ELECTRON- AND PHOTON-IMPACT IONIZATION OF O_2 †

J. William McGowan, E. M. Clarke,* Harold P. Hanson,‡ and R. F. Stebbings
John Jay Hopkins Laboratory for Pure and Applied Science,
General Atomic Division of General Dynamics Corporation, San Diego, California

(Received 21 September 1964)

Prior to this paper several publications[1-3] indicated that for diatomic molecules, electron-impact ionization proceeds directly through a Franck-Condon transition between a state of the target molecule and one of the product ion. In contrast, most photoabsorption and photoionization data[4] suggest that the primary mechanism is autoionization which requires a Franck-Condon transition between states of the molecule, the final state lying above the threshold of ionization. A rearrangement of the electrons in the excited molecule then quickly leads to an ion-electron pair, with the electron carrying off with it nearly all of the excess kinetic energy. It is predicted[5] that direct electron-impact ionization has a linear threshold dependence, while autoionization, like other excitation processes, proceeds according to a step function. Similarly, it is predicted that direct photoionization will proceed according to a step function, while photoexcitation, a resonance process, must be a delta function. A continuation of this reasoning suggests that the first derivative of the electron-impact ionization efficiency curve should be nearly equivalent to the photon-impact ionization efficiency curve, provided the same processes maintain.[5] For atoms like Kr and Xe, the latter appears to be established, the recent work of Morrison[6] presenting the strongest evidence.

Unlike previous electron-impact studies of diatomic molecules, our results for O_2 parallel those found for photon impact to a great degree, as shown in Fig. 1. First, the derivative of the ionization efficiency curve for $O_2{}^+ X\,{}^2\pi_g$ resembles the photoionization efficiency curve published by Nicholson.[4] Our data show clear maxima and minima instead of steps as one might expect if a simple linear threshold law applied. Secondly, the ionization potential (12.04 ± 0.02 eV) is found to be in good agreement with his value (12.065 ± 0.003 eV), but far removed from the other values found by electron impact which cluster near 12.2 eV.[2,3]

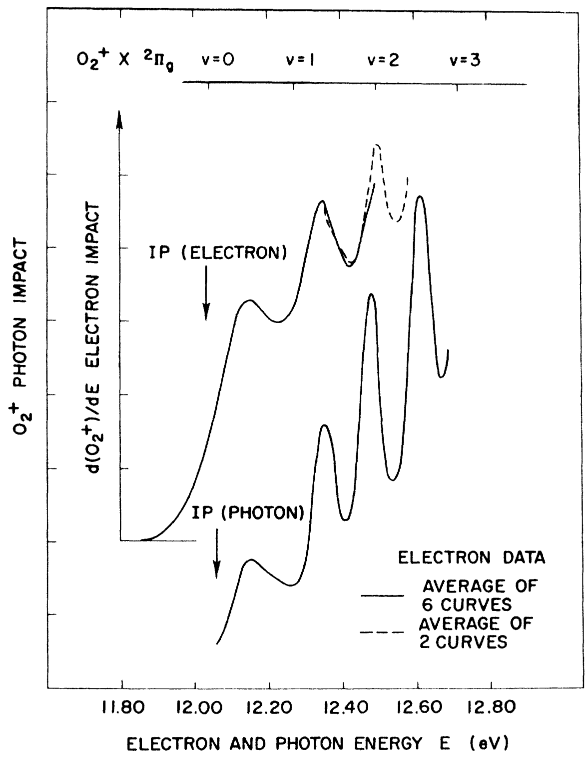

FIG. 1. Comparison of data from photon impact and electron impact of O_2. The vibrational intervals, taken from Herzberg, are normalized to the electron-ionization thresholds.

Some aspects of the modulated-beam apparatus[7] and the 127-deg electrostatic electron selector[1] used in these experiments have been described in previous publications. The details of our entire apparatus and approach will be discussed in a paper to follow. Here it suffices to mention that two selectors are mounted about the axis of the molecular beam; one produces the bombarding beam of electrons while the second, which is free to move in a plane perpendicular to the neutral-beam axis, measures the energy distribution of the bombarding electrons. At half-height, the widths of the distributions associated with the experiments described herein ranged from 0.04 to 0.07 eV.

