Electronic excitation in collisions of H and H^+ with O_2 †

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The 115–750-nm radiation produced in collisions of 1.5–25-keV H^+ and H with O_2 has been studied in an atomic-beam experiment under thin-target conditions. For both ion and neutral impact, the ($b\ ^4\Sigma_g^-$-$a\ ^4\Pi_u$) first-negative ($1N$) and ($A\ ^2\Pi_u$-$X\ ^2\Sigma_g^+$) second-negative ($2N$) band systems of O_2^+ are the most intense spectral features. Also observed are several emissions from excited states of O and O^+. Relative cross sections for individual bands of the O_2^+ $1N$ system, obtained by deconvolution of overlapped features in several vibrational sequences, were used to show that the vibrational population $P(v')$ for O_2^+ $b\ ^4\Sigma_g^-$ formed in both H^+ and H impact is in good agreement with the predictions of a simple Franck-Condon mechanism over the 2–25-keV energy range. Total cross sections for formation of O_2^+ $b\ ^4\Sigma_g^-$ in H^+ and H impact, determined from the latter results by normalization to previous proton-impact data, are in good agreement with values calculated via application of the semiempirical procedure developed recently by Edgar *et al*. For both projectiles the semiempirical approach gives a good prediction of the energy dependence and an adequate prediction of the magnitude of the cross sections for formation of O_2^+ $A\ ^2\Pi_u$ determined by integration of measured $2N$ band intensities.

I. INTRODUCTION

The interaction of precipitating protons with molecular oxygen in the Earth's auroral-zone atmosphere leads to the emission of band systems of O_2^+.[1] Nonetheless, very little work has been reported[2] on heavy-particle excitation of O_2 in the low-keV energy range in which, according to recent measurements, the majority of the precipitating hydrogen flux is found. At these low energies, electron capture and stripping collisions convert the incident flux to a charge-equilibrated mixture in which atomic hydrogen is the dominant component. Therefore, cross sections for electronic excitation of an O_2 target by both H and H^+ are required for hydrogen auroral analysis, but we are unaware of previous reports of excitation of O_2 by H impact. Several groups have, however, studied excitation in H^+ impact on O_2.[3–7]

In this paper we present the first determination of cross sections for hydrogen atom excitation of the O_2^+ ($b\ ^4\Sigma_g^-$-$a\ ^4\Pi_u$) first-negative ($1N$) bands and the O_2^+ ($A\ ^2\Pi_u$-$X\ ^2\Pi_g$) second-negative ($2N$) bands. Also reported are cross sections for excitation of these features in proton impact. The vibrational distribution of O_2^+ $b\ ^4\Sigma_g^-$ formed in H^+ and H impact is determined and compared with the predictions of a simple Franck-Condon excitation mechanism. In addition, total cross sections for formation of O_2^+ in the A and b states have been determined. Brief accounts of this work have been given elsewhere.[8,9]

In addition to providing data required for hydrogen auroral analysis, our experiments make possible further tests and refinements[1] of a semiempirical procedure recently developed[10] to predict H^+ and H impact excitation cross sections via scaling of electron-impact data. It is hoped that the development of this procedure, which relies partially on the systematics observed in heavy-particle as well as electron-impact collision phenomena, will allow us to circumvent the need for difficult *ab initio* calculations and allow us to predict excitation cross sections for unstable species such as atomic oxygen that are difficult to study in the laboratory.

II. EXPERIMENTAL

The apparatus and experimental techniques used in this study are described in detail in Ref. 11. Radiation emitted in the 115–750-nm interval during the impact of a beam of protons or hydrogen atoms on O_2 was analyzed with a 0.3-m vacuum monochromator.

For studies in the 200–500-nm range, the monochromator was equipped with a 2400-groove/mm plane grating blazed at 300 nm, giving a reciprocal dispersion of 1.33 nm/mm, and the analyzed light emerging from the exit slit was focused onto the cathode of an EMI 6256S photomultiplier which was chilled to −74 °C. For measurements at longer wavelengths, a 1200-groove/mm plane grating blazed at 750 nm was used, and the light was detected with EMI 9658R PM tube cooled to −25 °C. To reduce the interference from radiation at shorter wavelengths in the latter configuration owing to higher-order spectra and scattered light, a Corning 3-69 color filter could be placed between the condensing lens and the entrance slit. However, except for behavior associated with cut-on properties, no difference was observed between spectra

taken with and without the color filter. Several spectral scans were carried out in the 115–230-nm interval employing a magnesium-fluoride-coated 2400-groove/mm plane grating blazed at 150 nm and an EMR 542F-08 photomultiplier.

