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Calculation of Dissociative Attachment in Hot O_2†

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The very striking temperature dependence of the dissociative attachment cross sections found experimentally in O_2 has been reproduced by a semi-empirical calculation, assuming a Maxwell distribution of vibrational (v) and rotational (r) states. A recently derived expression for the cross section $\sigma_{v,r}$ is used, and the final-state potential curve of O_2^- is parametrized to fit the experiments. The temperature shift is found to be caused by the effect on excited vibrational states of the rapidly varying "survival probability," a measure of the competition between auto-ionization and dissociation. Byproducts of the calculation are the potential curve for the final dissociating state of O_2^{-*}, together with an estimate of its auto-ionization width $\Gamma_a(R)$, and also the contribution of this state to the total cross section for electron-energy loss to vibrational excitation and dissociation.

It has been found experimentally by Fite *et al.*[1] that the cross section for dissociative attachment (DA) of electrons to O_2 has an extraordinarily large dependence on the temperature of the O_2. The shift and broadening with temperature was such that at 2100°K the cross-section peak was shifted to lower energy by 1 eV while the apparent onset was reduced by over 2 eV. The present calculation was done in an attempt to provide some understanding of this remarkable effect.

It is first assumed that the direct effect of the temperature on the O_2 is to produce a Maxwell distribution of vibrational (v) and rotational (r) states. The cross section $\sigma(T,E)$, where E is the electron energy, is then the Boltzmann average of the cross sections $\sigma_{v,r}(E)$ from each of the individual excited states; thus

$$\sigma(T,E)=\sum_{v=v_{\min}}^{\infty}\sum_{r=r_{\min}}^{\infty}Ne^{-(E_v+E_r)/kT}\sigma_{v,r}(E)\,, \qquad (1)$$

where N is the Boltzmann normalization factor, $v_{\min}$ and $r_{\min}$ are subject to the threshold requirement for the process, viz., $E+E_v+E_r\geq 3.6$ eV, and the cross section $\sigma_{v,r}$ is given by the theoretical expression[2]

$$\sigma_{v,r}(E)=\frac{4\pi^2 g}{k^2}\frac{\Gamma_{a,X}}{\Gamma_d}\left|\tilde{\chi}_v\left(R_E-i\frac{\Gamma_a}{\Gamma_d}\right)\right|^2 e^{-\rho}\,. \qquad (2)$$

The Γ_a, Γ_d, and ρ as well as $\tilde{\chi}_v$ are evaluated at the final-state turning point $R_E(E,v,r)$. The exact definition of the quantities is given in Ref. 2. In particular, k is the electron's momentum, E is its energy, and g is an angular momentum and spin factor. Γ_a and $\Gamma_{a,X}$ are the total and partial (for the state X) auto-ionization widths, i.e., $\Gamma_a=\sum_j\Gamma_{a,j}$. Here Γ_d is a width for dissociation, χ_v is the vibrational wave function, R_E the turning point is in vibrational units, and ρ is twice the imaginary part of the final state phase shift δ_r. The factor $e^{-\rho}$ is called the survival probability[3] or survival factor. It is given approximately by

$$e^{-\rho}\simeq\exp\left[-\int_{R_E}^{R_c}\frac{\Gamma_a(R)dR}{\hbar v(R)}\right]=\exp\left[-\int\frac{\Gamma_a(R)dt(R)}{\hbar}\right], \qquad (3)$$

where v is the velocity of dissociation and t is the corresponding classical time. This factor results from the decay of the dissociating state by auto-ionization. Where the above expression is not sufficiently accurate, an exact expression can be used.[3] The effect of rotation in (2) is implicit. It adds a centrifugal term to the potential curves for initial and final vibrational motion, and at low energies it helps put the total energy above the threshold and thus determines $v_{\min}$ in Eq. (1).

The cross section (2) is completely determined when the potential energy curves V_i and V_f are specified including the width Γ_a of the latter, which is a resonance or autoionizing state. Since V_i, the ground-state curve for O_2, is well known,[4] it is necessary only to know the final curve V_f together with its width Γ_a in order to determine the entire family of cross sections given by (2). Accordingly, the procedure adopted in the present work was to *parametrize* this potential curve and its width. The parameters are then chosen with a view to fitting the experimentally determined $\sigma(T,E)$, in particular as given by Ref. 1, to the extent that this is possible. The curve V_f is first expanded in a series about $R_0=1.21$ Å (the O_2 equilibrium distance), as

$$V_f(R)=E_0-V'\Delta R+\tfrac{1}{2}V''\Delta R^2-\tfrac{1}{6}V'''\Delta R^3\,, \qquad (4)$$

where $\Delta R=R-R_0$. For the width, we may either parametrize $\Gamma_a(R)$ and then derive ρ from Eq. (3) or a more exact formula, or else parametrize $\rho(R)$ directly

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[1] W. L. Fite and R. T. Brackmann, *Proceedings of the Sixth International Conference on the Ionization Phenomena in Gases, Paris, 1963,* Vol. I, p. 21. W. L. Fite, R. T. Brackmann, and W. R. Henderson, *Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 100.

