuclear magnetons per rotational quantum number.

I. INTRODUCTION

CONSIDERABLE progress has been made in recent years in the field of molecular beam spectroscopy. Much of this progress is the consequence of the development and improvement of the electron bombardment detector.¹⁻⁴ Within our laboratories, a recently

constructed molecular beam magnetic resonance apparatus incorporating an improved electron-bombardment detector has greatly widened the scope of molecules to which this technique can be applied.⁴⁻⁷ In this paper, we wish to report the application of this molecular beam apparatus towards a study of the Zeeman hyperfine structure of the nitrogen molecule.

Molecular beam spectroscopy is an important tool towards the determination of certain interaction constants in the molecular hyperfine Hamiltonian. In particular, due to the collision-free conditions of a molecular beam, the method is suitable for the determination of those molecular or interaction constants, such

* Work supported by the National Science Foundation and the joint program of the U. S. Office of Naval Research and the U. S. Atomic Energy Commission.

† National Science Foundation Postdoctoral Fellow, 1960-61; Present address: Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California.

‡ Present address: Department of Physics, The Johns Hopkins University, Baltimore, Maryland.

¹ G. Wessel and H. Lew, *Phys. Rev.* **90**, 1 (1953).

² W. E. Quinn, A. Pery, J. M. Baker, H. R. Lewis, N. F. Ramsey, and J. T. LaTourrette, *Rev. Sci. Instr.* **29**, 935 (1958).

³ W. E. Quinn, J. M. Baker, J. T. LaTourrette, and N. F. Ramsey, *Phys. Rev.* **112**, 129 (1958).

⁴ M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, *Phys. Rev.* **121**, 807 (1961).

⁵ H. M. Nelson, J. A. Leavitt, M. R. Baker, and N. F. Ramsey, *Phys. Rev.* **122**, 856 (1961).

⁶ J. A. Leavitt, M. R. Baker, H. M. Nelson, and N. F. Ramsey, *Phys. Rev.* **124**, 1482 (1961).

⁷ N. F. Ramsey, *Am. Scientist* **49**, 509 (1961).