Single-photon–counting techniques were employed. Beam currents were measured with a digital charge integrator, and a differential-capacitance manometer was employed in target-pressure measurements. The digitized outputs from these experiments were recorded on magnetic tape for computer analysis. Matheson research-grade O_2 was used without further purification.

III. RESULTS

Scans over the vacuum uv region of the spectrum excited by H^+ and H impact on O_2 indicate the absence of molecular emission features at wavelengths below the onset of the O_2^+ $1N$ system at $\approx$187 nm. In particular, the O_2^+ $c\,^4\Sigma_u^- - b\,^4\Sigma_g^-$ Hopfield band system is not observed. Ignoring the variation of spectral sensitivity with wavelength, the observed intensity of the 130.4-nm O I ^3P-$^3S^\circ$ resonance line excited by 12.5-keV H^+ impact on O_2 is approximately twice that of H Lyman-α (L_α) at 121.6 nm and roughly an order of magnitude greater than the intensity of the 135.6-nm O I ^3P-$^5S^\circ$ feature. Therefore reference to our earlier L_α measurements[2] for H^+ collisions with O_2 indicates that the cross sections for excitation of these O I features by 12.5-keV protons are about 6×10^{-17} and 6×10^{-18} cm^2, respectively.

A. O_2^+ $b\,^4\Sigma_g^-$

Figure 1 shows the emission spectrum in the 490–750-nm wavelength range owing to impact of 20-keV protons on molecular oxygen. In this experiment, which was conducted in the *survey-scan mode*, the grating was positioned at fixed wavelength, and data were taken until either a preset amount of time had elapsed or a preset number of photon counts had been accumulated. The grating was then stepped to the next position in a wavelength increment smaller than the bandpass, and a new cycle was initiated. The spectral data are presented as a histogram, with the width of each bar denoting the wavelength step size.

The most intense features in this wavelength interval are the several sequences of the O_2^+ ($b\,^4\Sigma_g^- - a\,^4\Pi_u$) first-negative ($1N$) system. Also observed are a weak O I line at 615.7 nm and the Doppler-shifted Balmer-α (H_α) line of atomic hydrogen; however, the experimental configuration that we have employed is not suitable for the determination of H_α cross sections.[2]

Preliminary experiments were performed to ensure that our cross-section measurements would be uninfluenced by potential systematic errors.[12] At several beam energies in the 2–25-keV interval, the dependence of the count rate for the O_2^+ $1N$ bands on O_2 pressure was determined in order to demonstrate the absence of secondary collision effects such as contamination of the parent beam via charge-exchange collisions, production of O_2^+ $b\,^4\Sigma_g^-$ by secondary electrons, and collisional quenching of the b state of O_2^+ by O_2. With the O_2 pressure maintained below that at which secondary effects are important, it was then shown that the intensity of the O_2^+ $1N$ bands varied linearly with H^+ or H beam current. It was also demonstrated that the results for hydrogen atom impact are independent of both the gas used to neutralize the proton beam and the strength of the electric field used to deflect unneutralized H^+ and to quench metastable excited H atoms.

Most measurements of the radiative lifetime of the $v'=0$–2 levels of O_2^+ $b\,^4\Sigma_g^-$ have yielded results on the order of 1.2 μsec.[13] Since a thermal energy O_2^+ ion would travel only ~0.5 mm during this interval, the overwhelming majority of the excited ions would, in the absence of collisional quenching effects, radiate within the field of view of the monochromator. Copeland has recently reported[14] the O_2^+ b-state lifetime to be 170 nsec for $v'=0$–7, and, if this shorter lifetime were correct, the argument that O_2^+ $b\,^4\Sigma_g^-$ radiates before leaving the field of view of the monochromator would be strengthened; however, Copeland attributed the previously reported longer lifetime values to cascade from the $c\,^4\Sigma_u^-$ state. A careful search of our spectra excited by both H^+ and H impact on O_2

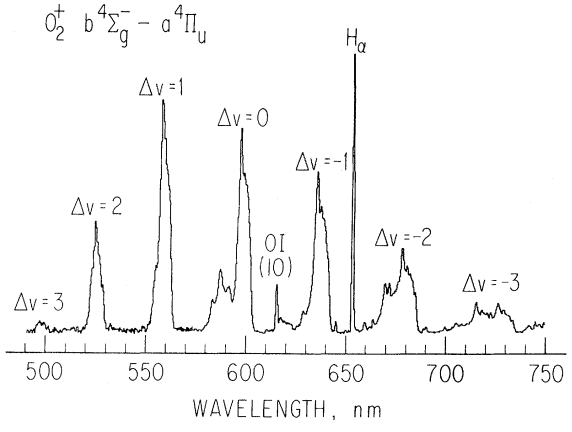

FIG. 1. Emission spectrum excited by 20-keV H^+ impact on O_2 taken at 1.0-nm bandwidth with 0.4-nm step size. No correction has been made for the variation of spectral sensitivity with wavelength.

