MOLECULAR PROCESSES IN COMETS

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Semiannual Progress Report No. 10

For the period 1 July through 31 December 1982

Principal Investigator
Dr. A. Dalgarno

Prepared for

National Aeronautics and Space Administration
Washington, D. C. 20546

December, 1982

Smithsonian Institution
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Cambridge, Massachusetts 02138

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Most of our effort has been devoted to preparing a paper on the dissociation cross section of OH arising from absorption into the repulsive $1^2\Sigma^-$ state. A copy of the paper, THE LOW-LYING $^2\Sigma^-$ STATES OF OH, by Ewine F. van Dishoeck, Stephen R. Langhoff and A. Dalgarno, is attached. It has been submitted for publication to the Journal of Chemical Physics.

We have also examined again photodissociation by predissociation of the $A^2\Sigma^+$ state. A preliminary version of a paper describing our results is attached as part of this report.

The Low-Lying $^2\Sigma^-$ States of OH

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Abstract

Potential energy curves for the two lowest $^2\Sigma^-$ states of OH are computed at the configuration-interaction level using four different basis sets. Electronic transition dipole moments connecting the excited $1^2\Sigma^-$ and $2(D)^2\Sigma^-$ states with each other and with the ground $X^2\Pi$ state are presented as functions of internuclear distance. The theoretical absorption oscillator strengths for the $D^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ transition are in good agreement with the empirical value derived from astronomical measurements. The photodissociation cross sections for absorption from the $v''=0$, 1 and 2 levels of the ground state into the continuum of the $1^2\Sigma^-$ state are calculated, and the interstellar and cometary photodissociation rates are derived.

1. Introduction

The hydroxyl radical OH is an important component in a diverse array of physical environments. We have reported recently[1] theoretical calculations of the properties of the excited $^2\Sigma^+$ electronic states of OH in which the oscillator strengths and radiative lifetimes of the $A^2\Sigma^+$, $B^2\Sigma^+$ and $C^2\Sigma^+$ states were derived. We present now calculations at a similar level of accuracy for the two lowest $^2\Sigma^-$ states. The lowest $1^2\Sigma^-$ state is known from predissociation of the $A^2\Sigma^+$ state. The state is repulsive and may provide an important path for the dissociation of OH in cometary atmospheres and in the interstellar gas. There are no measurements of the absorption cross sections. The second $2^2\Sigma^-$ state is the spectroscopic $D^2\Sigma^-$ state in the 1200 Å region studied in absorption by Douglas[2]. Observations of the absorption lines have yielded estimates of the oscillator strength and the abundance of OH in diffuse interstellar clouds[3].

Calculations of limited accuracy of the potential energy curves of the $1^2\Sigma^-$ and $D^2\Sigma^-$ states have been carried out by Lefebvre-Brion et al.[4] and Easson and Pryce[5]. The $D^2\Sigma^-$ state was classified as a Rydberg state[2,4]. No calculation has been reported of the $1^2\Sigma^-$-$X^2\Pi$ transition moment. The $D^2\Sigma^-$-$X^2\Pi$ transition moment has been computed at one internuclear distance by Ray and Kelly[6] in a ten-configuration self-consistent field calculation.

2. Theoretical Methods

We employed the configuration-interaction (CI) method for the determination of the electronic wavefunctions of the $^2\Sigma^-$ states using four different atomic orbital basis sets. Two of the basis sets, denoted I and II, consisting of Slater functions, and a third, denoted III, consisting of Gaussian functions, are given explicitly in Ref. 1. Since the $D^2\Sigma^-$ state contains substantial Rydberg character, an adequate representation requires diffuse basis set functions, in particular 3s and 3pσ functions centered on the oxygen nucleus. Basis sets II and III satisfy this requirement, but basis set I, which contains a diffuse s function only on the hydrogen nucleus, does not. Accordingly, we constructed a fourth basis set, denoted IA, that augments basis set I by adding diffuse 3s (exponents $\zeta = 1.0$ and 0.5), 4s ($\zeta = 0.5$ and 0.2), 3pσ ($\zeta = 1.0$ and 0.5) and 3pπ ($\zeta = 0.75$) functions centered on the oxygen nucleus. The 1s ($\zeta = 0.4$) and 2s ($\zeta = 1.557$) functions centered on the hydrogen nucleus were removed, to avoid linear dependencies. The resulting 22σ 11π 8δ basis should represent accurately both the compact and diffuse components of the wave function.

In the calculations with basis sets I and IA, the internally-consistent self-consistent field (ICSCF)[7] $X^2\Pi$ molecular orbitals were used for all the states. The configuration state functions (CSFs) that were explicitly included in the wave function were selected by Rayleigh-Schrodinger perturbation theory from the list of CSFs generated as single or double excitations from a zeroth-order wave function, ψ_o. Any CSF having a coefficient exceeding 0.08 in the wave functions for any of the states at any internuclear distance was included in ψ_o. For the $^2\Sigma$ states, the representation of ψ_o contained numerous terms, in part because the $^2\Sigma^+$ and $^2\Sigma^-$ states were considered together. In the calculations, those CSFs contributing more than 20 microhartrees (μh) to the energy were retained, and the energy contribution of those discarded was estimated by an extrapolation procedure[1]. Although these methods provide an accurate balanced description of the excited states, an uncertainty of about 0.05 eV exists in the energies resulting from the extrapolation procedures, and from difficulties in obtaining a uniform zeroth-order representation of the states as the internuclear distance varies.

In all CI calculations with basis set II, we used the $1^2\Sigma^-$ molecular orbitals as in the computations on the $^2\Sigma^+$ states. These orbitals have the advantage over the $X^2\Pi$ state orbitals that an additional orbital (4σ) is stabilized by the Hartree-Fock method. For the ground $X^2\Pi$ state and the first excited $1^2\Sigma^-$ state, a first-order CI (FOCI) calculation was performed which incorporated between 300 and 700 configurations[1]. For the FOCI calculation the molecular orbitals were partitioned into core orbitals 1σ, internal orbitals 2σ-4σ and 1π, and external orbitals 5σ-24σ, 2π-10π and 1δ-2δ. For the $D^2\Sigma^-$ state, the internal set consisted of the 2σ-10σ and 1π-4π orbitals and the external set contained the orbitals 11σ-24σ, 5π-10π and 1δ-2δ. A set of reference configurations was constructed which included all configurations with CI coefficients greater than 0.1 at any internuclear distance. All single excitations from the reference configurations and double excitations within the internal set were retained but double excitations out of the 2σ orbital were excluded. The selection process resulted in a CI matrix with 2400 configurations. The energies of this more elaborate calculation were shifted to the FOCI energies so that both yielded the same excitation energies for the $1^2\Sigma^-$ state.

The CI calculations with basis set III also used the $1^2\Sigma^-$ orbitals, and employed the Wuppertal-Bonn MRD-CI package of programs for the construction of the CI matrices. These programs select the CSFs on the basis of their energy lowerings in a secular equation with the reference configurations but the procedure is otherwise analogous to that described previously for bases I and IA. The selection threshold was set at 50 μh. An improved energy estimate was obtained by correcting the extrapolated CI energies for the effect of unlinked clusters[8,9]. This led to negligible improvement for the $^2\Sigma^+$ states and was not done in the earlier calculations[1]. Additional details of our CI methods are given in Ref. 1.

The bound-bound and bound-free absorption cross sections for transitions between electronic states depend on the electronic transition moment D(R). If the z-axis of the electron coordinates lies along the internuclear axis, D(R) is the expectation value, in atomic units, of the operators $\sum_j z_j$ or $\sum_j (x_j + iy_j)/\sqrt{2}$ for transitions in which $|\Delta\Lambda| = 0$ or 1, respectively. In terms of D(R), the electronic absorption oscillator strength at R for transitions from the $X^2\Pi$ state to the $^2\Sigma^-$ states is given by

$$f_{e\ell}(R) = \frac{2}{3}\, g\Delta E(R)\,|D(R)|^2 \qquad (1)$$

where g is a weighting factor which equals unity for $^2\Pi \rightarrow {}^2\Sigma^-$ transitions and $\Delta E(R)$ is the energy difference at R in hartrees. The band absorption oscillator strength for the transition from a bound vibrational level (v") of the ground state to a bound vibrational level (v') of a $^2\Sigma^-$ state is defined by

$$f_{v''v'} = \frac{2}{3}\, g\Delta E_{v'v''}\,|D_{v'v''}|^2 \qquad (2)$$

where $\Delta E_{v'v''}$ is the transition energy measured in hartrees and $D_{v'v''}$ is the transition matrix element

$$D_{v'v''} = (\chi_{v'}\,|D(R)|\,\chi_{v''}) \qquad (3)$$

obtained from the normalized vibrational wave functions $\chi_v(R)$ of the initial and final states. The vibrational wave functions $\chi_v(R)$ were determined by numerical integration of the radial Schrodinger equation for nuclear motion ignoring centrifugal distortion.

