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Studies of the electron-impact ionization cross section of vibrationally excited oxygen employing a shock-heated molecular beam

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The shock-heated molecular-beam technique was used to obtain vibrationally excited oxygen molecules. The vibrational distributions of these diatomic molecules, in argon gas as the "carrier" gas of a shock-heated molecular beam, have been calculated by considering atomic recombination, collisional excitation, and deexcitation during the expansion. The vibrationally excited molecules, which correspond to vibrational temperatures T_v, in the range 1800–7000 K, are used to examine the role played by vibrational excitation in both direct and dissociative electron-impact ionization cross sections over a range of electron energies from 50 to 500 eV. The results show that the dissociative electron-impact ionization cross section increases only slightly with increasing vibrational temperatures, and results agree with the theory based on the modified reflection method.

I. INTRODUCTION

The direct and dissociative ionization cross sections of vibrationally excited molecules by electron impact are not well understood at present. Great understanding of the role of vibrational excitation on the ionization of molecules has increased in importance as a result of recent developments in gaseous lasers, plasma-enhanced chemical-vapor deposition for the production of solar cells, impurity problems in nuclear fusion research, flame chemistry, and the chemistry of planetary atmospheres. There are few previously reported values of such processes leading to ionization. Spence and Dolder[1] suggested that the electron-impact cross section to O_2 to increase in value up to 50% at an electron energy of 200 eV and vibrational temperature of 3100 K using a shock-heated molecular beam (SHMB) with mass spectrometer. Crane and Stalker[2] estimated that the effect of vibrational excitation on total ionization is only less than 30% in nitrogen at an electron energy above 200 eV and vibrational temperatures ≤ 3100 K using the SHMB with ion sampling by a mass spectrometer. Micheja and Burrow[3] using a crossed-beam technique indicated that the effect of vibrational excitation on dissociative ionization is as much as 100% near the threshold for the first three vibrational levels of nitrogen. Evans *et al.*,[4] using the SHMB with the addition of a mass spectrometer (see Fig. 1) studied the dissociative ionization cross section of CO at a vibrational temperature of 3000 K, and obtained a factor of 5 times larger cross section compared with room-temperature values for an electron energy range of 100–400 eV. Theoretical studies, employing statistical methods to predict the roles of vibrational excitation in dissociative ionization, have been conducted by Dronin and Gorokhov,[5] Venugopalan,[6] and Jackson *et al.*[7] However, these theories only apply to larger molecules or are limited in threshold electron energy. For higher electron energies, the calculation has been done only for hydrogen.[8]

In this paper, direct and dissociative ionization cross sections of vibrationally excited oxygen molecules by electron impact are measured and evaluated by a theory based on the reflection method at elevated vibrational temperatures for oxygen molecules. The vibrationally excited molecules were produced by a shock-heated molecular-beam technique and the vibrational relaxation in the system was predicted numerically.

II. EXPERIMENTAL APPARATUS

A. Experimental apparatus

A schematic diagram of the shock-heated molecular-beam apparatus is shown in Fig. 1. It is seen to consist of a shock tube section, a beam formation region, ionization and detection sections.