failed to observe the 194.0–236.3-nm $c\,^4\Sigma_u^- - b\,^4\Sigma_g^-$ Hopfield band system.[15] From this negative result it can be shown that no more than ~2% of the O_2^+ $b\,^4\Sigma_g^-$ formed in our experiments results from cascade via the $c\,^4\Sigma_u^-$ state. Values of the cross section for quenching of O_2^+ $b\,^4\Sigma_g^-$ reported in the literature[14,16] range from 7.5×10^{-15} to 2×10^{-14} cm^2. Although the *absolute values* of the quenching cross sections would have to be revised if the shorter radiative lifetime were adopted, no reinterpretation is required to calculate the *ratio*, inferred from any one of these works, of the time between quenching collisions at a given O_2 density to the radiative lifetime. Using the 2×10^{-14}-cm^2 value of the quenching cross section (which had been derived[16] using a 1.2-μsec radiative lifetime) in a worst-case calculation, the radiative lifetime is about 70 times shorter than the time between quenching collision at an O_2 pressure of 5×10^{-4} Torr, which was typical of that used in cross-section measurements. Therefore, collisional quenching of O_2^+ $b\,^4\Sigma_u^-$ can be ignored under our experimental conditions.

No experimental measurement of an O_2^+ $1N$ emission cross section has yet been carried out in which the signal-to-noise ratio was good enough to allow resolution of the overlapping emissions from neighboring members of the sequences. Furthermore, currently available high-resolution-intensity data are not of sufficient accuracy to rigorously test recent calculations[17] of the rotational line strengths of the complex O_2^+ $1N$ system. It was therefore decided to adopt an approach outlined in Fig. 2 for the $\Delta v=1$ sequence in order to determine the contributions from individual bands. In this method, which was first used by Hughes and Ng[3] and was later employed by other workers,[5,18] one first obtains a reasonably high-resolution scan over a particular sequence. The solid curve in Fig. 2 was obtained in such a scan, and represents the sum of contributions from the (2, 1) and (1, 0) components of the $\Delta v=1$ sequence for 20-keV H^+ impact. It was assumed that the band shapes of these two components are identical, and that the peaks at 555.0 and 558.4 nm represent the same feature in the (2, 1) and (1, 0) bands, respectively. The 3.4-nm offset in position of these features is in good agreement with the spacing between the heads of the (2, 1) and (1, 0) bands, which occur at 559.8 and 563.2 nm, respectively.[19] The contribution from the (2, 1) band, indicated by the dashed curve in Fig. 2, was estimated by shifting the sequence 3.4 nm and normalizing the dashed and solid curves near 555 nm. The area under this curve was then subtracted from the total area under the sequence to give the contribution from the (1, 0) band.

The ratio $\sigma(559.8)/\sigma(563.2)$ of the cross sections for production of the (2, 1) and (1, 0) $1N$ bands is equal to the ratio of the areas under these features, and this information can be used to calculate the ratio $\sigma(v'=2)/\sigma(v'=1)$ of the cross sections for formation of O_2^+ $b\,^4\Sigma_g^-$ with $v'=2$ and $v'=1$ in the following manner. The cross section $\sigma(v')$ for formation of an electronically excited species in vibrational level v' can be calculated from the cross section $\sigma(\lambda_{v'v''})$ for production of the (v', v'') band through the relationship

$$\sigma(v') = \sigma(\lambda_{v'v''})/R_{v'v''}, \tag{1}$$

where the branching ratio $R_{v'v''}$ is related to the transition probabilities $A_{v'v''}$ as

$$R_{v'v''} = A_{v'v''}/\Sigma_v A_{v'v}. \tag{2}$$

The transition probability is in turn defined as

$$A_{v'v''} = q_{v'v''}\nu^3_{v'v''}R_e^2(\bar{r}_{v'v''}), \tag{3}$$

where $q_{v'v''}$ is the Franck-Condon factor, $\nu_{v'v''}$ is the band origin, $R_e(\bar{r}_{v'v''})$ is the electronic transition moment, and $\bar{r}_{v'v''}$ is the r-centroid of the $v'v''$ transition. Values of $A_{v'v''}$ for the O_2^+ $1N$ system were taken from Ref. 20(a).