The absorption cross section from a bound vibrational level v" of the ground state to the vibrational continuum of a $^2\Sigma^-$ upper state can be written

$$\sigma_{v''} = 1.23\times10^{-23} g\,|(\chi_k(R)\,|D(R)|\,\chi_{v''}(R))|^2 \Delta E \text{ cm}^2 \qquad (4)$$

where k is the wave number of the continuum state. In terms of k, the kinetic energy of relative motion in the final state is $E_k = k^2/2\mu$ where μ is the reduced mass, all quantities being in atomic units. The continuum wave function $\chi_k(R)$ is normalized to the asymptotic form

$$\chi_k(R) \sim \left(\frac{2\mu}{\pi k}\right)^{\frac{1}{2}} \sin(kR+\eta) , \qquad (5)$$

where η is an elastic phase shift. The spontaneous transition probability for the emission of a photon of wavelength λ Å from a bound $^2\Sigma^-$ upper state vibrational level v' to a lower $^2\Sigma^-$ continuum state with wavenumber k" is given by

$$A_{v'}(\lambda) = \frac{9.2\times10^{20}}{\lambda^5}\,|(\chi_{k''}(R)\,|D(R)|\,\chi_{v'}(R))|^2 \qquad (6)$$

measured in photons s^{-1} Å^{-1}.

3. Results and Discussion

3.1 Potential Energy Curves

The relative potential energies of the $X^2\Pi$, $(1)^2\Sigma^-$ and $D^2\Sigma^-$ states of OH calculated with basis sets I and IA, are presented in Table I and those corresponding to basis set I are illustrated in Fig. 1. The characteristics of the ground state $X^2\Pi$ potential resulting from calculations I-III have been discussed in detail previously[1]. The $1^2\Sigma^-$ potential is repulsive everywhere. The principal spatial occupancy occurring in the description of this state is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)(1\pi)(1\bar{\pi})$ at all internuclear distances, and it separates correctly at infinite distances into ground state oxygen and hydrogen atoms. In the separation, the 4σ orbital changes from an antibonding OH orbital at a distance of 1.85 a_o to a hydrogen 1s orbital at infinity. The calculated vertical excitation energy from the minimum in the $X^2\Pi$ state (R_e = 1.8342 a_o) to the $1^2\Sigma^-$ state is 8.00, 7.97, 7.20 and 7.81 eV for basis sets I, IA, II and III wave functions, respectively. The good agreement between the basis set I and IA results indicates that Rydberg functions are unimportant to the description of the $1^2\Sigma^-$ state. The basis set I and IA energies tend to be high because they use the $X^2\Pi$ orbitals, whereas the basis set II and III results may be low both because they used the $1^2\Sigma^-$ orbitals and because smaller CI wave functions were employed. From the larger CI calculations, it appears certain that the vertical excitation energy to the $1^2\Sigma^-$ state is 7.95 ± 0.1 eV. The precise location of the $1^2\Sigma^-$ state is crucial to the determination of the OH photodissociation rate in cometary atmospheres.

The $D^2\Sigma^-$ state is described principally by the spatial occupancy $(1\sigma)^2(2\sigma)^2(3\sigma)^2(5\sigma)(1\pi)(1\bar{\pi})$ at 1.85 a_o, where the 5σ orbital contains significant 3s and $3p\sigma$ Rydberg character. At larger distances, other spatial occupancies such as $(1\sigma)^2(2\sigma)^2(3\sigma)(4\sigma)(5\sigma)(1\pi)(1\bar{\pi})$ become important, in part because the molecular orbitals are themselves not optimum for the description of the $D^2\Sigma^-$ state. The $D^2\Sigma^-$ state dissociates to the excited $O(^3S)$ state of oxygen and a ground state hydrogen atom. In contrast to the repulsive $1^2\Sigma^-$ state, it is strongly bound. Using the experimental oxygen atom energy levels[10] and the excitation energy T_e of the $D^2\Sigma^-$ state[2] and dissociation energy D_e of the $X^2\Pi$ state[11], we obtain a binding energy of 3.95 eV for the $D^2\Sigma^-$ state. The calculated spectroscopic parameters T_e and R_e for the $D^2\Sigma^-$ state are compared with experiment in Table II. The basis set I results are in remarkable, though in part fortuitous, agreement with experiment[2], whereas the basis set IA results for both T_e and R_e are slightly too small. The basis set II wavefunctions overestimate R_e and underestimate T_e, whereas basis set III wave functions underestimate both, particularly R_e. The good agreement obtained for T_e with basis set I arises from a cancellation of errors. On the one hand, basis set I does not contain sufficiently diffuse 3s and 3pσ functions to describe accurately the $D^2\Sigma^-$ state and on the other hand it omits a larger amount of the correlation energy of the $X^2\Pi$ state than of the $D^2\Sigma^-$ state. Our methods yield about the same percentage, 70% for basis set I, of the valence correlation energy of the $X^2\Pi$ and $D^2\Sigma^-$ states, but because the total correlation energy is greater for the compact $X^2\Pi$ state than for the diffuse $D^2\Sigma^-$ state, a bias is created in favor of the $D^2\Sigma^-$ state. When the basis set deficiencies are removed by using basis IA, the predicted values of T_e and R_e are too small. This problem is more severe for the basis set III calculations, which account for the smaller fraction, 60%, of the valence correlation energy and for the basis set II calculations, where only 20% of the valence correlation energy was recovered. Similar arguments apply to the limited MCSCF calculations of Ray and Kelly[6].

3.2 Transition Moments

The calculated electronic transition moments of the $1^2\Sigma^- - X^2\Pi$ and $D^2\Sigma^- - X^2\Pi$ transitions obtained with basis sets I, IA, II and III are given in Tables III and IV and are illustrated in Figs. 2 and 3, respectively. The basis set I results for the $1^2\Sigma^- - X^2\Pi$ transition are not shown in Fig. 2. They are almost identical to the basis set IA results, demonstrating the insensitivity of the transition moment function to the addition of diffuse functions. The close agreement between all of the theoretical transition moment functions, especially for R values near the ground state minimum, indicates that the magnitude of the theoretical photodissociation cross sections should be reliable.

The theoretical $D^2\Sigma^- - X^2\Pi$ transition moment functions in Fig. 3 show larger discrepancies. There are substantial differences between the basis set I and IA results, particularly for $R < 2.25\ a_o$ where the diffuse character of the $D^2\Sigma^-$ state is most prevalent and reduces the magnitude of the transition moment. The basis set IA transition moment function is in reasonable agreement with the basis set II and III results for small internuclear distances, but rises more steeply at larger distances. Beyond 2.5 a_o the theoretical transition moment functions stay approximately constant. The $D^2\Sigma^- - X^2\Pi$ moment should approach 0.40 ± 0.04 at infinite separation, the value appropriate to the $O(^3P) - O(^3S)$ transition[12]. The MCSCF value of Ray and Kelly[6] computed at the equilibrium separation of the ground state is also shown in Fig. 3. It agrees well with the basis set II and III results.

The electronic dipole moments for the $D^2\Sigma^- - 1^2\Sigma^-$ transition obtained with basis sets IA and II are given in Table V and illustrated in Fig. 4. The magnitude of the transition moment decreases rapidly with increasing R. The two theoretical transition moments are in good agreement for $R \leq 2.5\ a_o$ where the transition moment has large amplitude.

3.3 Oscillator strengths and photodissociation cross sections

a) Absorption into the $D^2\Sigma^-$ state

The electronic absorption oscillator strengths f_{el} at the equilibrium separation of the ground state, and the 0-0 band absorption oscillator strength f_{00} for the $D^2\Sigma^- - X^2\Pi$ transition are tabulated in Table VI. The theoretical energy differences were used in computing f_{el}. To determine the band absorption oscillator strength f_{00}, we used the calculated potential energy curves in the equations for the vibrational wave functions, together with the corresponding transition moment function. The potential energy curves were shifted to be consistent with the experimental excitation energy. The basis set IA transition moments were used in conjunction with the basis set I potential curves. An empirical value of f_{00} has been obtained from astronomical observations of OH in diffuse interstellar clouds[3]. The derived value of 0.0108 ± 0.003 agrees closely with the theoretical values obtained with wave functions IA, II and III. The basis set I result of 0.016 is probably a reliable upper bound, because the lack of 3s and 3pσ oxygen basis functions tends to produce an overestimate of the $D^2\Sigma^- - X^2\Pi$ transition moment. These results rule out the earlier estimate of 0.1.[13]

Because the dipole moment changes rapidly with R, the close agreement obtained with wavefunctions II and III is partly fortuitous. If the basis set I potential energy curves, which are positioned closest to the experimental curves, are used together with the basis set II and III transition moments, changes of up to 30% in f_{00} are observed. The rapid variation of D(R) is the major source of the inaccuracy in the prediction of Ray and Kelly[6], which was carried out in advance of the astronomical determination. Table VII lists the absorption oscillator strengths $f_{0v'}$ of the $D^2\Sigma^- - X^2\Pi$

transition for upper state vibrational levels up to v'=3, calculated using the basis set I potential curves and basis set IA transition moment function.