The shock tube consists of a 7.1-m long, polished steel

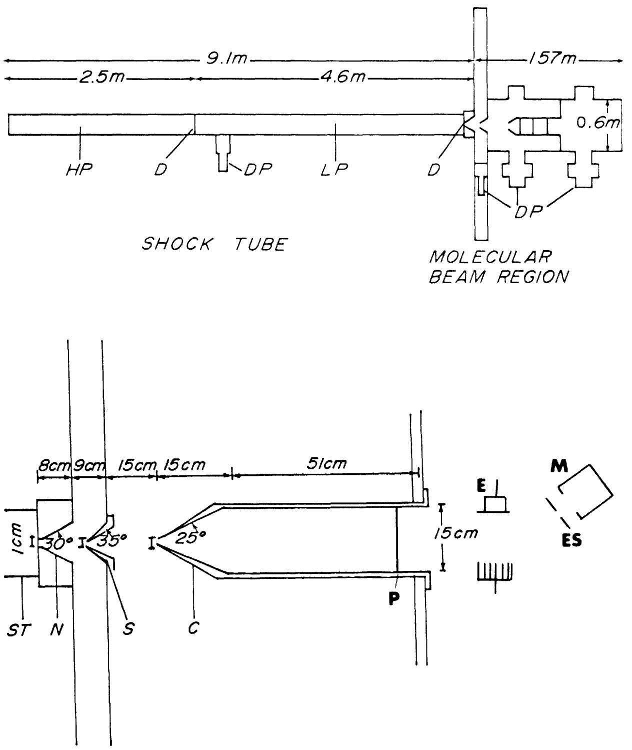

FIG. 1. Schematic diagram of the ionization cross-section measurement apparatus employing the shock-heated molecular beams (SHMB). (a) Shock-heated molecular-beam system, (b) detail of expansion nozzles and diagnostic section. ST = shock tube, N = nozzle, S = skimmer, M = mass spectrometer, C = collimeter, P = electrostatic probe, EG = electron gun.

tube of 10 cm internal diam. The low-pressure section is 4.1 m long and the driver section is 3.0 m long. By varying the shock tube diaphragm pressure ratio, diaphragm thickness or the driver and test gases, Mach numbers between 3 and 13 were achieved. The shock wave velocity was measured by four platinum, thin-film gauges and a piezoelectric pressure transducer.

The beam formation section consists of three vacuum chambers: the first, separating the nozzle and the skimmer, the second between the end of the skimmer and the collimator, and the third section past the collimator which contains the molecular-beam diagnostics section as shown in Fig. 1(a). The expansion vessels were made of 4-cm thick, 30-cm internal diam glass cylinders (QVF Co). The first section, which contains the skimmer and collimator, was 80 cm long, while the second section was 60 cm long. The electron gun, the grid, and collector constituted the ionization region. The electrons were obtained by heating a Ba-O coated cathode by a ceramic covered tungsten heater. To avoid arcs, the heater was held near cathode potentials. The voltage drop between heater and cathode was fixed at 6.3 V which led to a heater current of up to 0.85 A. The cathode voltage could be varied from 0 to 500 V. From the electron current-voltage characteristic, the electron gun was found to follow the Child-Langmuir space-charge law with a slope of 0.11 μm/V. The electron collector consists of about 150 razor blades (uncoated Schick injector blades) held tightly together and electrically isolated from ground. Due to the sharpness of the blades, most electrons are either absorbed on first impact or are reflected back into the blades and then collected. The potential of the collector could be varied from 0 to 500 V. A coarse copper grid, held over the collector and maintained at ground potential, was employed in order to avoid the collector voltage from accelerating electrons affecting the collection of ions. From the observed current-voltage characteristics, the range $100 \leq V \leq 80$ V was found to be an optimum condition to collect most of the electrons.

The positive ion detection section consists of an einzel lens leading to a quadrupole mass spectrometer and ion counter. The einzel lens consists of three parallel steel plates, each with a center-hole diameter of 1 cm. The voltage of the center plate could be varied from 0–250 V, positive or negative, with respect to ground. The outer two plates were electrically connected at voltages from 0–250 V, positive or negative. For the focal lengths used in this experiment, the lens acted as a thin convex lens. It was found by experiment that settings of -142 V for the inside plate and -60 V for the two outside plates of the einzel lens gave the optimum focusing characteristics (i.e., large signal with low signal distortion). The ion detector developed by Joshi *et al.*[9] was used in the present study.

B. Experimental procedure and calibration

The ion signal for a given run was obtained by varying the electron energy with a fixed constant voltage applied elsewhere. Thus, the intent was to reproduce, as best as possible, the same conditions for differing electron energies at a given vibrational excitation.

For each temperature condition, an argon and neon ionization cross-section curve was employed for calibration. The experimentally derived cross sections were normalized with the argon and neon cross sections from Rapp and Englander-Golden.[10] Since these cross sections should be independent of the vibrational temperature, they were employed as references. The calibrations and normalization procedure follow the usual sequence. The ion signal from the detector (I_+) is related to the cross section (σ) by

$$I_+ = \eta I_- n l \sigma \ , \tag{2.1}$$

where n is the neutral number density, l is the collisional path length of the electrons with the neutrals, I_- is the electron gun current, and η is the total collection efficiency which includes the einzel lens collection, transmission through the quadrupole mass spectrometer and ion detector gain. From Eq. (2.1), we can determine the absolute cross section for ionization of a gas N,σ, assuming η is the same for gas N as for argon A, by