The ions produced were accelerated along the neutral-beam axis, through a Paul mass filter, onto the face of an open multiplier. Techniques similar to those described by Foner and Hudson[8] were used, permitting counts due to the beam signal to be separated from those due to background noise. Counting times of one minute per point were used, and an interval between data points of either 0.01 or 0.02 V was used over the energy range studied. Nine sets of O_2^+ data were taken.

Six sets of data were averaged to give the electron-impact results shown in the figure (solid curve). The remaining three, though they exhibited the same structure, suffered badly from drift either in the electron current or in the molecular-beam intensity during the course of the experiment. Only two sets of data extended to high enough energies to define the final peak shown in the figure (broken line). One set extended to much higher energies and showed in the derivative a continuation of the undulations shown. However, in this region the statistical error in our signal was approaching the amplitude of the oscillations in the derivative.

The absolute energy scale of the individual curves was not determined; and for the purposes of averaging, the curves were displaced to superimpose the well-pronounced second maxima which in the photon work appears at 12.35 eV. The low-energy tailing on the composite curve results in part from the differences in the distributions between runs. At all times the tailing seemed to be wider than the electron distribution measured by the electrostatic analyzer. All data were mathematically smoothed in such a way that high-frequency oscillations and random noise were eliminated from the curves. It appeared that when the resolution of the selector was poorest (near 0.07 eV) the derivative of the raw data most closely resembled that shown in the figure; however, when the resolution and signal-to-noise were best (near 0.04 eV) there appeared to be more structure in the curves.

The similarity between the curves in the figure is striking and though the curves differ in some respects, the existence of the same processes in both electron- and photon-impact ionization is established. The peaks in photoionization and in the derivative of the electron-impact ionization can be associated with autoionization[5]

$$O_2 + h\nu = O_2'$$
$$\llcorner\; O_2^+ + e \text{ for photons,}$$

and

$$O_2 + e = O_2' + e$$
$$\llcorner\; O_2^+ + e \text{ for electrons.}$$

The peaks in the derivative of the electron-impact ionization efficiency curve are not as well resolved as they are in the photoionization efficiency curve. In part, this results from averaging and the fact that our electron-energy distribution is in some instances worse than the quoted photon-energy distribution. At present, a program is underway to remove the effects of the electron-energy distribution from the data. Provided that direct ionization is indeed competing with autoionization, we should find in the derivative marked peaks associated with autoionization superimposed on steps, the leading edges of which should correspond to the thresholds of direct vibrational excitation of the ion. At present, we have no explicit evidence of direct ionization. This apparently contradicts the work recently published by Brion.[2] Further, the intervals between structure in our ionization efficiency curves (shown as peaks in the derivative) do not correspond to vibrational intervals. Straight-line segments necessary to reproduce the Franck-Condon factors in no way resemble the experimental data.[9]

The appearance potential quoted by us is derived in two ways. First, 12.04 ± 0.02 eV is an average of the extrapolated values for eight of the ionization efficiency curves taken. The energy scales were fixed by a superposition of the structure in the photoionization curves with that in the derivative of the electron-impact ionization curves. Secondly, a value of 12.04 eV was also obtained by using the threshold for ionization[10] for $N_2^+\ X\,^2\Sigma_g^+$ 15.576 eV as the reference potential.

Recently Wacks and Krauss,[11] using Franck-Condon factors, constructed an ionization efficiency curve for O_2^+ which shows no structure due to electronically excited states. However, if new channels for autoionization become available at or near thresholds of electronic excitation, one might then expect to see structure similar to that observed in previously reported ionization efficiency curves.[2,3]

In summary, then, we wish to stress that through the first electron volt above the ionization threshold of O_2^+, autoionization is important and is indeed a dominant process. The danger associated with assigning linear segments to ionization efficiency curves is once again emphasized. More detailed results for oxygen will soon be submitted for publication along with results for nitrogen, hydrogen, and the rare gases.

