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Dynamics of OH Λ -doublet production through photodissociation of water in its first absorption band. I. Formal theory

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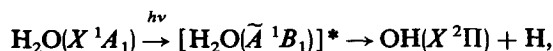
The formal theory is presented for the photofragmentation of water into a hydrogen atom and an OH radical in its ground $^2\Pi$ state. Full account is taken of the electron spin angular momentum, the electronic orbital angular momentum, and the angular momentum generated by motion of the nuclei. A formula is presented which permits the calculation of the differential cross section for the production of individual OH($X^2\Pi$) Λ -doublet states. From this formula others for less detailed cross sections are derived. In particular, an expression is presented for the integral photodissociation cross section for the production of OH Λ -doublet fragments. In all cases the formulas are specialized to apply to the $\tilde{A}^1B_1 \leftarrow X^1A_1$ photodissociative transition of water. The general formalism that is developed however, transcends this particular application. It is clearly apparent how the formalism may be extended to apply to many other cases of current experimental interest. Simplified formulas are derived to permit approximate Franck-Condon estimates of the photodissociation cross sections and product state distribution to be made.

I. INTRODUCTION

Photodissociation and photofragmentation dynamics of small molecules, especially triatomics, are now being exposed to the full power of modern high resolution spectroscopic techniques.¹⁻²⁰ The primary observations of such experiments are the quantum state distributions of the molecular fragments produced by the photodissociation process. In some cases the angular distribution of the fragments or their polarization properties may also be measured.

The initial parent molecule is normally in a singlet spin state possessing a closed shell electronic structure. The molecular fragments are, however, almost invariably radicals, with both nonzero spin and electronic angular momenta. The theory of photofragmentation processes available to date²¹⁻³⁰ has not, except in the case of diatomic photodissociation,³¹ taken cognizance of the extra complications caused by the presence of these additional angular momenta. Consequently, this theory is not able to explain the finer details of the actually observed experimental data.

In this paper the theory of photofragmentation and photodissociation processes²¹ is generalized to apply to processes which produce molecular fragments having both electronic orbital and spin angular momenta. The theory is not developed in an abstract general way, rather it is formulated with the specific process,¹²



in mind. Thus the resulting theory yields both differential and integral photofragmentation cross sections for the production of specific OH Λ -doublet states. The fact that the initial state in the photofragmentation process is a well defined electronic state, and that the electronic excitation process is to a well defined excited electronic state of the system, leads to a considerable simplification of the formalism. This simplification is exactly analogous to that arising in the scattering dynamics²¹ of photofragmentation from the fact that

the initial state may be taken to possess a well specified total angular momentum J_i .

The theory presented below is very similar to that developed by Shapiro and Kaplan³² in connection with their discussion of $\text{H} + \text{OH}(^2\Pi)$ collisions and interstellar OH maser action. The differences between their theory and that given below will be indicated at the appropriate points in the text. They arise mainly through the fact that a body-fixed coordinate system is used here while Shapiro and Kaplan³² use a space-fixed axis system.

In Sec. II the basic formula for the photodissociation cross section is given and the $\text{H}_2\text{O}(\tilde{A}^1B_1 \leftarrow X^1A_1)$ dissociation process is discussed in general terms. The angular momentum coupling theory needed to describe the dissociating fragments is discussed in Sec. III. Section IV details the expansion of the continuum wave function while in Sec. V the coupled differential equations which must be solved for the radial channel wave functions arising in the expansion of the continuum wave function are derived. Section VI defines the photofragmentation T matrix elements and gives expressions for several of the most important types of cross sections in terms of them. The exact evaluation of these T matrix elements is discussed in Sec. VII, while in Sec. VIII useful approximate formulas based on a simplified "Franck-Condon" type analysis,^{33,34} are derived for the product OH Λ -doublet quantum state distribution. Section IX summarizes the present work.