$$\sigma = \frac{I_+(V,N,T)\sigma_A(V)}{I_+(V,A,T)X} \ , \tag{2.2}$$

where $I_+(V,N,T)$ is the ion signal from the detector measured at an electron beam voltage of V for species N at temperature T, $\sigma_A(V)$ is the ionization cross section of argon from Rapp and Englander-Golden[10] measured at 300 K V, and X is the present concentration of molecules in argon. From the argon and neon curves for different shock-reflected-region temperatures, a weak mass discrimination effect and molecular-beam velocity effect on the collection efficiency has been observed.

III. VIBRATIONAL RELAXATION IN A SHOCK-HEATED MOLECULAR BEAM

A. Method of calculation and the procedure employed

In order to determine vibrational temperature in a molecular beam, the following numerical procedure was conducted. As the molecular plasma is expanded through a nozzle, and the translational, rotational, and vibrational energy modes come into equilibrium at different rates. The translational and rotational relaxation times are typically in the order of a few collisions; the vibrational relaxation time is much longer. In the present work, the vibrational distribution function of the molecular beam is computed as a function of time, assuming translational and rotational equilibrium, and using a method similar to that developed by Yau.[11] In particular, the molecule is assumed only to be vibrationally excited and relaxation in the molecular beam is characterized by the reactions

$$X_2(v)+M \leftrightarrows X_2(v')+M, \quad |v-v'|=1 \,, \tag{3.1}$$

$$X_2(v)+M \rightleftarrows 2X+M \,, \tag{3.2}$$

where $X_2(v)$ is the diatomic molecule in the vth vibrational level and M is the major constituent of the gas.

The first reaction considers collisional excitation and deexcitation while the second reaction considers dissociation and recombination. The diatomic molecule X_2 is assumed to be at sufficiently small concentrations so that X_2-X_2 collisions can be ignored. Excitation and deexcitation is also assumed to occur only from adjacent vibrational levels are all in the ground electronic state.

The time-dependent population of the vth level $n_v(t)$ is given by the master equation

$$\frac{dn_v(t)}{dt}=[M]\left[\sum_{v'=0}^{m-1} g_{v'v}n_{v'}(t)-\sum_{v'=0}^{m} g_{vv'}n_v(t) + g_{mv}n_m^2(t)\right], \quad v\le m-1 \tag{3.3}$$

and

$$\frac{dn_m(t)}{dt}=[M]\left[2\sum_{v'=0}^{m-1} g_{v'm}n_{v'}(t)-n_m^2(t)\sum_{v'=0}^{m-1} g_{mv'}\right], \tag{3.4}$$

where $g_{vv'}$ is the transition probability from v to v'. As a consequence of detailed balancings

$$\tilde{n}_v g_{vv'}=\tilde{n}_{v'}g_{v'v}, \quad \tilde{n}_v g_{vm}=\tilde{n}_m^2 g_{mv} \,, \tag{3.5}$$

where $\tilde{n}_v$ is the equilibrium population of the state v. Also, for a given diatomic molecule X_2 and inert gas M, $g_{vv'}$ is a function of the temperature of the inert gas.

The solution to the master equation is drastically simplified by linearizing the $n_m^2(t)$ term. By defining

$$a_m=\tfrac{1}{2}\tilde{n}_m+\Delta \quad \text{and} \quad \Delta=n_m(t)-\tilde{n}_m \,,$$

we obtain

$$n_m^2=\tilde{n}_m^2+2\tilde{n}_m\Delta+\Delta^2 \,,$$

so that near equilibrium, $\Delta\approx 0$, and $n_m^2\approx 2n_m a_m$ in the above equation. The details of the procedure and method of numerical solutions can be found in Yau.[11]

In order to integrate the above differential equations, the gas density as a function of the downstream distance along the present SHMB apparatus was evaluated in time steps. The initial values at the beginning of the program (i.e., in the shock-reflected region) were calculated from the JPL program of Horton and Menard.[12] The temperatures and argon gas density decay in the molecular beam from the nozzle to the freeze-out point (or free molecular point) were obtained from the numerical results of Evans *et al.*,[13] in which it is assumed that the small admixture of molecular gases in argon does not affect the neutral beam flow properties.