Extension of this analysis to the other sequences of the O_2^+ $1N$ system shown in Fig. 1 allows the determination of the complete vibrational distribution $P(v')$ for O_2^+ $b\,^4\Sigma_g^-$. Values of this quantity, which is defined as

$$P(v') = \sigma(v')/\Sigma_v\sigma(v), \tag{4}$$

are given in Table I. Repeating this analysis at several energies in the 2–25-keV range for both

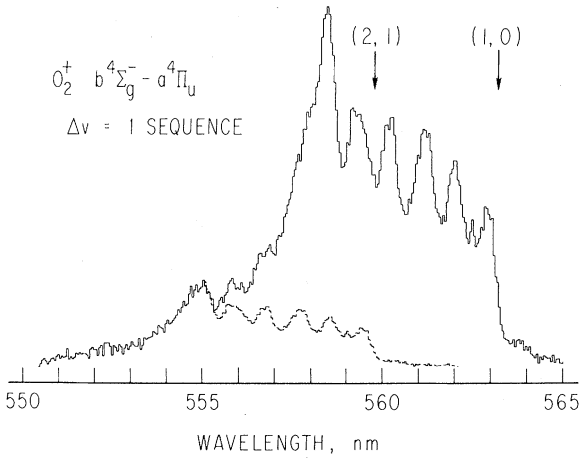

FIG. 2. Deconvolution of the O_2^+ $(b\,^4\Sigma_g^- - a\,^4\Pi_u)$ $\Delta v=1$ sequence excited by 20-keV protons. The solid curve, which gives the primary data, was recorded at 0.4-nm bandpass with 0.05-nm step width. The dashed curve gives the contribution from the (2, 1) band, and the arrows indicate the band origins for the labeled transitions.

H^+ and H projectiles demonstrated that, within an experimental uncertainty of ±10%, the vibrational distribution of $O_2^+ b\,^4\Sigma_g^-$ formed in proton impact is identical to that produced in H atom bombardment and is independent of the collision energy in this interval. Analysis of previously published cross-section data[3-5] for H^+ impact on O_2 yields values of $P(v')$ in good agreement with our results.

Inspection of Table I shows that the measured vibrational distribution of $O_2^+ b\,^4\Sigma_g^-$ is in excellent agreement with the distribution $P_{FC}(v')$ calculated by assuming that $P(v')$ is proportional to the Franck-Condon factor for ionization of an isolated $X\,^3\Sigma_g^-$ oxygen molecule in its $v=0$ level to yield $O_2^+ b\,^4\Sigma_g^-$ in vibrational level v'.

Having established the energy independence of the vibrational distribution at several selected energies, the total relative cross section for excitation of the $\Delta v=1$ sequence was determined at a number of energies in the 2–25-keV range by scanning over this sequence in an *integration mode*, in which the grating was advanced in wavelength step size equal to the bandpass. The contribution from the (1,0) $1N$ band was determined using the procedure described above, and the resulting cross sections $\sigma_p(563.2)$ and $\sigma_a(563.2)$ for excitation of this band in proton and hydrogen atom impact, respectively, are shown in Fig. 3. Our results were made absolute by normalization of the H^+ measurements to the earlier proton-impact data of Hughes and Ng.[3] The values of $\sigma(563.2)$ shown in Fig. 3 were used in conjunction with the branching ratio R_{10} and the probability $P(1)$ in Table I to calculate the total cross section $\sigma_p(b\,^4\Sigma_g^-)$ and $\sigma_a(b\,^4\Sigma_g^-)$ for formation of $O_2^+ b\,^4\Sigma_g^-$ in H^+ and H impact given in Table II.

The *relative* error in $\sigma_p(563.2)$ is estimated to be $\leq 12\%$ based on a random propagation of a $\leq 7\%$ uncertainty in the cross section for the $\Delta v=1$ sequence and a $\leq 10\%$ uncertainty in the ratio $\sigma_p(559.9)/\sigma_p(563.2)$. The former includes contributions from errors in measurement of the beam current and photomultiplier counts as well as from nonlinearities in measurement of the O_2 pressure in the scattering chamber. Uncertainties in the secondary electron emission coefficient used to calculate the H beam flux introduce an additional relative error of about 10% in $\sigma_a(563.2)$. The largest source of error in the absolute value of the cross sections is the uncertainty of $\leq 40\%$ in the data to which our results were normalized.

At low energies, uncertainties in the parent beam energy could lead to modest errors in the shape of the rapidly changing cross-section curve. It has been shown[21] that the mean energy of the beam produced by rf ion sources similar to the one used in our experiments can exceed the applied extraction potential by 100–400 eV. Taking a value of 250 eV as representative of the energy

TABLE I. Relative vibrational distribution of $O_2^+ b\,^4\Sigma_g^-$ produced by 2–25-keV H^+ and H impact on O_2.