[2] T. F. O'Malley, Phys. Rev. **150**, 14 (1966).

[3] J. N. Bardsley, A. Herzenberg, and F. Mandl, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 415.

[4] F. R. Gilmore, J. Quant. Spectay. Rad. Trans. **5**, 369 (1965).

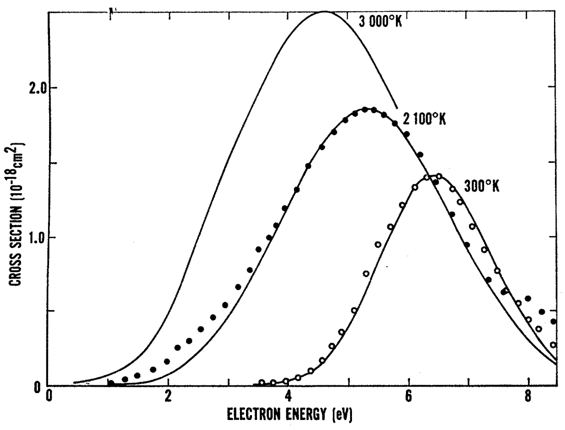

FIG. 1. Dissociative attachment cross sections at 2100 and 300°K. The solid curves are from the present calculation with a broad electron spread included. The circles are the experimental points of Fite *et al.*, normalized to the result of Ref. 5. The experimental 2100° curve has been normalized to the present calculation, as discussed in the text. The theoretical curve for 3000° is also shown.

and derive Γ_a. The latter course proved easiest and was done in the form

$$\rho(R)=\rho'(R_c-R)^n,\quad (R\leq R_c) \tag{5}$$

and $\rho=0$ beyond R_c. Lest the form of (5) appear arbitrary, this is actually the exact form which follows from (3) in the limit that the potential curve V_f is approximately linear between R_E and R_c and Γ_a has its threshold behavior $\Gamma_a\propto(R_c-R)^{L+(1/2)}$ where L is the electron's asymptotic angular momentum. In this case, n would be equal to $L+1$. However, the present results cover a wider range, and so (5) represents simply a 3-parameter approximation to the true behavior. R_c is interpreted as the crossing point between V_f and the target potential curve into which it auto-ionizes, which is where the partial auto-ionization width $\Gamma_{a,j}$ and therefore its contribution to ρ goes to zero in the Born-Oppenheimer approximation.

It was found that the best fit to the experimental results[1] was obtained with the parameters in (4) and (5) chosen as follows:

$$\begin{aligned} &E_0=7.8\pm0.2\text{ eV}, && V'=27\pm2\text{eV/Å},\\ &V''=110\pm20\text{ eV/Å}^2, && V'''=300\pm100\text{ eV/Å}^3, \end{aligned} \tag{6}$$

and

$$n=1.5\pm0.5,\quad \rho'=41\pm3\text{ Å}^{-3/2},\quad R_c=1.44\pm0.03\text{ Å}. \tag{7}$$

The uncertainties expressed for the various quantities are meant to indicate the sensitivity of the fit to the various parameters and do not necessarily reflect any judgment as to absolute errors.

The resulting cross sections at 300 and at 2100°K are plotted in Fig. 1 together with the experimental results at these temperatures. The theoretical curve for 3000° is also shown. The normalization of the 300° cross section was taken mainly from the work of Schulz.[5] The theoretical curves in Fig. 1 have been averaged over a broad distribution of electron energies chosen to approximate that employed in the experiment

$$\sigma_{\rm av}(T,E)=\int dE'f(E')\sigma(T,E'), \tag{8}$$

where the electron-distribution function $f(E')$ was taken to be a shifted Maxwellian corresponding to about 2800°K. The experimental 2100°K cross section represents the experimental signal normalized to agree in magnitude with the presently calculated 2100° cross section, which is 1.3 times as large as that at room temperature. Though the magnitude of the cross section (as opposed to the signal) is not given explicitly in Ref. 1, the ratio of 1.3 found here is consistent with the cross sections implied by the discussion in these papers.