The $D^2\Sigma^-$ state can radiate to the lower repulsive $1^2\Sigma^-$ state, which leads to dissociation of the molecule. The continuous spectra emitted in the transition from the $D^2\Sigma^-$ state to the $1^2\Sigma^-$ state are shown in Figure 5 for v'=0 and 1, obtained using the basis set I potential curves and the basis set IA transition moment function. The integrated transition probability, $\int A_{v'}(\lambda)d\lambda$, is $3.4\times10^7\ s^{-1}$ for v'=0 and $3.2\times10^7\ s^{-1}$ for v'=1, values which agree to within 10% with those obtained with the basis set II potential curves and transition moments. The $D^2\Sigma^-$ state can also radiate into the ground electronic state. The summed transition probability into the discrete levels of the ground $X^2\Pi$ state we calculate to be $2.3\times10^8\ s^{-1}$ for v'=0 and $2.4\times10^8\ s^{-1}$ for v'=1 using the basis set I curves and the basis set IA moments. With the basis set II results we obtain $1.5\times10^8\ s^{-1}$ for v'=0 and $1.6\times10^8\ s^{-1}$ for v'=1. Thus, about one fifth of the absorptions into the $D^2\Sigma^-$ v'=0 and 1 levels lead to dissociation of the molecule. With the oscillator strengths and wavelengths of Table VII, the dissociation rate corresponding to the interstellar radiation field used by Roberge _et al._[14] is $1.0\times10^{-11}\ s^{-1}$ in the optically thin limit.

b) Absorption into the $1^2\Sigma^-$ state

Absorption into the $1^2\Sigma^-$ state leads directly to dissociation. The effective oscillator strength has been estimated as 8×10^{-4} by Solomon[15] and as 10^{-2} by Tarafdar and Das.[16] We obtain at R = 1.85 a_o a value of 3.4×10^{-2} for $f_{e\ell}$ so that absorption into the $1^2\Sigma^-$ state is a major destruction mode for OH in diffuse interstellar clouds and in comets.

The photodissociation cross sections obtained with wave functions IA, II and III for absorption from the v"=0 level of the $X^2\Pi$ state are illustrated in fig. 6 as a function of incident photon energy. The cross section shapes obtained with the three wave functions are similar but, consistent with the different vertical excitation energies, there are small shifts in the effective thresholds. Table VIII contains the numerical values obtained with basis set IA.

The cross sections listed in table VIII lead to a photodissociation rate of $2.2 \times 10^{-6}\ s^{-1}$ at the mean Earth-Sun distance (1 A.U.) in conditions of average solar intensities, the rate changing by less than a factor of two between solar maximum and minimum. The solar spectrum is varying rapidly in the vicinity of the effective threshold for absorption of photons into the $1^2\Sigma^-$ state. The uncertainty of 0.1 eV in the calculated excitation energy produces an uncertainty of 25% in the solar induced photodissociation rates.

The interstellar radiation field is nearly uniform in the spectral region where absorption into the $1^2\Sigma^-$ state occurs, and the interstellar photodissociation rate is insensitive to the detailed location of the threshold. Corresponding to the radiation field used by Roberge et al.,[14] we obtain in the optically thin limit a rate of $1.3 \times 10^{-10}\ s^{-1}$.

In experimental situations, OH is often vibrationally excited.[17] Figs. 7 and 8 illustrate the photodissociation cross sections for absorption from the excited v"=1 and v"=2 levels of the ground state using the basis set IA potential curves and transition moments. The structure reflects that of the initial vibrational wave function.

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Table I

The $X^2\Pi$, $1^2\Sigma^-$ and $D^2\Sigma^-$ potential energies in eV calculated using basis set I and IA

$R(a_o)$	$X^2\Pi$		$1^2\Sigma^-$		$D^2\Sigma^-$	
	I	IA	I	IA	I	IA
1.30	4.07	-	-	-	-	-
1.50	1.18	1.20	10.03	10.00	12.05	11.76
1.75	0.06	0.06	8.31	8.29	10.57	10.28
1.8342	0.00	0.00	8.00	7.97	10.37	10.10
2.00	0.14	0.15	7.55	7.50	10.22	9.98
2.25	0.70	0.74	6.94	6.91	10.31	10.12
2.50	1.37	1.43	6.35	6.33	10.63	10.48
2.75	2.06	2.12	5.86	5.82	11.05	10.97
3.00	2.66	2.68	5.46	5.47	11.48	11.46
3.25	3.16		5.16		11.96	
3.50	3.54		4.95		12.40	
3.75	3.82		4.80		12.77	
4.00	4.03		4.68		13.10	
4.50	4.26		4.55			
5.00	4.38		4.48			
6.00	4.47		4.43			

Table II

Spectroscopic parameters for the $D^2\Sigma^-$ state of OH

Parameter	Basis Set I	 IA	 II	 III	Ray and Kelly[6]	Experiment[2]
$R_e (a_o)$	2.05	2.02	2.06	1.95		2.043
T_e (eV)	10.22	9.98	9.16	9.93	<9.4	10.20[a]

[a] The value of 10.20 eV was obtained by correcting the reported T_o value by the difference in zero-point energies between the $D^2\Sigma^-$ and $X^2\Pi$ states.

Table III

Theoretical $1^2\Sigma^- - X^2\Pi$ electronic transition moments of OH in a.u.[a]

$R(a_o)$	Basis Set			
	I	IA	II	III
1.00	-	-	0.480	-
1.20	-	-	-	0.481
1.30	-	-	0.482	-
1.50	0.456	0.463	0.472	0.468
1.75	0.422	0.430	0.439	0.433
1.8342	-	0.412	-	-
1.85	-	-	0.416	-
2.00	0.353	0.363	0.368	0.359
2.25	0.272	0.278	0.276	0.254
2.50	0.209	0.215	0.205	0.174
2.75	0.165	0.170	-	-
3.00	0.131	0.136	0.126	0.098
3.25	0.105	-	-	-
3.50	0.084	-	0.080	0.061
3.75	0.066	-	-	-
4.00	0.050	-	0.048	0.036
4.50	0.029	-	-	-
5.00	0.012	-	-	-
6.00	0.003	-	-	0.002

[a] The operator is $(x+iy)/\sqrt{2}$

Table IV

Theoretical $D^2\Sigma^- - X^2\Pi$ electronic transition moments for OH in a.u.[a]

	Basis Set				
$R(a_o)$	I	IA	II	III	Ray and Kelly[6]
1.30	-	-	0.127	-	
1.50	0.218	0.153	0.148	0.143	
1.60	-	-	0.162	-	
1.75	0.276	0.216	-	0.175	
1.8342	-	0.246	-	-	0.190[b]
1.85	-	-	0.211	0.197	
2.00	0.351	0.310	0.247	0.238	
2.25	0.402	0.394	0.301	0.308	
2.50	0.412	0.435	0.329	0.347	
2.75	0.402	0.446	-	-	
3.00	0.411	0.456	0.331	0.354	
3.25	0.384		-	-	
3.50	0.352		0.332	0.339	
3.75	0.324		-	-	
4.00	0.291		0.340	0.291	

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[a] The operator is $(x+iy)/\sqrt{2}$

[b] Their result in the velocity formulation is 0.179

Table V

Theoretical $D^2\Sigma^- - 1^2\Sigma^-$ electronic transition moments for OH in a.u.

$R(a_o)$	Basis Set	
	IA	II
1.30	-	2.373
1.50	2.292	2.310
1.60	-	2.239
1.75	2.018	-
1.8342	1.831	-
1.85	-	1.886
2.00	1.399	1.536
2.25	0.815	0.887
2.50	0.501	0.490
2.75	0.195	-
3.00	-0.299	0.141
3.50		-0.134
4.00		-0.218
8.00		-0.482

Table VI

The absorption oscillator strengths of the $D^2\Sigma^- - X^2\Pi$ transition

	Basis Set				Ray and Kelly[6]	Observation[3]
	I	IA	II	III		
f_{el}[a]	0.023	0.015	0.010	0.010	0.008	-
f_{00}[b]	0.016	0.012	0.011	0.011	0.004[c]	(0.0108 ± 0.003)

[a] See Eq. 1 for definition. The theoretical excitation energies were used.

[b] See Eq. 2 for definition. The experimental T_o value was used. In the vibrational analysis, the theoretical potentials were used.

[c] Obtained assuming a constant transition moment, and a Franck-Condon factor of 0.45, based on a Morse representation of the potentials.

Table VII

Band absorption oscillator strengths and wavelengths for the $D^2\Sigma^-(v')-X^2\Pi(v''=0)$ transitions[a]

v'	$f_{0v'}$	$\lambda(\mathring{A})$
0	1.2(-2)	1222.1
1	4.4(-3)	1188.7
2	5.8(-4)	1158.4
3	9.6(-6)	1130.9

[a] Calculated using the basis set I potential curves and the basis set IA transition moment function.

Table VIII

Calculated photodissociation cross sections for absorption into the $1^2\Sigma^-$ state from the $X^2\Pi(v''=0)$ level using the basis set IA potential curves and transition moment function

E(eV)	$\sigma(10^{-18}\mathrm{cm}^2)$
6.50	0.01
7.00	0.28
7.20	0.70
7.40	1.42
7.60	2.28
7.80	2.90
7.90	3.01
8.00	2.97
8.20	2.54
8.40	1.84
8.60	1.14
8.80	0.59
9.00	0.25
9.50	0.01

Figure Captions

Fig. 1 - Theoretical basis set I potentials for the $X^2\Pi$, $1^2\Sigma^-$ and $D^2\Sigma^-$ states of OH.