B. Numerical results

Numerical vibrational population distributions for 1% oxygen gas seeded in the argon carrier gas are shown in Fig. 2 for various locations x along the axis and down-

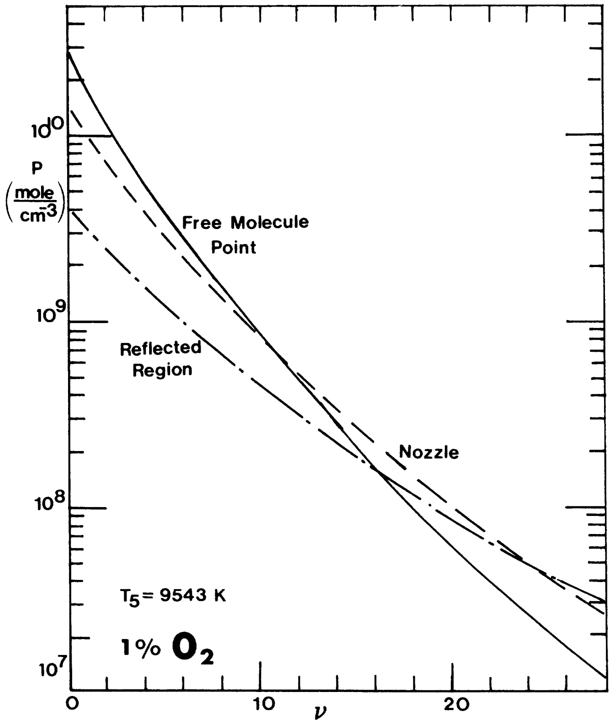

FIG. 2. Vibrational population distributions for 1% oxygen gas seeded in the argon gas for various locations along the axis and downstream and the expansion nozzle at $T_5=9543$ K.

stream of the expansion nozzle at $T_5=9543$ K, where T_5 is the temperature in the shock-reflected region. Figure 2 shows that the vibrational population distribution becomes non-Boltzmann almost immediately after the expansion nozzle. Numerical vibrational population distributions at the free molecular point for oxygen molecules seeded in the argon carrier gas are shown in Fig. 3 for various shock-reflected region temperatures. Figure 3 shows that none of the vibrational distributions of the molecular points are Boltzmann-like above $T_5 \simeq 6000$ K. The larger concentrations of vibrationally excited molecules ($v > 5$) (relative to their equilibrium values) are observed also in Fig. 3 for T_5 greater than about 6900 K. The resulting vibrational temperature at a free molecular point is shown in Fig. 4 from which it is clear that the vibrational temperature at a free molecular point increases nonlinearly with the shock-reflected-region temperature. It should be recalled that the vibrational temperatures are determined from the slopes of the population distribution at small vibrational levels ($v \leq 5$) (since the populations of vibrational levels above about 5 are orders of magnitude smaller than $v \leq 5$). Then a highly vibrationally excited molecular beam can be developed in the present apparatus.

IV. ESTIMATE OF THE EFFECT OF VIBRATIONAL EXCITATION ON THE DISSOCIATIVE IONIZATION CROSS SECTION

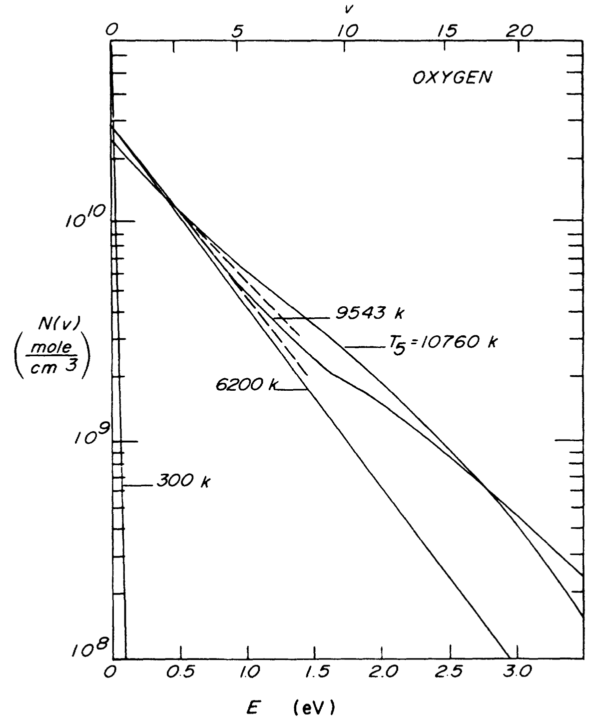

FIG. 3. Numerical vibrational population distributions of oxygen at the free molecular point for various T_5.