The theoretical fit to the experiments may be seen from Fig. 1 to be good, except that it falls somewhat below at the lowest electron energies. The experimental plateau above 8 eV is apparently due to some other cause. In Table I, the calculated cross sections $\sigma(T,E)$ are tabulated for a number of temperatures. Note that unlike the values given in Fig. 1, these are not averaged over the electron distribution of Eq. (8).

In the course of the fitting process, it was found that the three parameters E_0, V', and V'' of the potential curve V_f are essentially determined by the room temperature data, except that E_0 is raised by the presence of $e^{-\rho}$. The quantity V''' does not affect the 300° result and was chosen mainly for its influence on $D(E)$ (see below). The expansion (4) of V_f should hold till roughly $R=1.55$ Å.

The final-state potential curve V_f for the system O_2^{-*} is shown in Fig. 2, together with other relevant

TABLE I. Dissociative attachment cross sections $\sigma(T,E)$ from Eq. (1) at various temperatures, in units of 10^{-21} cm^2. The electron energy E is in eV and T in °K. A sharply defined electron energy is assumed.

T \ E	2600°K	2200°K	1800°K	1400°K	300°K
1.0	5	1	0	0	0
1.5	22	4	0	0	0
2.0	98	27	4	0	0
2.5	312	119	29	3	0
3.0	650	306	104	20	0
3.5	1070	610	271	77	0
4.0	1530	1010	560	224	1
4.5	1920	1430	940	500	21
5.0	2120	1750	1340	890	155
5.5	2070	1870	1610	1280	520
6.0	1810	1750	1650	1500	1040
6.5	1420	1440	1450	1440	1380
7.0	1000	1050	1100	1160	1310
7.5	630	670	720	770	930
8.0	360	381	405	434	520
8.5	183	190	197	206	229
9.0	82	83	83	83	83

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[5] G. J. Schulz, Phys. Rev. **128**, 178 (1962). See also D. Rapp and D. D. Briglia, J. Chem. Phys. **43**, 1480 (1965).

states of O_2 and O_2^- taken from Gilmore's curves.[4] It is believed that this potential curve together with the approximation (5) and (7) to the width (see also Ref. 6) constitutes a significant byproduct of the present work. Note that the curve goes below the dissociation limit at about $R=1.44$ Å and becomes attractive. The dotted line from about $R=1.55$ to 2.1 Å represents the way in which this curve is assumed to connect up with the known asymptotic form of the $^2\Pi_u$ curve for O_2^{-*}. Although no use is made of this dotted region of the curve, the $^2\Pi_u$ configuration is fully consistent with the assumed electronic structure of the state. But whatever its spin and parity (since these are only tentative at present), it follows that this state probably has a dissociation energy of the order of $1\pm\frac{1}{2}$ eV.

The heuristics of choosing the parameters for ρ in (7) may be of interest. They were chosen to fit the 2100° cross section. The primary feature, namely, the shift of the peak by 1 eV, was easily reproduced by simply varying the amplitude ρ'. However, the obvious choice of $n=\frac{1}{2}$ (corresponding to a constant Γ_a) gave a cross section that was either nearly square in shape or double-peaked, depending on R_c. It was only when n was varied to between 1 and 2 that bell-shaped curves resulted. The value of 1.5 which fit best is gratifyingly close to the assumed correct threshold value, which as mentioned would give $n=2$. Finally, fitting the observed cross section width fixed R_c loosely at 1.44 ±0.03 Å. The value 1.44 for R_c was a little surprising. Reference to Fig. 2 shows that this lies squarely between the crossing of the A C system at $R<1.39$ and the crossing of the states X, a, b at $R\geq1.55$. R_c had been expected to coincide with one or the other of these crossings. The intermediate value, somewhat closer to A and C, is interpreted as meaning that there is considerable auto-ionization to all of the 5 allowed states, with the largest part going to A and C. The value of 1.44 is therefore taken as an average or compromise value.[6]