---

†Work supported in part by Project DEFENDER of the Advanced Research Projects Agency, Department of Defense, under Office of Naval Research Contract No. Nonr-2786(00), and in part by the Defense Atomic Support Agency under Contract No. DA49-146-XZ-041.

*Present address: St. Francis University, Antigonish, Nova Scotia.

‡Present address: University of Texas, Austin, Texas. Robert A. Welch Foundation Grantee.

[1] Ionization in H_2: P. Marmet and L. Kerwin, Can. J. Phys. **38**, 972 (1960); L. Kerwin, P. Marmet, and E. M. Clarke, Can. J. Phys. **31**, 1240 (1960). Ionization in N_2: P. Marmet and J. D. Morrison, J. Chem. Phys. **36**, 1238 (1962).

[2] C. E. Brion, J. Chem. Phys. **40**, 2995 (1964).

[3] C. E. Melton and W. H. Hamill, J. Chem. Phys. **41**, 546 (1964); and references pertinent to ionization of O_2.

[4] A. J. C. Nicholson, J. Chem. Phys. **39**, 954 (1963); and references pertinent to photoionization of O_2.

[5] G. H. Wannier, Phys. Rev. **100**, 1180 (1956); S. Geltman, Phys. Rev. **102**, 171 (1956); and an excellent extension of this work by F. H. Dorman, J. D. Morrison, and A. J. C. Nicholson, J. Chem. Phys. **32**, 378 (1960).

[6] J. D. Morrison, J. Chem. Phys. **40**, 2488 (1964).

[7] W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1141 (1958).

[8] S. N. Foner and R. L. Hudson, J. Chem. Phys. **36**, 2681 (1962).

[9] At the moment we can suggest but one possible explanation for this discrepancy. Indirect heating of the gas by the filament might have a much larger effect on the ionization efficiency curve than previously suspected. In our experiments we are presently using a chopped room-temperature beam which passes unimpeded through the collision region. Preliminary experiments in which we preheat the beam give ionization efficiency curves which somewhat resemble those previously published. (See references 1 and 2 above.)

[10] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

[11] M. E. Wacks and M. Krauss, J. Chem. Phys. **35**, 1902 (1961).

SCATTERING CROSS SECTION OF IDEAL GASES FOR NARROW LASER BEAMS

O. Theimer*
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

(Received 8 October 1964)

Recent experiments by George *et al.*[1] have indicated that Rayleigh's theory may not be valid for scattering of narrow laser beams by ideal gases. It will be shown in this Letter that interference phenomena do, in fact, produce deviations from Rayleigh's theory which are significant if the scattering volume satisfies certain criteria of smallness, and that these interference effects can explain some of the above-mentioned striking experimental results.

For a derivation of the modified scattering formula, consider a system of N molecules with polarizability α in a large cubical volume $V=L^3$. The scattering volume v is that section of the incident laser beam which is seen by the detector and is assumed much smaller than V. In many practical cases v is approximately a parallelepiped, as shown in Fig. 1. Its volume is

$$v = abc/\sin\theta, \tag{1}$$

where θ is the scattering angle, and a, b, c are, respectively, the width and height (along z) of the laser beam, and the width of the scattered beam (determined by diaphragms). According to Eq. (1), the scattering volume and with it the intensity are proportional to $1/\sin\theta$. This is characteristic for scattering of narrow beams,[2] but it appears that this trivial angle dependence has been neglected by George *et al.*

An incident monochromatic radiation field with frequency ω and space dependence

$$\vec{E}(\vec{r}) = \vec{E}\exp(i\vec{k}\cdot\vec{r}), \quad k = 2\pi/\lambda, \tag{2}$$

induces a dipole moment

$$\vec{p}(\vec{r}_j) = \alpha\vec{E}(\vec{r}_j) = \vec{p}\exp(i\vec{k}\cdot\vec{r}_j) \tag{3}$$

in the molecule located at $\vec{r}_j$. $\vec{p}$, oscillating with the frequency ω, is the source of a scattered radiation field[3]

$$\vec{E}_j'(\vec{D}) = f(\vec{R}, \lambda, \theta)\exp[i(\vec{k}\cdot\vec{r}_j + kR)], \tag{4}$$