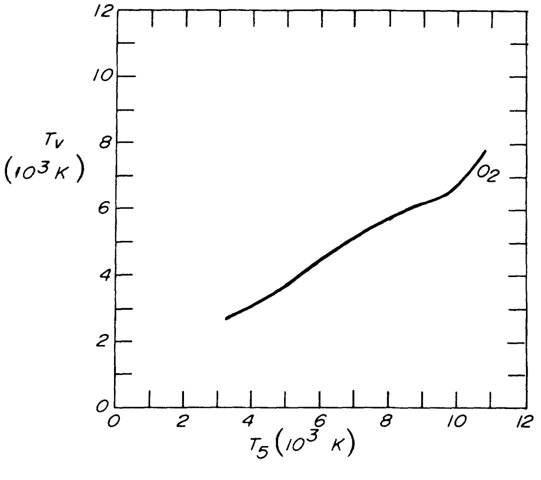

FIG. 4. Vibrational temperature at a free molecular point vs T_5 for O_2 additives.

The electron ionization reactions for oxygen in the present electron energy ranges and partial pressures are direct and dissociative ionization as follows:

$$O_2+e \rightarrow O_2{}^+ + e \quad \text{(direct ionization)}$$

$$\rightarrow O^+ + O + e \quad \text{(dissociative ionization)}\ .$$

The theory presented here for the effect of vibrational excitation on the dissociative ionization cross section of O_2 by electron impact is based on an approximate method given by Winans and Stuckelberg[14] and sometimes called the reflection method (Herzberg[15]). This theory is applied in the case of electron energies above 50 eV.

Since the "Stuckelberg" method approximates the continuous wave functions in the upper ionization states by a δ function as the turning point, the Franck-Condon density for a transition from the lower bound state $\Psi_{v''}$ is given by

$$\begin{aligned} g_{v'v''} &= \left| \int_0^\infty \psi_{v''}\psi_{v'}dr \right|^2 \\ &= \left| \int_0^\infty \delta(r-r_1)\psi_{v''}dr \right|^2 \\ &= |\psi_{v''}(r_1)|^2 \,, \end{aligned} \qquad (4.1)$$

where r is the internuclear separation and r_1 is the value of the internuclear separation at the turning point of the upper state continuous wave function.

The condition for the transition limit to the ionization electronic potentials above the dissociation is that the internuclear separation becomes less than a critical value r_c.[16] The latter is defined as the interatomic distance corresponding to the state of the molecular ion at which the potential energy at the turning point equals its dissociation energy [i.e., $r_1=r_c$ in Eq. (4.1)]. This condition contains in part the Franck-Condon principle.

It thus follows that the amount of O^+ produced relative to $O_2{}^+$ for a single transition from the ground state of O_2 to an ionization state of O_2 can be described by

TABLE I. Parameters and molecular constants used in the calculation of the dissociative ionization cross section of vibrationally excited O_2.

State k	$\tau(k)$[a]	r_c (Å)[b]	r_e (Å)[c]	D_e	β_e	w_e	$w_e x_e$	$\sum_{v'} q^{d}_{v''v'}$	Max. v' considered
$X\,^2\Pi_g$	0.140	0.94	1.1164	6.92057	1.6913	1904.77	16.259	~1.00	10
$a\,^4\Pi_u$	0.294	1.14	1.38138	3.2000	1.10466	1035.69	10.39	~0.90	8
$A\,^2\Pi_u$	0.270	1.19	1.40905	1.8421	1.06160	898.25	13.573	~0.85	6
$b\,^4\Sigma_g^-$	0.206	1.10	1.27914	2.5977	1.28729	1196.77	17.09	~1.00	3
$B\,^2\Sigma_g^-$	0.09	1.14	1.298	1.8828		1156	22		
$D\,^2\Delta_g$	small	1.10	1.33	2.1863		920	12		

[a] Normalized transition probabilities from $O_2 X\,^3\Sigma_g^-$ to the kth state of O_2^+ from Watson *et al.*

[b] From Morse potential extension of the Klein-Dunham potentials of McCallum *et al.*

[c] Molecular constants from Hubner and Herzberg.