Fig. 2 - Theoretical $1^2\Sigma^- - X^2\Pi$ electronic transition moments. The Δ's, □'s and o's represent the basis set IA, II and III results, respectively.

Fig. 3 - Theoretical $D^2\Sigma^- - X^2\Pi$ electronic transition moments. The ∇'s, Δ's, □'s and o's represent the basis set I, IA, II and III results, respectively. The MCSCF result of Ray and Kelly[6] at $R = 1.8342\ a_o$ in the length formulation is denoted by the x.

Fig. 4 - Theoretical $D^2\Sigma^- - 1^2\Sigma^-$ electronic transition moments. The Δ's and □'s represent the basis set IA and II results, respectively.

Fig. 5 - The continuous emission spectra originating from the v'=0 and v'=1 levels of the $D^2\Sigma^-$ state in the transition to the $1^2\Sigma^-$ state.

Fig. 6 - The photodissociation cross section for absorption from the v"=0 level of the $X^2\Pi$ state into the $1^2\Sigma^-$ state calculated with wave functions IA, II and III.

Fig. 7 - The photodissociation cross sections for absorption from the v"=1 level of the $X^2\Pi$ state into the $1^2\Sigma^-$ state calculated with wave function IA.

Fig. 8 - As for Fig. 7 for the v"=2 level.

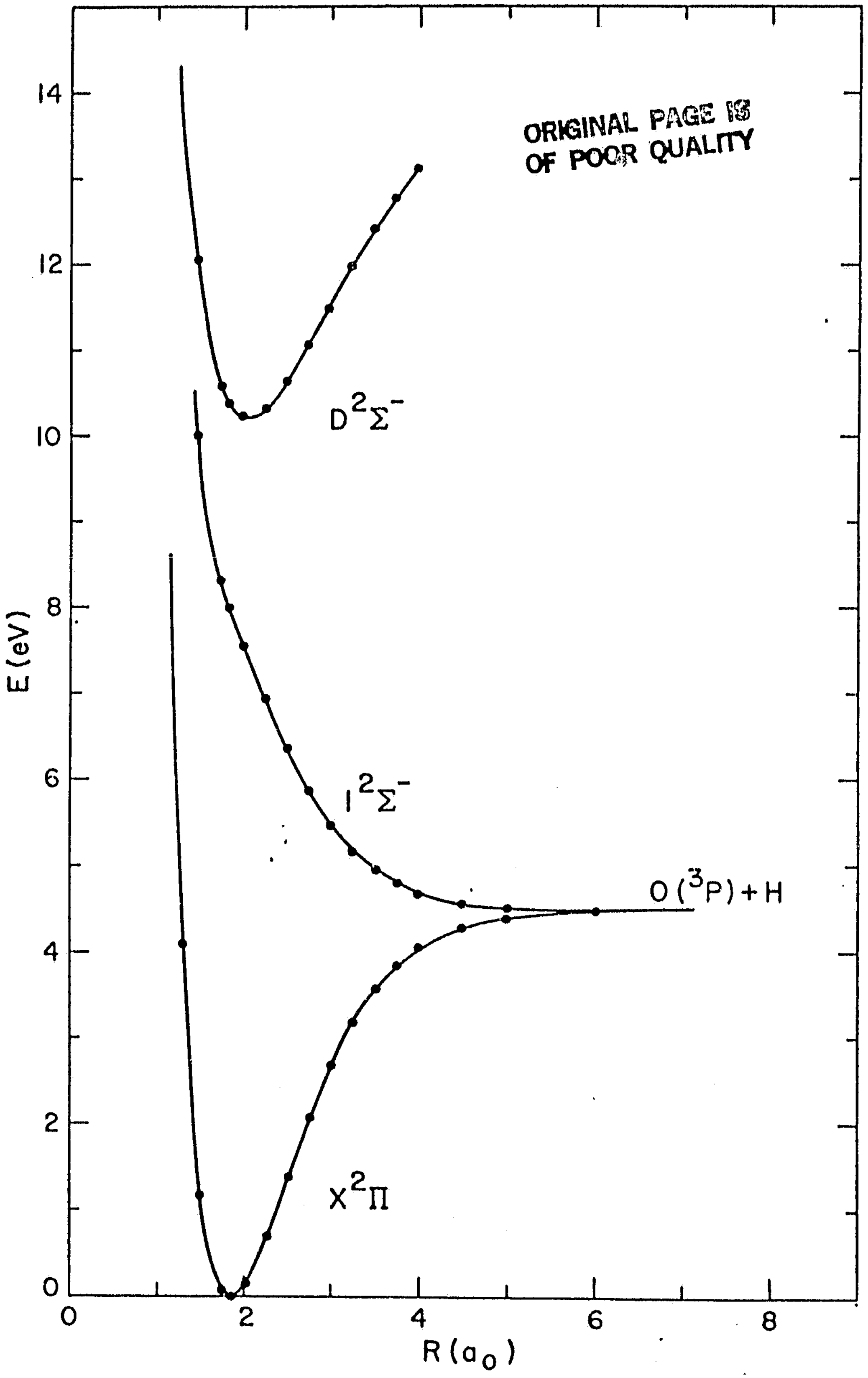

Figure 1

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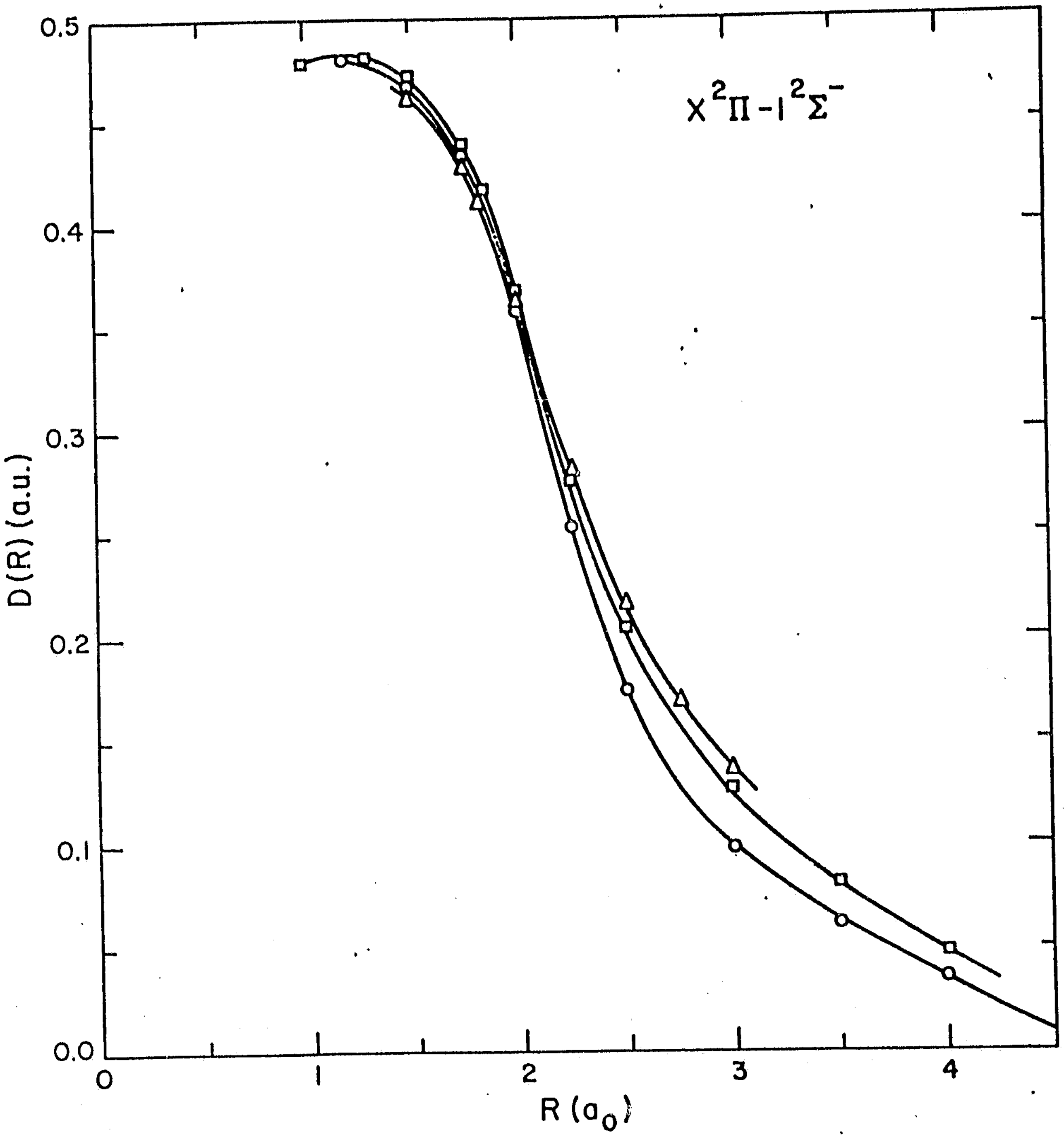