II. THE PHOTOFRAGMENTATION CROSS SECTION AND OVERVIEW OF THEORY

For photodissociation of water in its first absorption band ($\tilde{A}^1B_1 \leftarrow X^1A_1$) by a weak electromagnetic field, we may write the probability of observing the OH fragments in a state with quantum numbers vjm_i scattered into a solid angle $d\Omega (\equiv \sin \theta_R d\theta_R d\phi_R)$ about a direction $\hat{k} (\equiv \theta_R, \phi_R)$ as²¹

$$\begin{aligned} & \sigma(\hat{\mathbf{k}}E, vjmi, m_s | E_i J_i M_i P_i) \frac{\rho(\hat{\mathbf{e}})}{h\nu} d\Omega dv \\ &= \frac{8\pi^3}{h^2 c} \rho(\hat{\mathbf{e}}) |\langle \Psi_f^- (\hat{\mathbf{k}}E, vjmi, m_s) | \\ & \quad \times \hat{\mathbf{e}} \cdot \hat{\boldsymbol{\mu}} | \Psi_i (E_i J_i M_i P_i) \rangle|^2 d\Omega dv, \end{aligned} \quad (1)$$

where Ψ_f^- is the scattering wave function in the final dissociative electronic state of the system and Ψ_i is the initial bound state wave function. Both Ψ_f^- and Ψ_i represent the complete wave functions for the systems and are functions of both the nuclear and electronic coordinates. In the case of the continuum or scattering wave function the superscript “ $-$ ” sign on Ψ_f^- indicates that the wave function corresponds asymptotically³⁵ to a pure outgoing plane wave traveling in direction $\hat{\mathbf{k}}$ with total energy E . The quantum numbers $vjmi$ denote the vibrational and rotational state of the OH fragment and i enumerates the Λ -doublet state of which there are four (see below), s and m_s are the spin quantum numbers of the hydrogen atom, which is assumed to be in its lowest electronic state. The s quantum number, which is always $+\frac{1}{2}$, is omitted for brevity from many of the cross sections and wave functions. $E_i J_i M_i P_i$ specify the energy and quantum numbers of the initial state, while $\hat{\mathbf{e}}$ is a unit vector in the direction of polarization of the electric field and $\hat{\boldsymbol{\mu}}$ is the dipole moment operator. The meaning of all the other symbols is as specified in our previous paper.²¹

In the present paper consideration is given only to the photodissociation of water to form ground electronic state fragments; $\text{OH}(X^2\Pi) + \text{H}(^2S)$. The theory will therefore apply to the photodissociation of H_2O after excitation to its first excited \tilde{A}^1B_1 state. Molecules excited to the second excited \tilde{B}^1A_1 state can dissociate either to^{36,37} $\text{OH}(^2\Sigma)$ or $\text{OH}(^2\Pi)$, and this process is therefore beyond the scope of the present paper. The theory of $\text{H} + \text{OH}(^2\Pi)$ collisions given by Shapiro and Kaplan,³² unlike that given here, includes consideration of the $\text{OH}(^2\Sigma)$ state. In any scattering problem, the scattering wave function must be expanded in the asymptotic channel eigenfunctions. In the present case these are the antisymmetrized (with respect to exchange of electrons) products of hydrogen atom [$1s(r_1)\alpha(\sigma_1)$ or $1s(r_1)\beta(\sigma_1)$] and $\text{OH}(X^2\Pi)$ Λ -doublet wave functions. As the Λ -doublet wave functions involve the coupling of nuclear rotational, electronic orbital, and electronic spin angular momenta, there is no way of avoiding the proper consideration of the electronic degrees of freedom when discussing the scattering wave function.