[d] From Krupenie for $v''=0$.

$$A=\frac{\int_0^{r_c}|\psi_{v''}(r)|^2dr}{\int_{r_c}^{0}|\psi_{v''}(r)|^2dr}\ .$$

This expression must be summed over all vibrational levels in a given electronic state. Then all electronic states must also be summed; hence, the expression to be evaluated is

$$\frac{[0^+]}{[0_2{}^+]}=\sum_{\substack{\text{state}\\ k}}\sum_{v''}\tau(k)\frac{\int_0^{r_c(k)}\psi^2_{v''}(r)dr}{\int_{r_c(k)}^{0}\psi^2_{v''}(r)dr}\ , \qquad (4.2)$$

where $\tau(k)$ is the electronic transition probability from the electronic ground state of O_2 to the upper ionization state k.

The electronic ground-state wave functions of O_2 for $v=1\rightarrow20$ were obtained by McCallum, Nicholls, and Jarmain.[17] The various values of $r_c(k)$ were obtained from the upper vibrational states given in Krupenie,[18] and a Morse potential extrapolation was made from this point using the known molecular constants (Huber and Herzberg[19]). The values of $\tau(k)$ were obtained from the semiempirical study by Watson *et al.*[20]

Table I lists values of $\tau(k)$, r_c, and the molecular constants used for the states considered. Two assumptions made in the above theory could be checked. First, all transitions to a given state with $r>r_c$ are bound transitions. The Franck-Condon factors are normalized by

$$\sum\!\!\!\!\!\!\int_{v'} q_{v''v'}dv'=1\ , \qquad (4.3)$$

where $\sum$ is taken over the Franck-Condon factors of the bound state and $\int$ is taken over the Franck-Condon densities (Nicholls[21]). Hence, by summing the Franck-Condon factors up to the highest vibrational level, an estimate of the accuracy of this assumption can be achieved. This is summarized in Table I.

It can be seen from Table I that most transitions proceed to a bound state. Furthermore, a study of the behavior of the $\sum q_{v''v'}dv'$ for the various molecular states considered here indicates that it is generally small compared to $\sum_{v'} q_{v''v'}$ (Nicholls[22]).

The second assumption is that the transition probabilities $\tau(k)$ are independent of electron energy, i.e., Eq. (4.2) is independent of electron energy. This is verified to within 5% for electron energies above 70 eV and less than 1000 eV by noticing that $[O^+]/([O_2{}^+]+[O^+])$ measured by Rapp Englander-Golden[10] becomes nearly constant in this energy range and that the partial ionization cross sections measured by Watson *et al.*[20] are nearly constant with electron energy for energies above 50 eV.

By studying the spectrum of energies of the O^+ fragment, created by dissociative ionization at room temperature, it has been shown that a significant percentage of this dissociation occurs by predissociation.[23-25] However, since this process must occur from the bound transition of the excited states of $O_2{}^+$ (mainly the $B\,^2\Sigma_g^-$ state and the $D\,^2\Delta_g$ state, Locht and Schopman[24]), the effect of vibration should be quite small compared to the direct dissociation, as discussed above. This is because the overlap of the wave functions is more sensitive at the turning point than it is over the rest of the wave function.

Figure 5 shows a plot of the computed partial cross sections for the dissociative ionization of O_2 normalized to 1 for $v''=0-20$. It can be seen that major contribu-

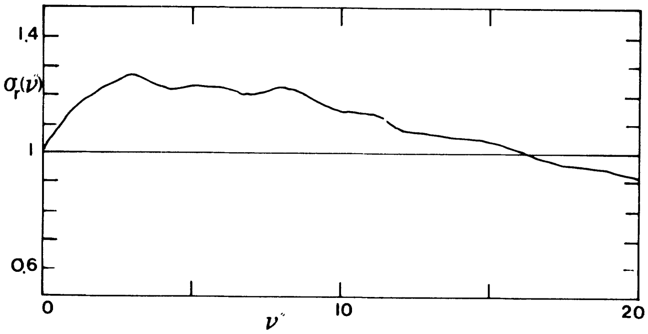

FIG. 5. Theoretical dissociative ionization partial cross section of O_2 vs initial vibrational level v'' of the ground electronic state. σ_r is the cross section normalized to the ground vibrational level.