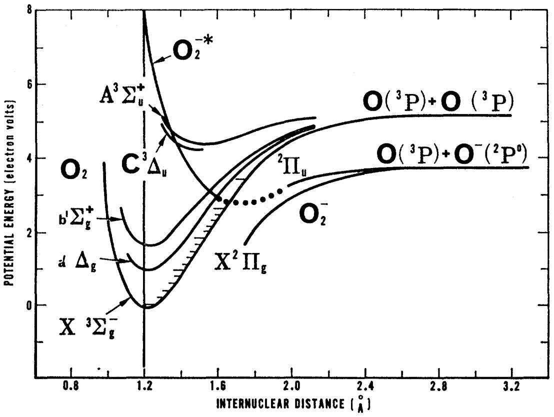

FIG. 2. Potential energy curves for the O_2^- and O_2 system. The result of the present calculation, labeled O_2^{-*}, is shown in relation to the pertinent O_2 curves (from Ref. 4). The dotted portion of the curve is an extrapolation and shows schematically how the O_2^{-*} curve is assumed to connect up with the known portion of the $^2\Pi_u$ curve.

TABLE II. Activation energies $D(E)$, experimental and theoretical in different approximations. D's are in eV. D_{av} comes from σ_{av} of Eq. (8), i.e., with electron spread. D corresponds to σ with no electron spread. C is the corresponding coefficient from Eq. (10) in units of 10^{-18} cm². The value of D_v was computed with rotation entirely neglected (vibration only).

E	D_{exp}	D_{av}	D	D_v	$C(E)$
1.0	···	1.59	2.43	2.61	370
1.5	···	1.36	2.05	2.12	280
2.0	1.0	1.14	1.64	1.66	200
2.5	0.92	0.93	1.18	1.18	72
3.0	0.79	0.72	0.89	0.91	39
3.5	0.58	0.55	0.67	0.68	23
3.75	···	0.47	0.59	0.58	19
4.00	0.29	0.40	0.50	0.50	15
4.25	···	0.34	0.42	0.42	12
4.50	0.15	0.28	0.35	0.35	10
4.75	···	0.22	0.28	0.28	8

The foregoing results, (6) and (7), were derived with the cross sections arbitrarily normalized. Taking the 300° normalization of 1.4×10^{-18} cm² from Ref. 5 allows $\Gamma_{a,X}$ in (2) to be determined. First, assuming the O_2^- state to be $^2\Pi_u$, it follows that the weighting factor g equals $\frac{2}{3}$. Further, it follows from $n=1.5$ in (7) that the width Γ_a is roughly linear in electron energy. Substituting all this into Eq. (2) with $v=0$ and r small yields for the partial capture width from the state X,

$$\Gamma_{a,X}=0.034E. \tag{9}$$

This was incorporated in Fig. 1 and Table I. The *total* width Γ_a also can be computed[2] from ρ as determined by (5) and (7). Because Γ_a is not used directly, this was done only roughly, in a linear approximation, with the result $\Gamma_a(R)\approx4(1.44-R)$. Near the cross-section peak, then, $\Gamma_{a,X}$ is somewhat more than $\frac{1}{4}$ of Γ_a, which is also believable.

An analysis of the physical content of the calculation is made in Fig. 3, where the 2100° cross section is plotted in five successive approximations. In curve a, we set $v=r=\rho=0$. This would correspond to the low temperature cross section without ρ. Including excited vibrational states in b broadens the curve considerably. Applying the rapidly varying survival factor $e^{-\rho}$ shifts b to c, while the narrower curve a is shifted only to c′. (Differences in magnitude are suppressed in Fig. 3.) To a good approximation for O_2, the difference between c and c′ represents the entire temperature effect.[7] If $\rho(E)$ or its energy variation were small, as

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[6] Strictly speaking, one should put at least two terms like (5) into ρ, one for each set of states. This was tried and found to give essentially the same cross section. The parameters were found very roughly to be (with $n=1.5$) $R_{C1}=1.52$, $\rho_1'=16$; $R_{C2}=1.39$, $\rho_2'=27$. This gives approximately $\Gamma_1=1.5$ $(1.52-R)$ and $\Gamma_2=2.6$ $(1.39-R)$, while $\Gamma_X\approx0.6\Gamma_1$. However, the relative magnitude of ρ_1 and ρ_2 was found to be somewhat arbitrary without additional experimental information.

[7] This is in agreement with the qualitative suggestion of Y. N. Demkov, Phys. Letters 15, 235 (1965). See also Ref. 2.

for some other molecules, then the curves a and b would describe the effect and there would be broadening but no shift. Curves d and e, representing σ and σ_{av}, respectively, show the modest shift caused by rotational states (agreeing with the analysis of Ref. 2) and the shift and tailing effect of a broad electron distribution. It can be seen from *d* that excited rotational states are of negligible importance compared to vibrational states.