III. ANGULAR MOMENTUM COUPLING AND THE BASIS FUNCTIONS FOR THE EXPANSION OF THE CONTINUING WAVE FUNCTION

The $\text{OH}(X^2\Pi)$ Λ -doublet wave functions are represented by $|jmi\rangle$. They are eigenfunctions of the total angular momentum (for OH) and of its space-fixed z component. The index i runs from 1 to 4 and enumerates the four different possible Λ -doublet states for any given values of j and m . These wave functions may be written in the general form^{32,38–41}

TABLE I. Expansion coefficient for OH Λ -doublet wave functions [Eq. (2)]. The index i runs in order of increasing energy (Ref. 40). $a_j = [(X - |\lambda - 2|)/4X]^{1/2}$; $b_j = [(X + |\lambda - 2|)/4X]^{1/2}$; $X = [4(j + \frac{1}{2})^2 + \lambda(\lambda - 4)]^{1/2}$; $\lambda = A/B = (-7.50$ for OH). A and B are the spin-orbit and electronic angular momentum-nuclear rotation coupling constants, respectively. Detailed energy expressions are presented in Ref. 39.

State	A_{ji}	B_{ji}	C_{ji}	D_{ji}
$i = 1$	a_j	a_j	b_j	b_j
$i = 2$	a_j	$-a_j$	b_j	$-b_j$
$i = 3$	$-b_j$	b_j	a_j	$-a_j$
$i = 4$	$-b_j$	$-b_j$	a_j	a_j

$$\begin{aligned} |jmi\rangle &= \left(\frac{2j+1}{4\pi}\right)^{1/2} \{A_{ji}|\Omega = \tfrac{1}{2}\rangle D_{(1/2)m}^j(\omega) \\ &+ B_{ji}|\Omega = -\tfrac{1}{2}\rangle D_{-(1/2)m}^j(\omega) \\ &+ C_{ji}|\Omega = \tfrac{3}{2}\rangle D_{(3/2)m}^j(\omega) + D_{ji}|\Omega = -\tfrac{3}{2}\rangle D_{-(3/2)m}^j(\omega)\}, \end{aligned} \quad (2)$$

where $|\Omega = \frac{1}{2}\rangle$, for instance, denotes the OH electronic wave function with electronic plus spin angular momentum component of $\Omega = \frac{1}{2}$ about the OH molecular axis. $\omega \equiv \phi, \theta, 0$ and represents the Euler angles of the OH molecular axis in the space fixed coordinate system. The definitions of Edmonds⁴² are used throughout this paper for all angular related quantities [i.e., the rotation matrices $D_{(1/2)m}^j(\omega)$], and for the rotations relating different coordinate systems. The coefficients A_{ji} , B_{ji} , C_{ji} , and D_{ji} are listed in Table I.

The OH Λ -doublet wave functions $|jmi\rangle$ are first coupled to the spin angular momentum of the second hydrogen atom, to give wave functions with a resultant angular momentum quantum number k . The wave function $|sm_s\rangle$ is used to denote an electron in a $1s$ orbital on the departing hydrogen atom with spin quantum numbers “ sm_s ”. Coupling the j and s angular momenta we therefore obtain

$$|km_k; ji\rangle = \sum_{mm_s} |jmi\rangle |sm_s\rangle (jmsm_s | jskm_k), \quad (3)$$

where $(jmsm_s | jskm_k)$ is a Clebsch–Gordan coefficient.⁴²

As will be discussed more extensively below, the notation $|jmi\rangle |sm_s\rangle$ implies a complete electronic and nuclear wave function for the triatomic system. This wave function must be properly antisymmetrized with respect to interchange of all electrons. The antisymmetrization operator,

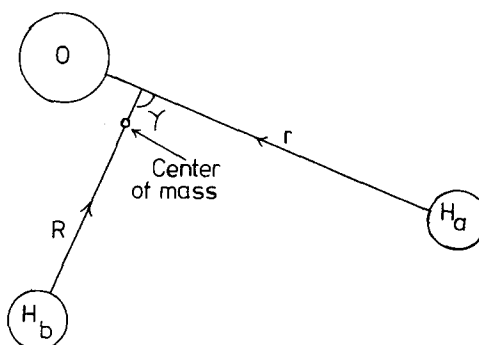


FIG. 1. Coordinates used in description of H_2O photodissociation.

which accomplishes this process, is always understood to be present although it is not explicitly written down.