Figure 2

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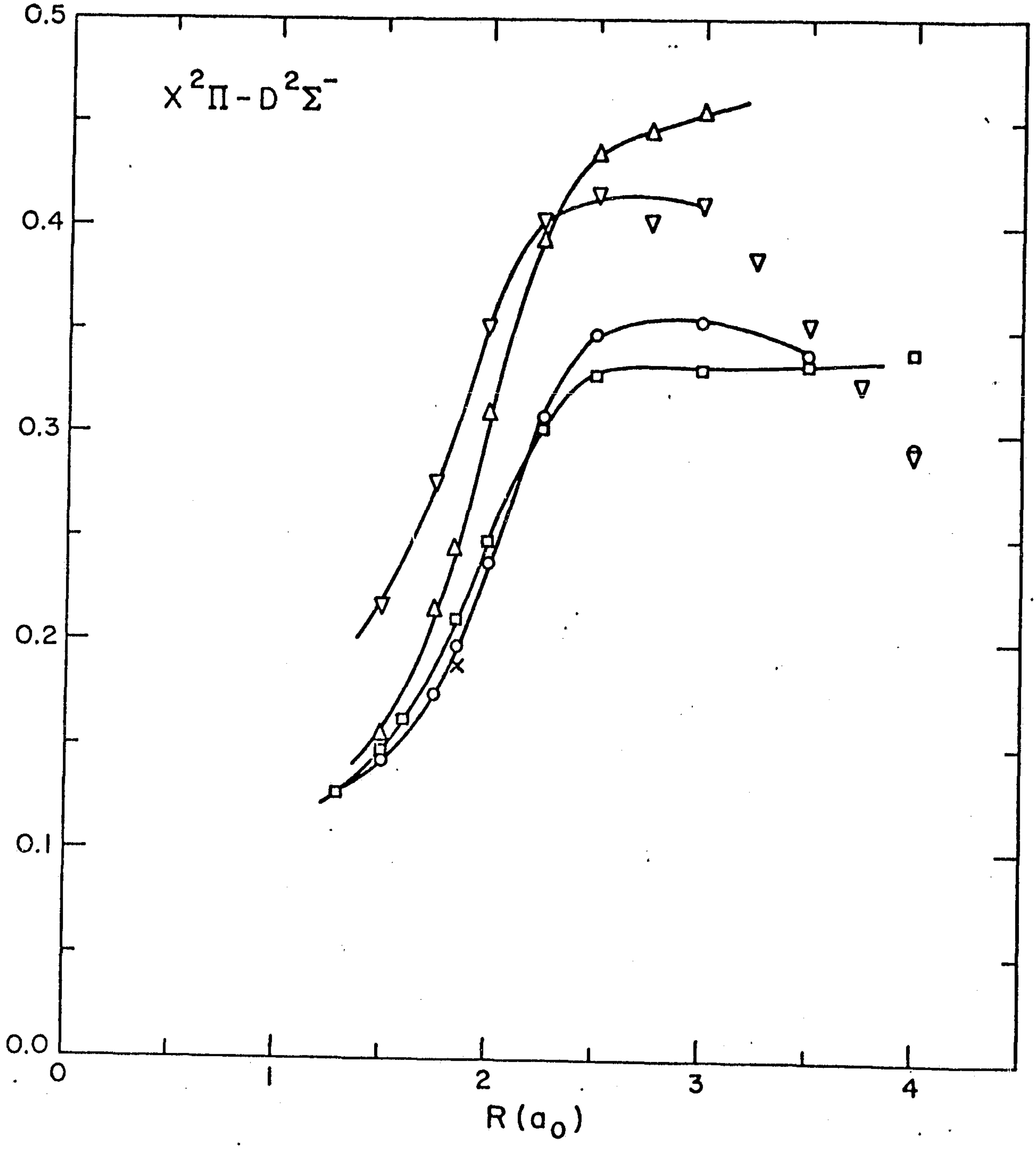

Figure 3

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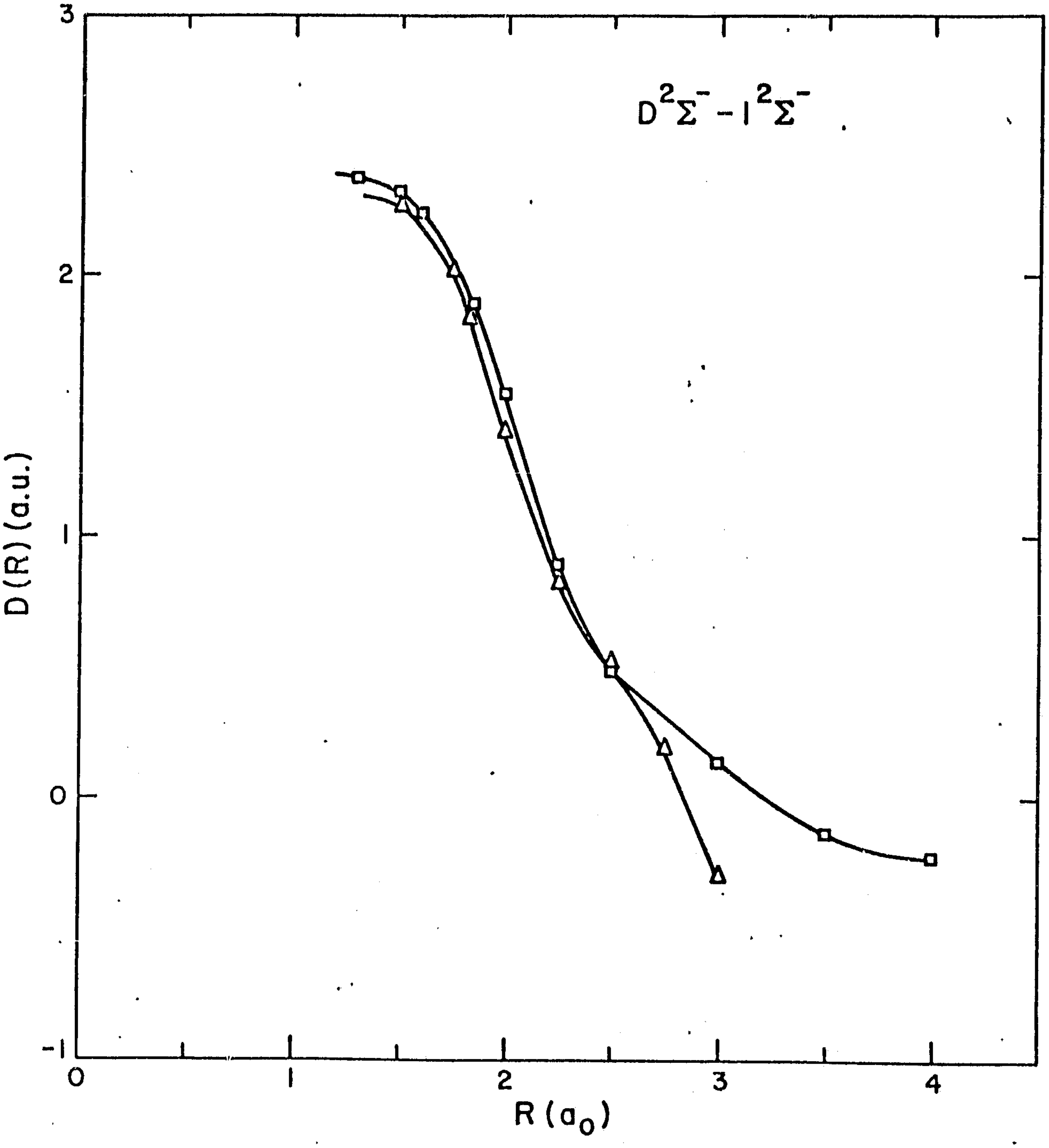