In Fig. 4, the calculation is analyzed from a slightly different point of view. The cross sections σ_v for attachment from the vth state are plotted individually. (The small dependence on r is here suppressed.) For each increase in v, there is a large shift to the left and a substantial increase in magnitude (σ_5 is 20 times as large as σ_0). Note that each cross section is cut off below its threshold ($E+E_v=3.6$ eV). These curves show graphically the basis for the observed shift and the large low energy tail.

A very interesting aspect of the work of Fite *et al.* was the finding that at the lower energies ($E \lesssim 5$ eV and $T \gtrsim 1000$°K) the cross sections follow very closely the formula

$$\sigma(T,E)=C(E)e^{-D(E)/kT}. \tag{10}$$

Exactly the same was found for the presently computed results. In Fig. 5, $\log\sigma$ is plotted against $1/T$ and the data are seen to lie on straight lines from roughly 800 to 3000°K. The slopes, $D(E)$, which were called activation energies, have a clear interpretation in the present work. They are the average internal energy (vibrational plus rotational) of the molecule which maximizes the summand in Eq. (1), showing the internal states which contribute most strongly to the temperature averaged cross section. In columns 1 and 2 of Table II, the experimental values $D_{\text{expt.}}(E)$ are compared with the theoretical values $D_{av}(E)$ taken from σ_{av} of Eq. (8). The agreement is seen to be within 0.1 eV everywhere. (Probably the discrepancy at the largest E's would be reduced if the experimenters had plotted σ rather than the uncorrected current.) The third column shows $D(E)$, the present result with sharply defined electron energies from Eq. (1). The very large difference between D and D_{av} is due to the tailing effect of the broad electron distribution. In the fifth column, the corresponding coefficient $C(E)$ from Eq. (10) is listed. The fourth column, labeled D_v, was calculated with vibrational states only (no rotational excitation). This corresponds to the data plotted in Fig. 6, which differ very little from Fig. 5. The difference between D and D_v is some measure of the relative importance of rotation, which seems to be very small except below about 2 eV. This is in disagreement with the assessment of Fite *et al.*[1] In this connection, it was found that at 2100° rotational states with $E_r \gg kT$ never contributed significantly to the sum in Eq. (1) (unlike the situation with the vibrational states), until E fell below about 2 eV. Even at the lowest energy of 1.0 eV, the average excitation of the rotational states contributing to (1) was not much more than 20% of that of the average vibrational state ($v \approx 13$).

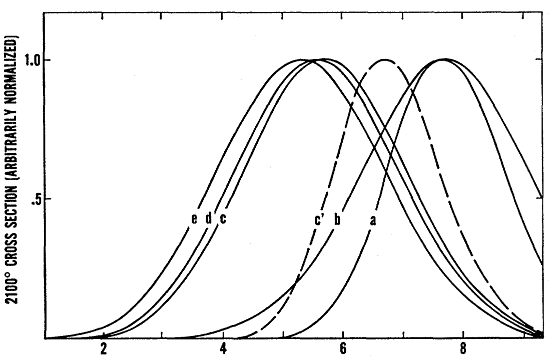

FIG. 3. The 2100° attachment cross section in successive approximations, all arbitrarily normalized. In curve a, $v=r=\rho=0$. Curve b includes excited vibrational states. In c, the factor $e^{-\rho}$ is also included. (Curve c′ is curve a times $e^{-\rho}$. This is essentially the room temperature cross section, to be compared with c.) In d, rotation is included, giving σ of Eq. (1). Curve e is σ_{av} of Eq. (8), with a broad electron spread. If drawn to scale, curves a and b would be nearly two orders of magnitude larger than the others.

It is interesting to note in Table II that for electron energies well below the threshold of 3.6 eV the values of $D(E)$ (not D_{av}) converge more or less to (3.6 eV)$-E$, the internal energy necessary to raise the system above the threshold.[8] This would indicate that the results for very high vibrational states are no longer sensitive to the details of the wave functions, but that these may