	$P(v')$	
v'	Measured	Franck-Condon
0	0.40±0.04	0.42±0.03
1	0.37±0.04	0.35±0.03
2	0.16±0.016	0.17±0.009
3	0.072±0.010	0.064±0.004

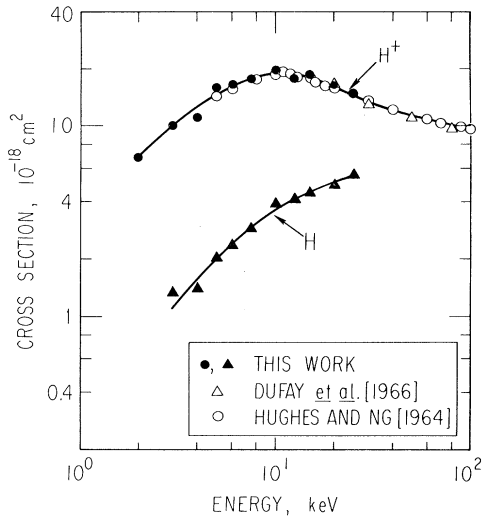

FIG. 3. Cross sections for emission of the 563.2-nm O_2^+ ($b\,^4\Sigma_g^- - a\,^4\Pi_u$) (1, 0) band in collisions of 1–100-keV H^+ and H with O_2. Also shown are the H^+ data of Dufay *et al.* (Ref. 4) and Hughes and Ng (Ref. 3).

TABLE II. Total cross sections in units of 10^{-17} cm^2 for formation of $O_2^+ A\,^2\Pi_u$ and $O_2^+ b\,^4\Sigma_g^-$ in collisions of 1.5–25-keV H^+ and H with O_2.

Energy	$O_2^+ A\,^2\Pi_u$		$O_2^+ b\,^4\Sigma_g^-$	
(keV)	σ_p ($A\,^2\Pi_u$)	σ_a ($A\,^2\Pi_u$)	σ_p ($b\,^4\Sigma_g^-$)	σ_a ($b\,^4\Sigma_g^-$)
1.5	2.3	•••	•••	•••
2.0	3.3	•••	2.9	•••
2.5	3.9	•••	•••	•••
3.0	4.1	•••	4.2	0.57
3.5	4.3	•••	•••	•••
4.0	4.5	0.73	4.7	0.60
5.0	5.2	0.79	6.8	0.86
6.0	4.6	0.92	6.8	1.00
7.5	4.2	0.99	7.5	1.24
10.0	4.2	1.06	8.2	1.66
12.5	3.9	1.22	7.6	1.74
15.0	3.4	1.11	7.9	1.90
20.0	3.2	1.29	6.9	2.0
25.0	3.1	1.32	6.3	2.4

anomaly, this effect would induce a systematic error in the impact energy amounting to ≈12, 5, and 1% at apparent beam energies of 2, 5, and 25 keV, respectively.

B. $O_2^+ A\,^2\Pi_u$

The 200–400-nm emission spectrum excited by 10-keV proton impact on O_2 is shown in Fig. 4. A correction has been made in this figure for the wavelength dependence of the spectral sensitivity of the detection system, which was determined using the molecular-branching-ratio method described in Ref. 11. This wavelength region is dominated by the double-headed red-degraded bands of the $O_2^+ A\,^2\Pi_u$-$X^2\Pi_g$ second-negative ($2N$) system. At each projectile energy studied, hydrogen atom impact on O_2 excited a spectrum having wavelength dependence identical to, but an intensity lower than, that for H^+ bombardment.

Also shown in Fig. 4 is a calculated $O_2^+ A$-X spectrum in which the height of the line located at the wavelength of the origin of the (v', v'') band is proportional to $P_{FC}(v')q_{v'v''}\nu^3_{v'v''}$.

The Franck-Condon factors for the $O_2^+ A\,^2\Pi_u$-$O_2\ X^3\Sigma_g^-$ ionization system originating on $v''=0$ used to calculate $P_{FC}(v')$ and the product $q_{v'v''}\nu^3_{v'v''}$ for the O_2^+ $2N$ system were taken from Ref. 20(b). The intensity distribution in the measured spectrum is in generally good agreement with that of the theoretically calculated spectrum; however, owing to the complicated structure of the $^2\Pi_u$-$^2\Pi_g$ transition,[22] and since the separation of the two heads of the bands (≈1.0–3.0 nm) is comparable to or greater than displacement between the band origins of adjacent intense features, there is substantial band overlap in the O_2^+ $2N$ system. Also, the data from which the theoretical spectrum was calculated are limited to $v' \leq 8$, whereas the proton-impact-induced emission spectrum in Fig. 5 indicates that a number of $2N$ bands originating from substantially higher v' are weakly excited. Therefore, a detailed quantitative comparison with the FC vibrational distribution was not attempted.