Figure 4

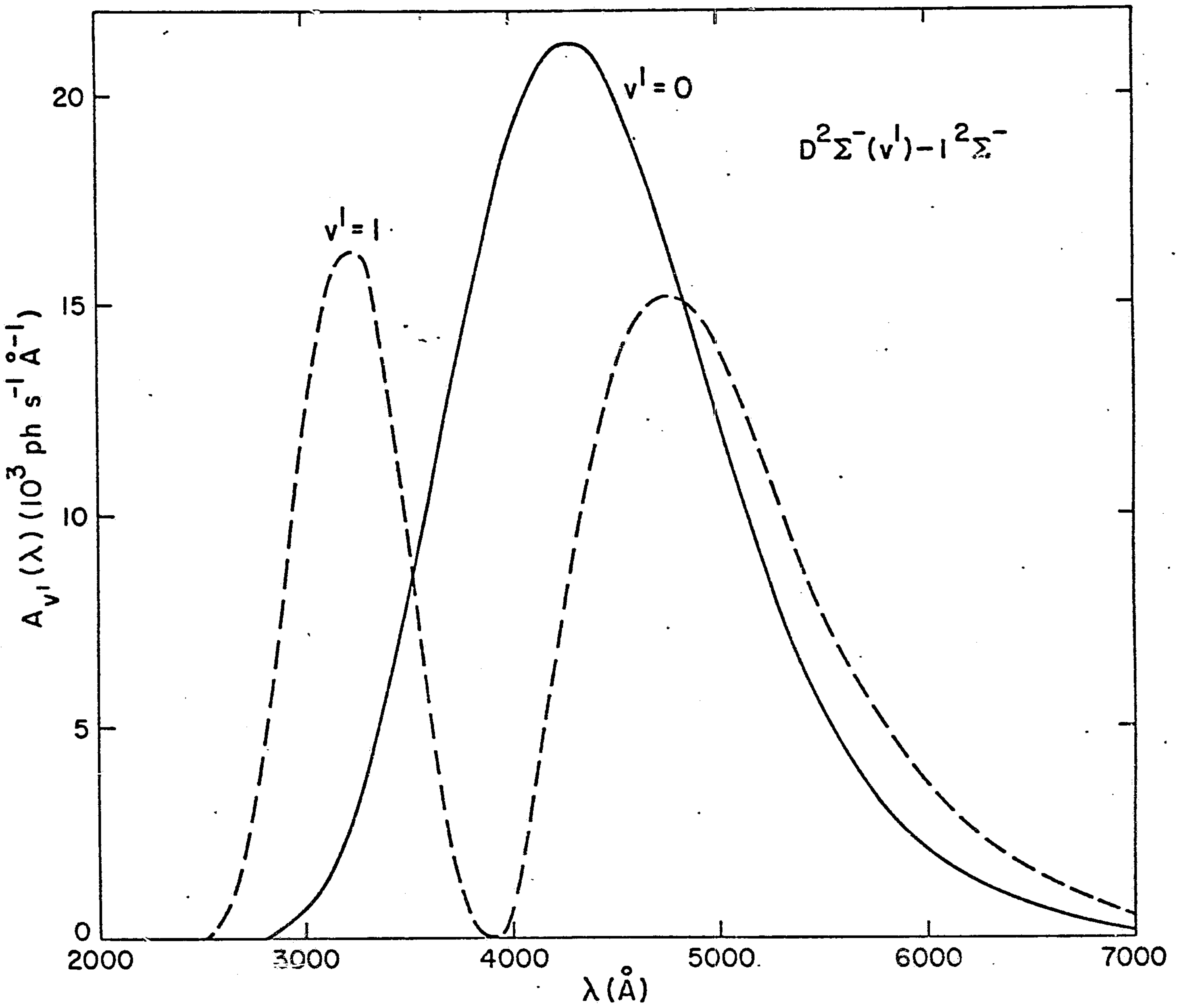
$A_{v'}(\lambda)$ (10^3 ph s^{-1} Å^{-1})
0
5
10
15
20
2000
3000
4000
5000
6000
7000
λ(Å)
$v' = 1$
$v' = 0$
$D^2\Sigma^-(v') - 1^2\Sigma^-$

Figure 5

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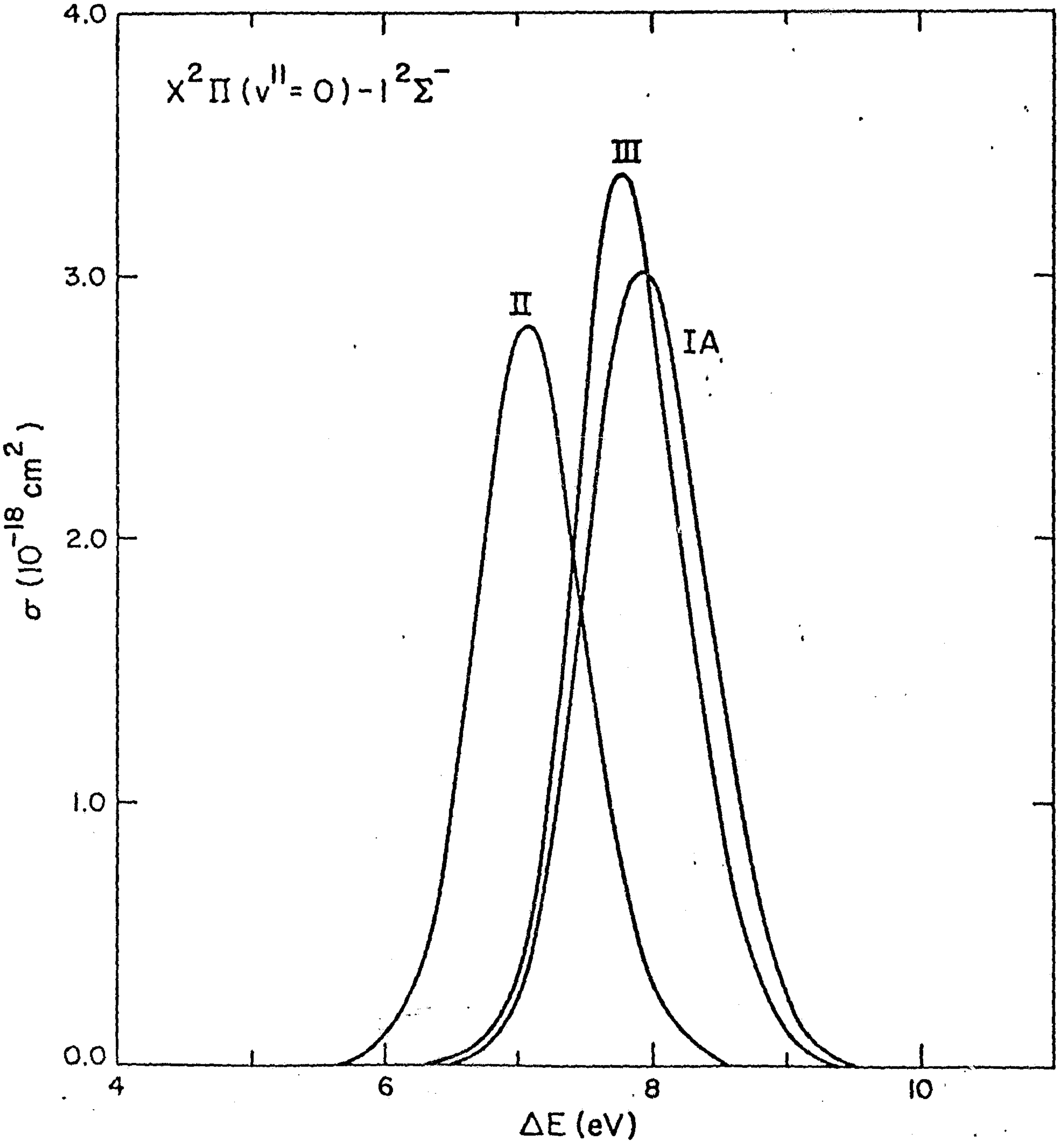

Figure 6

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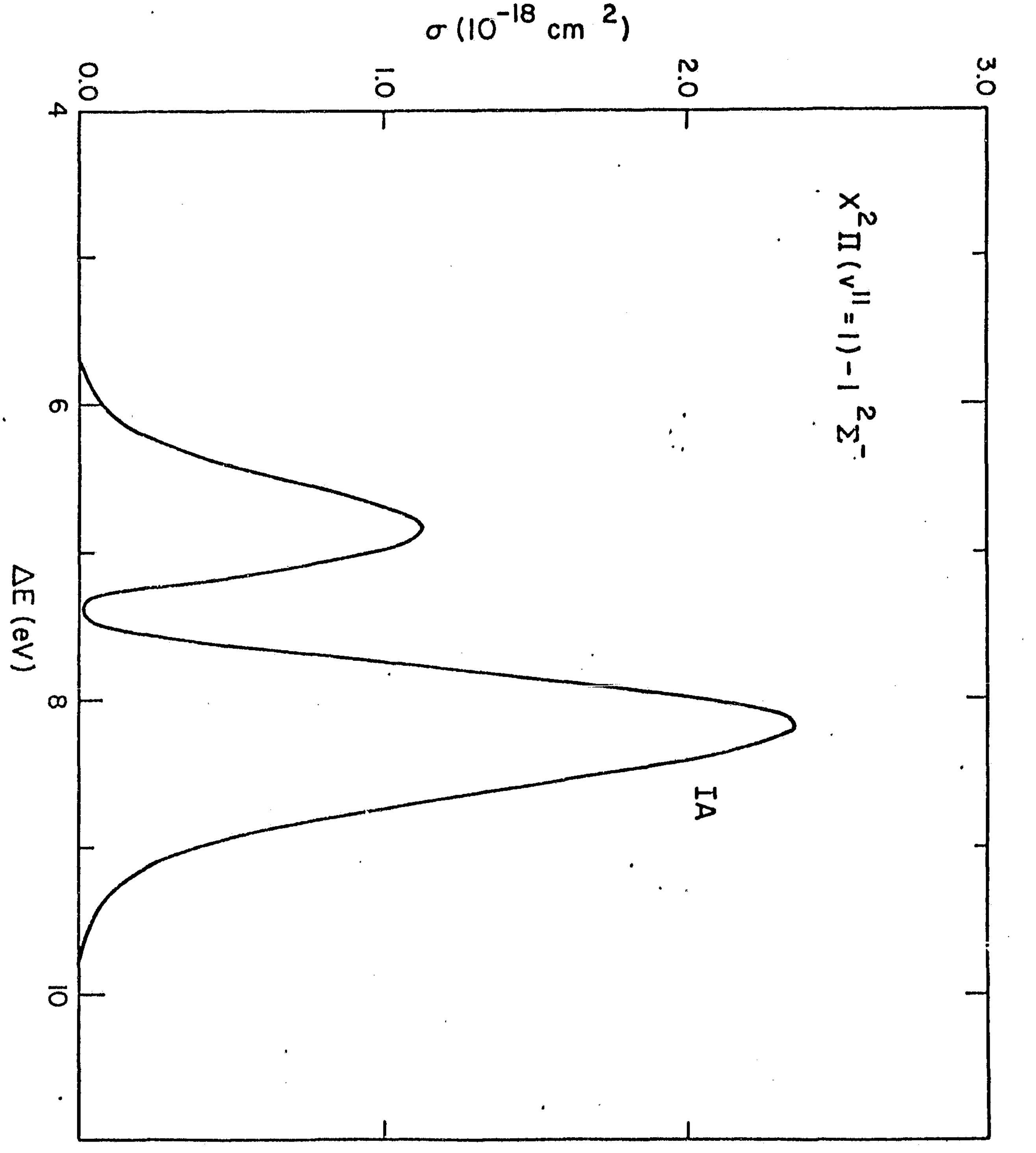