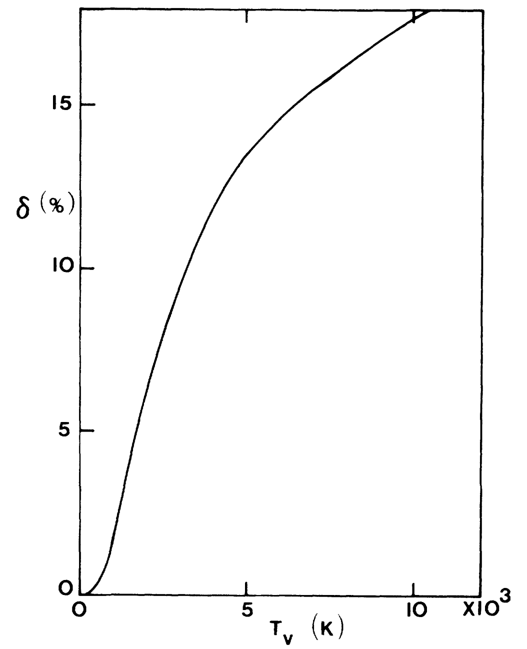

FIG. 6. Theoretical percent change of the dissociative ionization cross section of O_2, $\delta\%$ vs the vibrational temperature T_v.

tions will occur even for modest vibrational excitation. Figure 6 shows the dissociative ionization cross section, normalized to room temperature, for vibrational temperatures from 300 to 10 500 K and electron energies above 70 eV. Thus, for vibrational temperatures from 1500 to 4000 K, this theory predicts at most an increase in the dissociative ionization cross section of approximately 4–12%.

V. ELECTRON-IMPACT IONIZATION CROSS-SECTION MEASUREMENTS OF AN OXYGEN MOLECULE IN A HIGH VIBRATIONAL STATE

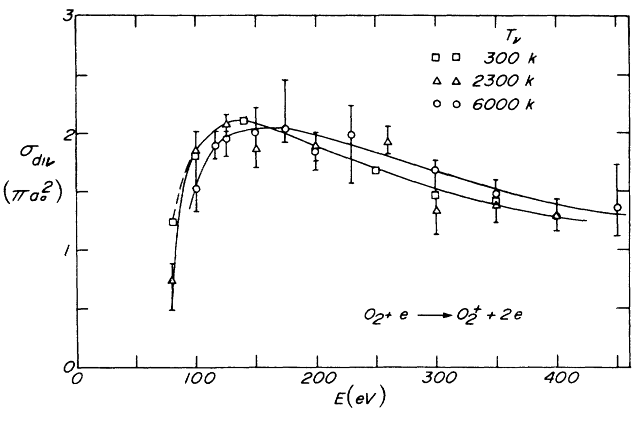

FIG. 8. The effect of vibrational temperature on direct ionization cross section of oxygen.

Typical electron-impact measurements reported here in the case of direct ionization of oxygen with $T_v = 5300$ K are shown in Fig. 7 and are compared with results reported by other workers at $T_v = 300$ K. Figure 7 shows that the cross sections reported here agree both in order of magnitude and in the shape of the curve with the other results. The effects of vibrational temperature on this cross section are shown in Fig. 8. The latter indicates that the cross section at a vibrational temperature of 2300 K is identical to the present $T_v = 300$ K results. The measurements at $T_v = 6000$ K show some small systematic variations of the cross sections. It is also seen to vary for electron energy $E \geq 200$ eV. At $E \leq 200$ eV, the maximum in the cross section seems to be shifted towards higher electron energy with increasing vibrational temperatures.