Because of the large number of $2N$ bands that are excited, the count rate for any feature was too low to allow us to attempt to alleviate the band-overlap problem by working at higher spectral resolution. Therefore, the cross sections $\sigma(A\,^2\Pi_u)$ shown in Fig. 6 and tabulated in Table II were determined directly by integration over the entire $2N$ system. These experiments were carried out with the monochromator operated in the *integration mode*.

The results were made absolute via normalization to the $N_2^+ B^2\Sigma_u^+$-$X^2\Sigma_g^+$ cross sections of de Heer and Aarts,[23] as described in detail in Ref. 11. Auxiliary experiments of the type described above demonstrated the absence of secondary collision

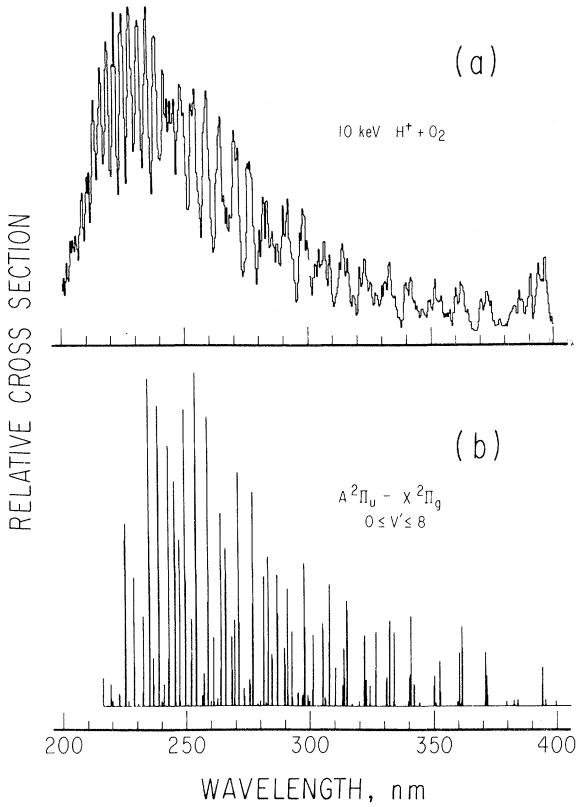

FIG. 4. (a) Emission spectrum excited by 10-keV H^+ impact on O_2 taken at 1.0-nm bandwidth with 0.4-nm step size. The spectrum has been corrected for the variation of spectral sensitivity with wavelength. (b) Calculated $O_2^+ A\,^2\Pi_u$-$X^2\Pi_g$ emission spectrum for $0 \leq v' \leq 8$.

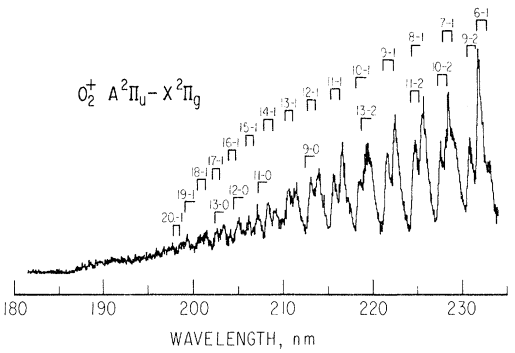

FIG. 5. Short-wavelength emission spectrum excited by 20-keV H^+ impact on H_2 recorded at 0.4-nm bandwidth with 0.075-nm step size. The spectrum has not been corrected for the variation of spectral sensitivity with wavelength. The positions of the double-headed $A\,^2\Pi_u - X^2\Pi_g$ bands were taken from Ref. 19.

effects. Based on the measured value of the radiative lifetime for $O_2^+ A\,^2\Pi_u$ of 7×10^{-7} sec [13] and a cross section[13(b)] of 7×10^{-15} cm^2 for quenching the A state of O_2^+ by O_2, the interval between quenching collisions at an O_2 pressure of 5×10^{-4} Torr is more than 300 times longer than the radiative lifetime, and therefore collisional quenching of $O_2^+ A\,^2\Pi_u$ is negligible under our experimental conditions.