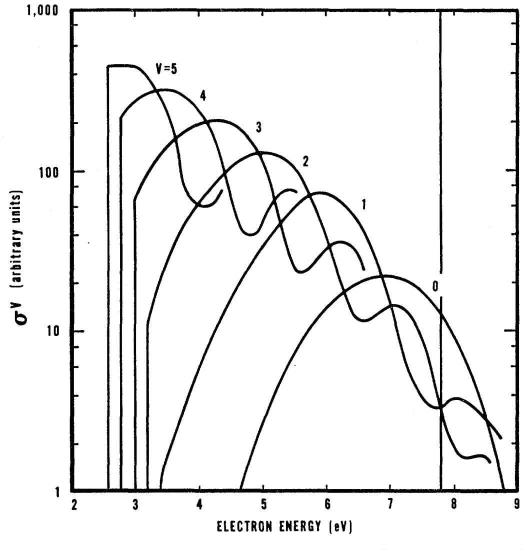

FIG. 4. Cross sections σ_v for attachment from the vth vibrational state, plotted against energy for $v=0$ through 5. The lack of symmetry about the vertical line (7.8 eV) and the increase in magnitude with increasing v is due to the variation of the survival factor $e^{-\rho}$ with electron energy. A Boltzmann average of these cross sections (including higher v's) reproduces the observed temperature dependence of the cross section $\sigma(T,E)$.

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[8] This relation was obtained previously by M. A. Fineman from similar experiments done by J. W. McGowan (private communication).

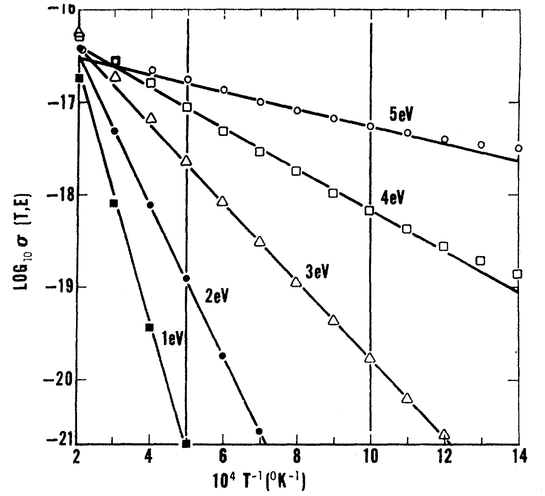

FIG. 5. Log$\sigma(T,E)$ from the present calculation is plotted versus $1/T$ for various electron energies of 5 eV and below. The empirical formula (10) represents straight lines on this plot. Like the experimental results, which were plotted in the temperature region between the vertical straight lines, the calculated results also fall on straight lines. See text for discussion.

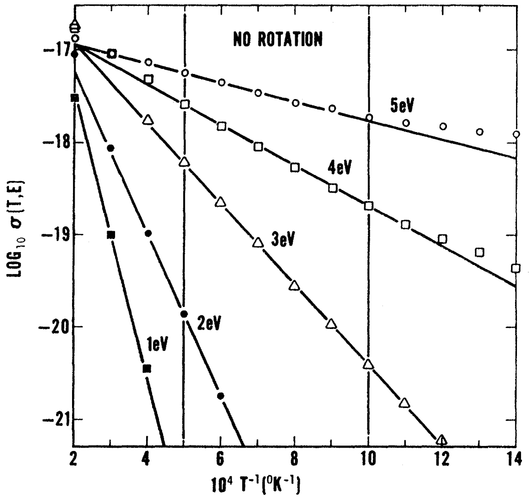

FIG. 6. The same as Fig. 5 but from a calculation done without excited rotational states. The straight-line behavior indicates that the relation given by Eq. (10) does not necessarily depend on rotational excitation.

be replaced by a suitable average value, in the statistical spirit. Thus, the simple concept of an activation energy does become appropriate in this limit. It seems, however, that at the very lowest energies (below 2 eV) the dynamical effects of rotation tend to bring $D(E)$ (not, however, D_v) below the simple threshold value of (3.6 eV)$-E$.

Finally, the consequences of the present analysis for processes other than dissociative attachment should be pointed out. Consider only the low-temperature cross section for simplicity. The accepted interpretation[3] of Eq. (2) is that the DA cross section is equal to a capture cross section to the state V_f of O_2^{-*} times $e^{-\rho}$, the chance of surviving to dissociate before auto-ionizing to some vibrational level of one of the five lowest O_2 states. Given the presently determined parameters (6) and (7), it follows that the capture cross section $e^{+\rho}\sigma_{\mathrm{DA}}$ is roughly 70 times that for DA, with a peak value of about 1.0×10^{-16} cm^2 at 7.8 eV. From $R_c=1.44$, we would expect that at least half[9] of this capture cross section will decay to the states A and/or C, resulting in dissociation, while the remainder auto-ionizes to the states X, a, and b (about half of it to X), resulting in excitation of most of the vibrational levels of these states. Whether the contribution of this to the respective cross sections is significant is not clear at present.

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[9] See also Ref. 6.