Figure 7

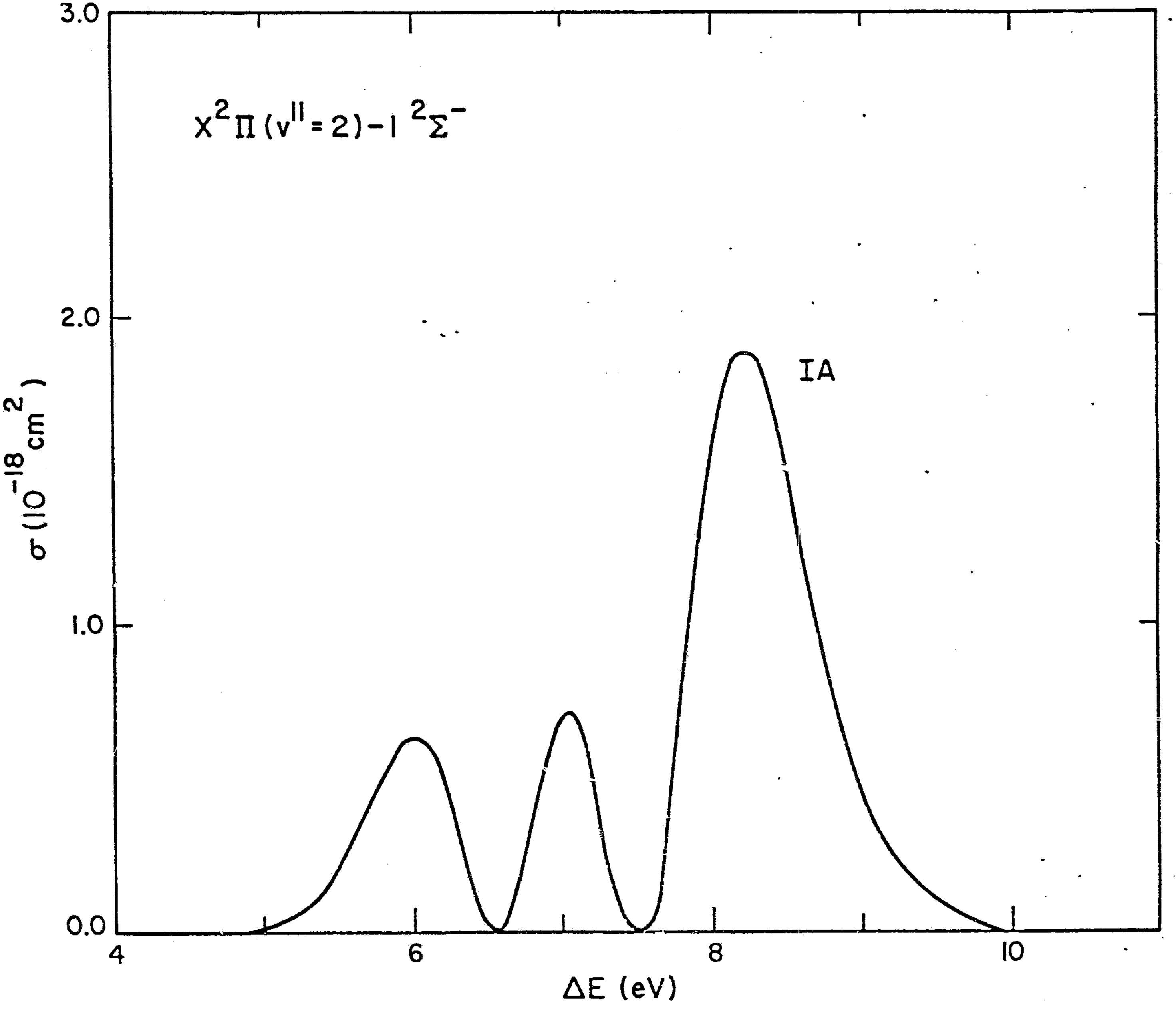

Figure 8

The photodissociation lifetimes of the OH and OD radicals in comets

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The rates of photodissociation of the OH and OD molecules from absorption of solar radiation in the $X^2\Pi - A^2\Sigma^+$ electronic transition are calculated to lie between 2.0 and 3.7×10^{-6} s^{-1} for OH and to be about 2.4×10^{-7} s^{-1} for OD at 1 AU from the Sun. The corresponding lifetimes which are upper bounds to the actual lifetimes are generally consistent with the observational cometary data.

1. Introduction

Jackson (1980) has pointed out that the OH radical in cometary atmospheres is destroyed by a photodissociation process initiated by the absorption of solar radiation into high vibrational levels of the excited electronic $A^2\Sigma^+$ state. The vibrational levels of the $A^2\Sigma^+$ state with quantum numbers $v' \geq 2$ undergo predissociation with an efficiency close to unity for all rotational levels (Brzozowski, Erman and Lyyra 1978). Because the dissociation is stimulated by line absorption in a wavelength region where the solar spectrum is rapidly varying the corresponding lifetime of OH depends upon the radial velocity of the comet (Jackson 1980). The deuterated molecule OD is destroyed by a similar process at, as we shall argue, a much slower rate. We take the opportunity to present improved estimates of the photodissociation rate of OH.

2. Photodissociation of OH

Detailed calculations of the populations of the rotation-vibration levels of the ground electronic $X^2\Pi$ state of OH (Mies 1974, Biraud et al. 1974, Elitzur 1981, Despois et al. 1982, Schleicher and A'Hearn 1982) show that at a distance of 1 AU from the sun, about 97% of the OH molecules reside in the $J''=3/2$, $N''=1$, $v''=0$ level of the $X^2\Pi_{3/2}$ state. The calculations are consistent with observational data and in particular with high resolution ultraviolet spectra obtained from the IUE satellite (Jackson et al. 1979, Feldman et al. 1980).

For each band, six allowed absorption lines occur labelled

$P_1(1)$, ${}^QP_{21}(1)$, $Q_1(1)$, ${}^RQ_{21}(1)$, $R_1(1)$ and ${}^SR_{21}(1)$. The excitation rate for the absorption of solar radiation into vibrational level v' of the $A^2\Sigma^+$ electronic state is given for unit density of OH by the sum over the individual lines

$$\sum_{J',N'} B_{0v'}(\tfrac{3}{2}, 1-J',N')\ \rho_{\nu'}(\tfrac{3}{2}, 1-J',N')\ s^{-1}$$

where $\rho_{\nu'}$ is the mean radiation density of the solar flux in units of ergs cm^{-2} at the wavenumber ν' in cm^{-1} of the transition from the level $(J''=\frac{3}{2}, N''=1, v''=0)$ of the $X^2\Pi$ state to the level (J', N', v') of the $A^2\Sigma^+$ state and $B_{0v'}(\frac{3}{2}, 1-J', N')$ is the corresponding Einstein B coefficient for absorption in units of cm^2 $ergs^{-1}$ s^{-1}. The B coefficient may be written in terms of the coefficient $A_{v'0}(J', N'-\frac{3}{2}, 1)$ for spontaneous emission according to

$$B_{0v'}(J''N''-J'N') = \frac{1}{8\pi hc\nu'^3}\ \frac{(2J'+1)}{2(2J''+1)}\ A_{v'0}(J'N'-J''N'') \quad .$$

In terms of the absorption oscillator strength $f_{0v'}(J''N''-J'N')$,

$$A_{v'0}(J'N'-J''N'') = \frac{8\pi^2e^2\nu'^2}{mc}\ \frac{2(2J''+1)}{(2J'+1)}\ f_{0v'}(J''N''-J'N') \quad .$$

To a close approximation, the line absorption oscillator strength may be expressed in terms of the band oscillator strength $f_{0v'}$ by the relationship

$$f_{0v'}(J''N''-J'N') = \frac{S(J''N''-J'N')}{(2J''+1)}\ f_{0v'}$$

where S(J"N"-J'N') are Hönl-London factors normalized according to

$$\sum_{J''} \frac{S(J''N''-J'N')}{(2J''+1)} = 1 \quad .$$

In the expression used by Jackson (1980) for the Einstein B coefficient, the Hönl-London factors appear to be normalized incorrectly.