The only previous study of H^+ impact excitation of the $O_2^+ 2N$ system was carried out by Dufay *et al.*,[4] who measured the cross sections for the features at 339–345 and 382–388 nm for 30–120-keV protons. Although these authors assigned these features exclusively to the (0, 6) and (0, 8) bands, respectively, consideration of $P_{FC}(v')$ and $q_{v'v''}\nu_{v'v''}^3$ for features in this wavelength interval indicate the strong participation of additional O_2^+ $2N$ bands. Therefore, the values of $\sigma_p(A\,^2\Pi_u)$ of Dufay *et al.* shown in Fig. 6 have been determined from their reported values of $\sigma_p(339.8)$ by renormalization via extrapolation of our values of $\sigma_p(A\,^2\Pi_u)$.

The relative error in $\sigma_p(A\,^2\Pi_u)$ is estimated to be $\lesssim$17% based on a random propagation of a $\lesssim$7% uncertainty in the integrated $O_2^+ A$-X cross section (uncorrected for the wavelength-dependent spectral sensitivity) and a $\lesssim$15% uncertainty in the determination of the detection efficiency as a function of wavelength. Combining this with the 15% error quoted by de Heer and Aarts leads to an estimated uncertainty of ±23% in the absolute values of $\sigma_p(A\,^2\Pi_u)$. The errors induced by the ion-source energy anomaly and, for H impact, by the uncertainty in the emission coefficient are identical to those described above for $O_2^+ b\,^4\Sigma_g^-$ formation.

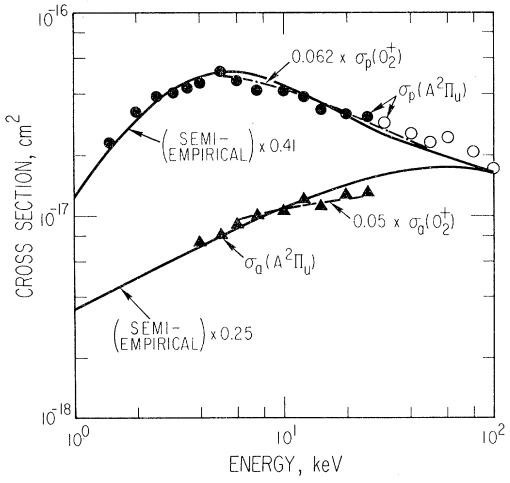

FIG. 6. Total cross section $\sigma(A\,^2\Pi_u)$ for formation of $O_2^+ A\,^2\Pi_u$ in collisions of 1–25-keV H^+ (●) and H (▲) with O_2. Also shown are the H^+ impact data of Dufay *et al.* (Ref. 4) (○), as well as the total cross section $\sigma(O_2^+)$ for formation of O_2^+ and H^+ (Ref. 24) (dash-dotted line) and H (Ref. 25) (dashed line) impact. The solid curves give the total semiempirical cross sections for the A state derived by Edgar *et al.* (Ref. 1) from our measurements and from electron-impact data.

IV. DISCUSSION

Figures 6 and 7 compare our cross sections for formation of the A and b states of O_2^+ with the total cross sections $\sigma_p(O_2^+)$ [24] and $\sigma_a(O_2^+)$ [25] for formation of O_2^+ in all electronic states via H^+ and H impact on O_2. In the energy range in which a comparison is possible it is seen that 5–6% of the O_2^+ molecule ions are formed in the A state for both projectiles. On the other hand, below about 10 keV, the fraction of O_2^+ formed in the b state decreases with decreasing collision energy. Also, reference to Figs. 6 and 7 shows that the maximum in $\sigma_p(b\,^4\Sigma_g^-)$ occurs at roughly twice the collision energy of the peak in $\sigma_p(A\,^2\Pi_u)$.

Direct ionization to form O_2^+ in the A state with $v=0$ requires 17.04 eV, and proceeds by removal of a $1\pi_u$ electron from O_2 (the electronic configuration of the $X\,^3\Sigma_g^-$ ground state of O_2 is $KK2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$), while 18.17 eV is needed to remove a $3\sigma_g$ electron to form O_2^+ in the b state with $v=0$.[19] The shift of the maximum in the cross section to higher projectile energy as the electron to be removed becomes more strongly bound is consistent with previous results for an N_2 target[11,26]; however, the finding that, for

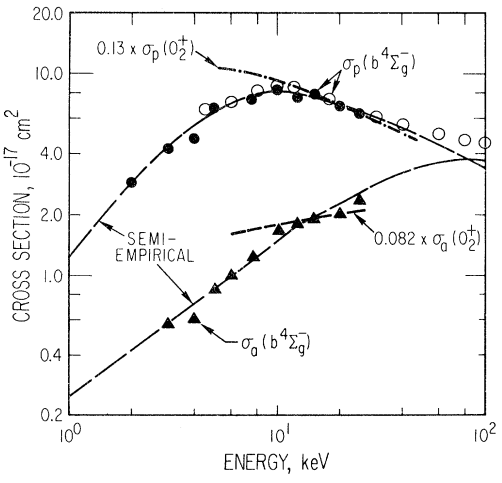

FIG. 7. Total cross section $\sigma(b\,^4\Sigma_g^-)$ for formation of $O_2^+ b\,^4\Sigma_g^-$ in collisions of 1–25-keV H^+ (●) and H (▲) with O_2. Also shown are the H^+ impact data of Hughes and Ng (Ref. 3) (○). The broken curves have the same significance as in Fig. 6.