The quantum number m_s refers to the component of the spin angular momentum about the space fixed z axis. If m'_s is used for the quantum number corresponding to the component of the hydrogen electron spin angular momentum about the body-fixed OH z axis (i.e., the OH bond), we can

write [see Edmonds⁴² Eq. (4.1.4)]:

$$|sm_s\rangle = \sum_{m'_s} D_{m'_s m_s}^{1/2}(\omega) |sm'_s\rangle. \quad (4)$$

This transformation, involving $D_{m'_s m_s}^{1/2}(\omega)$, is not included in the theory of Shapiro and Kaplan.³²

Now combining Eqs. (2)–(4), we obtain

$$\begin{aligned} |km_k; ji\rangle = & \sum_{m'_s} \left(\frac{2k+1}{4\pi} \right)^{1/2} (-1)^{s+m'_s} \{ A_{ji} |\Omega = \frac{1}{2}\rangle |sm'_s\rangle D_{m'_s + \frac{1}{2}, m_k}^k(\omega) (s - m'_s k, m'_s + \frac{1}{2} |skj\Omega) \\ & + B_{ji} |\Omega = -\frac{1}{2}\rangle |sm'_s\rangle D_{m'_s - \frac{1}{2}, m_k}^k(\omega) (s - m'_s k, m'_s - \frac{1}{2} |skj\Omega) \\ & + C_{ji} |\Omega = \frac{3}{2}\rangle |sm'_s\rangle D_{m'_s + \frac{3}{2}, m_k}^k(\omega) (s - m'_s k, m'_s + \frac{3}{2} |skj\Omega) \\ & + D_{ji} |\Omega = -\frac{3}{2}\rangle |sm'_s\rangle D_{m'_s - \frac{3}{2}, m_k}^k(\omega) (s - m'_s k, m'_s - \frac{3}{2} |skj\Omega) \}, \end{aligned} \quad (5)$$

where the following relationships have been used:

$$\sum_{mm_s} D_{\Omega m}^l(\omega) D_{m'_s m_s}^{1/2}(\omega) (jmsm_s | jskm_k) = D_{\Omega + m'_s, m_k}^k(\omega) (j\Omega sm'_s | jsk, \Omega + m'_s) \quad (6)$$

[see Edmonds⁴² Eqs. (4.3.2), (3.7.3), and (3.5.4) and Rose⁴³] and

$$\left(\frac{2j+1}{4\pi} \right)^{1/2} (j\Omega sm'_s | jsk, \Omega + m'_s) = \left(\frac{2k+1}{4\pi} \right)^{1/2} (-1)^{s+m'_s} (s - m'_s k, \Omega + m'_s | skj\Omega) \quad (7)$$

[see Edmonds⁴² Eq. (3.5.1s)].

The orbital angular momentum of the nuclear motion of the hydrogen atom relative to the OH molecule (quantum number l) must now be coupled to k to give a total angular momentum J for the triatomic system. Thus,

$$|JM; klji\rangle = \sum_{m_k m_l} |km_k; ji\rangle Y_{lm_l}(\theta_R \phi_R) (km_k lm_l | k l J M). \quad (8)$$