Many estimates have been made of the absorption oscillator strengths of the $A^2\Sigma^+-X^2\Pi$ transition in OH. Boring, Wadt and Cartwright (1982) have reviewed the experimental and theoretical data and they recommend a radiative lifetime of 688 ns for the $A^2\Sigma^+$ state which corresponds to an oscillator strength f_{00} of $1.02\mathrm{x}10^{-3}$. Recently McDermid and Laudenslager (1982) have measured a lifetime of 721 ± 9 ns corresponding to $f_{00} = (0.976 \pm 0.012) \times 10^{-3}$. Their value may be affected by rotational excitation. Wang and Killinger (1979) and Chidsey and Crosley (1980) have shown that f_{00} decreases slowly with increasing rotational quantum number. For the rotationless limit Wang and Huang (1980) recommend the value $(1.09 \pm 0.04) \times 10^{-3}$ and Smith and Crosley (1981) the value $(1.10 \pm 0.03) \times 10^{-3}$.

The values of $f_{0v'}$ for higher values of v' are uncertain. The limited experimental data (cf. Crosley and Lengel 1975) suggest that f_{01}/f_{00} is about 0.3 but no reliable information exists on f_{02}. Because of extreme cancellation in the evaluation of the vibrational matrix elements the theoretical predictions are sensitive to details of the transition dipole moment as a function of internuclear distance. Table 1 lists the calculated band oscillator strengths corresponding to the dipole moment of Chu et al. (1974) and to the dipole moments of Langhoff et al. (1982) obtained with their case I and case III wave functions. Comparison with the experimental data on the 0-0 transition suggests a slight preference for the values derived from the dipole moment of Chu et al. (1974) and we adopt them.

The value of $5.4\text{x}10^{-5}$ for f_{02} is equivalent to a spontaneous vibrational emission transition probability A_{20} of $1.06\text{x}10^{5}$ s^{-1}. The approximate estimate made earlier by Jackson (1980) is equivalent to the much smaller rate of $1.05\text{x}10^{4}$ s^{-1}. The discrepancy is attributable mainly to the variation with internuclear distance of the transition moment which is not taken into account in the procedure followed by Jackson (1980).

The Honl-London factors S(J"N"-J'N') depend upon the coupling constant a of the X^2 state (cf. Dieke and Crosswhite 1962, Schleicher and A'Hearn 1982). For v" = 0, a = -7.547 (Dieke and Crosswhite 1962, Moore and Richards 1971). We present in table 2 the Hönl-London factors and the wavelengths of the six absorption lines from the J"=3/2, N"=1, v"=- level to the optically allowed J', N', v'=2 levels.

The solar radiation densities at the transition wavelengths have been calculated by Jackson (1980) for a range of cometary radial velocities between ± 60 km s^{-1}. Using them we may calculate the rates of photodissociation of OH by absorption of solar photons into the v'=2 level. The values are compared with the results of Jackson (1980) in table 3. At a distance of 1 AU from the Sun, they range from $3.16\text{x}10^{-6}$ s^{-1} for a radial velocity towards the sun of 58 km s^{-1} to $1.20\text{x}10^{-6}$ s^{-1} for a radial velocity away from the sun of 60 km s^{-1}. They are smaller than the rates calculated by Jackson (1980) by factors of about four.

The contribution to photodissociation from absorption into the v'=3 level was considered briefly by Jackson (1980). The corresponding absorption line wavelengths are listed in table 2. The ratio of the absorption oscillator strengths f_{03}/f_{02} is about 0.15 and the ratio of the solar intensities near 245 nm and 261 nm is about 0.6 (cf. Mount and Rottman 1981) so that the inclusion of the v'=3 channel increases the photodissociation rates by 9%. Because the increase is small, we ignore any dependence on the radial velocity of the comet and simply add to the rates for v'=2 listed in Table 3 a factor 0.09 of the zero velocity v'=2 value. Absorptions into levels v'>3 are negligible in comparison.

3. Photodissociation of OD

A similar analysis may be carried through for OD with the interesting difference that the v'=2 level of the $A^2\Sigma^+$ state of OD does not undergo significant predissociation and it is absorptions into the v'=3 and v'=4 levels that determine the resulting photodissociation rate. We have calculated the absorption oscillator strengths $f_{0v'}$ of the $X^2\Pi - A^2\Sigma^+$ transition of OD using empirical potential energy curves and the dipole transition moment function of Chu et al. (1974). The values are given in table 4.

Bergeman, Erman, Haratym and Larsson (1981) have carried out measurements of the lifetimes of rotational levels of the v'=0-3 vibrational states of OD. Their analysis of the data suggests a predissociation rate for low-lying rotational levels of the v'=3 state of about 6.9×10^{5} s^{-1} out of a total rate of about 2×10^{6} s^{-1}. The corresponding predissociation efficiency η is 0.34. The absorption lines occur at wavelengths near 2575 Å (Clyne, Coxon and Woon Fat 1973) and the corresponding photodissociation rate at zero velocity is about $2.0 \times 10^{-7} s^{-1}$. No estimate is available for the predissociation efficiency η for v'=4. We adopt a value of unity. The absorption lines lie near 2450 Å. With an oscillator strength of 1.2×10^{-6}, the absorption into the v'=4 level leads to a photodissociation rate of approximately 3.5×10^{-8} s^{-1}. The total photodissociation rate of OD at 1 AU from the Sun through absorption into the excited $A^2\Sigma^+$ state is $2.4 \times 10^{-7} s^{-1}$, leading to the possibility of a substantial enhancement in the relative abundance of OD/OH compared to [D]/[H]. However there are other dissociation mechanisms, one such being that due to absorptions into the repulsive $1^2\Sigma^-$ state (van Dishoeck, Langhoff and Dalgarno 1983), which will limit the enhancement.

Because of the additional paths, the predicted lifetimes from absorption into the $A^2\Sigma^+$ state are upper bounds to the actual lifetimes. The analyses of cometary data on OH in comets (Keller and Lillie 1974, Blamont and Festou 1974, Feldman and Brune 1976, Feldman et al. 1980, Festou 1981, Despois et al. 1981, Weaver et al. 1981) yielded lifetimes of the same order but generally below and hence consistent with the calculated values. A study of the additional destruction processes is in progress.

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Table 1

Theoretical band oscillator strengths of OH corresponding to different calculations of the transition dipole moment.

	$f_{0v'}$	Chu	Langhoff et al. Case I	Langhoff et al. Case III
v'	0	1.1×10^{-3}	1.2×10^{-3}	1.15×10^{-3}
	1	3.1×10^{-4}	3.1×10^{-4}	2.9×10^{-4}
	2	5.4×10^{-5}	5.2×10^{-5}	4.4×10^{-5}
	3	8.5×10^{-6}	8.5×10^{-6}	6.6×10^{-6}
	4	1.4×10^{-6}	1.5×10^{-6}	1.4×10^{-6}

Table 2

Hönl-London factors and transition wavelengths for $X^2\Pi_{3/2}(J''=3/2,\ N''=1,\ v''=0) - A^2\Sigma^+(J',\ N',\ v'=2,\ 3)$

Line	Wavelength nm v'=2	$\frac{S(J''N''-J'N')}{(2J''+1)}$	Wavelength nm v'=3
$P_1(1)$	261.63	0.1471	245.00
$^QP_{21}(1)$	261.42	0.0979	244.83
$Q_1(1)$	261.42	0.1404	244.83
$^RQ_{21}(1)$	261.00	0.0616	244.49
$R_1(1)$	261.00	0.0413	244.49
$^SR_{21}$	260.38	0.0117	243.97

Table 3

Photodissociation rates by predissociation of OH at 1 AU as a function of heliocentric radial velocity v in units of 10^{-6} s^{-1}.

	Rate (10^{-6} s^{-1})		
v (km s^{-1})	(v'=2)	total	Jackson (1980)
-58	3.16	3.39	13.09
-46	3.46	3.69	14.58
-31.9	1.95	2.18	8.70
-23	2.58	2.81	11.36
0	2.58	2.81	4.85
46.6	3.24	3.47	13.51
60	1.80	2.03	7.41

Table 4

Theoretical band oscillator strengths $f_{0v'}$ of OD*

v'	0	1	2	3	4
$f_{0v'}$	1.1×10^{-3}	3.2×10^{-4}	5.6×10^{-5}	8.2×10^{-6}	1.2×10^{-6}

*The dipole moment of Chu et al. (1974) was used in the calculation of $f_{0v'}$.