The effects of vibrational temperature on the oxygen electron-impact dissociative ionization are shown in Fig. 9, together with the results of Rapp *et al.*[26] at 300 K. Figure 9 shows general correlation with the results of Rapp *et al.*[26] However, a more definite shift to higher E is observed in the current measurement of the cross sec-

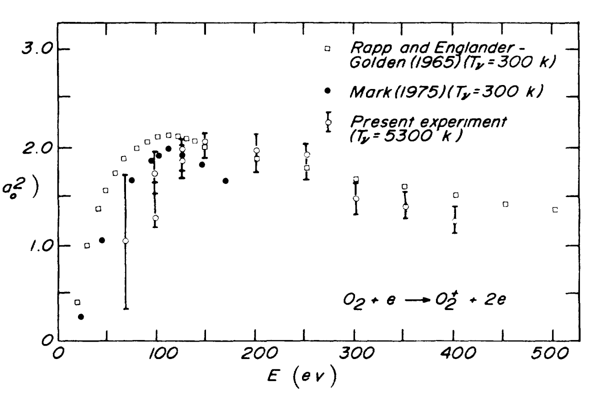

FIG. 7. Direction ionization cross section of oxygen $\sigma_{\rm div}$ at $T_v = 5300$ K.

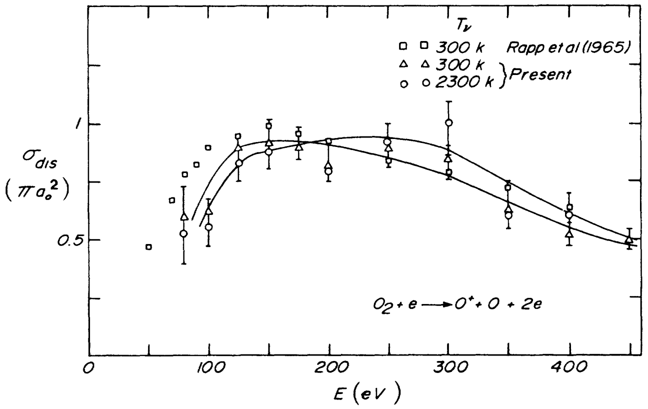

FIG. 9. The effect of vibrational temperature on dissociative ionization cross section of oxygen $\sigma_{\rm dis}$.

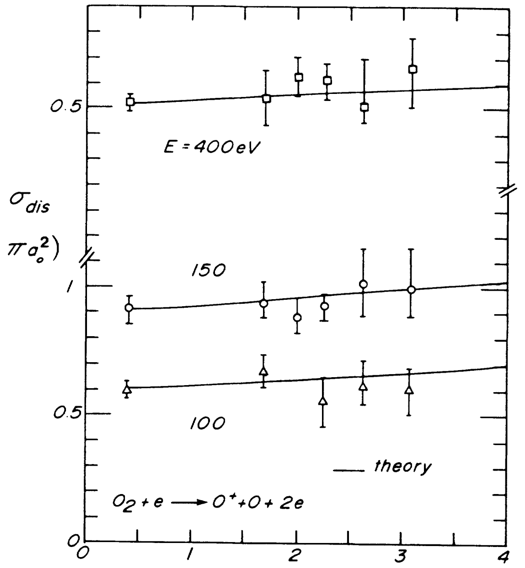

FIG. 10. Comparison of experimental σ_{dis} with theory.

tion for dissociative ionization. Finally, the σ_{diss} for oxygen is plotted as a function of vibrational temperature and compared with the theoretical predictions of Sec. III in Fig. 10, which are strictly only valid for higher values of E. Nevertheless, they are seen to be in substantial agreement with the experimental values. The disagreement between these results and the much larger shift determined by Spence and Dolder[1] could well be due to an inadequate allowance for η in this case.

VI. CONCLUSIONS

The measurement of ionization cross section by electron impact has been conducted, employing a shock-heated molecular beam, and the relaxation of vibrational temperature in the system is predicted numerically. This leads to the following conclusions. (1) For shock-reflected temperatures T_5 larger than 6000 K, the vibrational population distribution at the free molecular (freeze-out) point is non-Boltzmann for any mixture ratio with argon. (2) For concentrations of seeded molecules less than 10%, the vibrational population distribution was near Boltzmann and independent of partial pressure for $T_5 \leq 3000$ K. (3) The vibrational temperature at a free molecular point increases nonlinearly with the temperature in the shock-reflected regions. (4) There are some small systematic variations of the cross sections for both dissociative and direct electron-impact ionization with vibrational temperature. (5) The experimental results agree with theoretical values obtained using a modified reflection method for the dissociative ionization cross section of oxygen.

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