TABLE III. Ionization cross-section parameters.[a]

Cross section	W (keV)	ν	J (keV)	a (keV)	Ω
$\sigma_{ip}(A\,^2\Pi_u)$	1.70×10^{-2}	1.1	170.3	5.25	0.60
$\sigma_{ia}(A\,^2\Pi_u)$	1.70×10^{-2}	0.51	79.0	6.87	0.87
$\sigma_{ip}(b\,^4\Sigma_g^-)$	1.82×10^{-2}	1.1	142.4	3.19	0.58
$\sigma_{ia}(b\,^4\Sigma_g^-)$	1.82×10^{-2}	0.77	80.1	3.25	0.69

[a]Taken from Ref. 1.

TABLE IV. Electron-capture cross-section parameters.[a]

Cross section	A	B	C	p	q	r
$\sigma_{10}(A\,^2\Pi_u)$	2.10	12.0	77.0	−1.54	0.67	3.7
$\sigma_{10}(b\,^4\Sigma_g^-)$	4.70	11.0	65.0	−1.34	0.64	3.7

[a]Taken from Ref. 1. The parameters A, B, and C are in keV, while p, q, and r are dimensionless.

both projectiles, the magnitude of the b-state cross section equals or exceeds that for A-state formation is contrary to the trend with electron-binding energy observed for N_2. The occurrence of the maxima in $\sigma_p(A\,^2\Pi_u)$ and $\sigma_p(b\,^4\Sigma_g^-)$ at low energies and the observation that in the 1–25-keV range the proton-impact cross sections are substantially larger than those for H projectiles suggest that electron-capture collisions are responsible for a large fraction of the electronically excited molecule ions formed via proton impact; however, photon-particle coincidence experiments[27] are required to verify this assertion.

Figures 6 and 7 also compare our results with semiempirical cross sections derived by Edgar *et al.*[1] from our data and from scaling of previous electron-impact results. For H impact their result is represented by the relationship

$$\sigma_a = \sigma_{ia}, \tag{5}$$

where the cross section σ_i to yield the state of interest via direct target ionization is given parametrically as a function of the impact energy E (in keV) by the expression

$$\sigma_i = 10^{-16}\frac{(Za)^{\Omega}(E-W)^{\nu}}{J^{\Omega+\nu}+E^{\Omega+\nu}}. \tag{6}$$

Table III gives the values of the parameters for ionization of O_2 by H^+ and H to yield the $A\,^2\Pi_u$ and $b\,^4\Sigma_g^-$ states of O_2^+.

In H^+ impact one must also account for formation of the excited state in charge-exchange collision via the expression

$$\sigma_p = \sigma_{ip} + \sigma_{10}, \tag{7}$$

in which the component σ_{10} of the total cross section owing to electron capture is related to the impact energy (in keV) as

$$\sigma_{10} = 10^{-16}\left[\left(\frac{E}{A}\right)^p + \left(\frac{E}{B}\right)^q + \left(\frac{E}{C}\right)^r\right]^{-1}. \tag{8}$$

Parameters for electron capture from O_2 to yield the $A\,^2\Pi_u$ and $b\,^4\Sigma_g^-$ states of O_2^+ are given in Table IV.

As indicated in Figs. 6 and 7, the energy dependence of the semiempirical cross sections of Edgar *et al.* are in good agreement with our experimental results. Also, for excitation of O_2^+ $b\,^4\Sigma_g^-$, the agreement in magnitude between semiempirical and experimental cross sections is quite good. On the other hand, based on the systematics observed in the electron-impact data as well as in H^+ and H impact excitation of other targets, Edgar *et al.* predict that the cross sections $\sigma_p(A\,^2\Pi_u)$ and $\sigma_a(A\,^2\Pi_u)$ are larger by a factor of 2.4 and 4.0, respectively, than those we measured. The source of the discrepancy is not understood but, considering the developmental stage of the semiempirical scaling method and the considerable uncertainty in the measured values of $\sigma(A\,^2\Pi_u)$, the agreement in magnitude is acceptable.

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