The angles $\theta_R \phi_R$ are those of the H–OH vector \hat{R} in the space-fixed axis system. The coordinates used are shown diagrammatically in Fig. 1. It is desirable that the final wave function, which is to be used for calculations, should be expressed in the H₂O body-fixed axis system. In the H₂O body-fixed axis system, the z axis points along the H–OH direction,²¹ i.e., the θ_R, ϕ_R direction in the space-fixed system. The H–OH nuclear orbital angular momentum therefore has zero component along the H₂O body-fixed axis system. Furthermore, the Euler angles required to rotate the OH body-fixed axis system into the H₂O one are “OγO” where γ is the angle between the H_B–OH_A and H_A–O directions. Note that the molecular plane is the zx plane in the H₂O body-fixed axis system. Expressing the wave functions in the H₂O body-fixed system [see Eq. (B6) of Ref. 21] the eigenfunctions of the total angular momentum equation (8) can be written in the form:

$$\begin{aligned} |JM; klji\rangle = & \left(\frac{2l+1}{4\pi} \right)^{1/2} \left(\frac{2k+1}{4\pi} \right)^{1/2} \sum_{\lambda} \left\{ \sum_{m'_s} (-1)^{s+m'_s} \right. \\ & \times [A_{ji} |\Omega = \frac{1}{2}\rangle |sm'_s\rangle D_{m'_s + \frac{1}{2}, \lambda}^k(0, \gamma, 0) D_{\lambda M}^J(\phi_R \theta_R \psi) (s - m'_s k, m'_s + \frac{1}{2} |skj\frac{1}{2}) \\ & + B_{ji} |\Omega = -\frac{1}{2}\rangle |sm'_s\rangle D_{m'_s - \frac{1}{2}, \lambda}^k(0, \gamma, 0) D_{\lambda M}^J(\phi_R \theta_R \psi) (s - m'_s k, m'_s - \frac{1}{2} |skj-\frac{1}{2}) \\ & + C_{ji} |\Omega = \frac{3}{2}\rangle |sm'_s\rangle D_{m'_s + \frac{3}{2}, \lambda}^k(0, \gamma, 0) D_{\lambda M}^J(\phi_R \theta_R \psi) (s - m'_s k, m'_s + \frac{3}{2} |skj\frac{3}{2}) \\ & \left. + D_{ji} |\Omega = -\frac{3}{2}\rangle |sm'_s\rangle D_{m'_s - \frac{3}{2}, \lambda}^k(0, \gamma, 0) D_{\lambda M}^J(\phi_R \theta_R \psi) (s - m'_s k, m'_s - \frac{3}{2} |skj-\frac{3}{2}) \right] \} (k\lambda l 0 | k l J \lambda). \end{aligned} \quad (9)$$

This equation may be slightly simplified by using the relationship

$$D_{\nu, \lambda}^k(0, \gamma, 0) = d_{\nu, \lambda}^k(\gamma)$$

[see Edmonds⁴² Eq. (4.1.12)].

The angular functions $D_{\lambda M}^J(\phi_R \theta_R \psi) d_{\nu, \lambda}^k(\gamma)$, now occurring in Eq. (9), do not possess a definite parity. We therefore define a new set of normalized angular functions $F_{k\lambda\nu}^{JMp}(\phi_R \theta_R \psi \gamma)$ which are parity eigenfunctions with parity $(-1)^J p$:

$$F_{k\lambda\nu}^{JMp}(\phi_R \theta_R \psi \gamma) = t_{\lambda} \left(\frac{2J+1}{8\pi^2} \right)^{1/2} \left(\frac{2k+1}{2} \right)^{1/2} [D_{\lambda M}^J(\phi_R \theta_R \psi) d_{\nu, \lambda}^k(\gamma) + p(-1)^J D_{-\lambda M}^J(\phi_R \theta_R \psi) d_{-\nu, -\lambda}^k(\gamma)], \quad (10)$$

where $\lambda > 0$ and $t_{\lambda} = 1/\sqrt{2}$ for $\lambda > 0$, $t_{\lambda} = 1/2$ for $\lambda = 0$. With this new definition, the eigenfunctions of the total angular momentum, its space-fixed z component and the parity may be written in the form;

$$\begin{aligned}
|JMp;klji\rangle = \sum_{\lambda} (-1)^{k-\lambda} 2t_{\lambda} \left\{ \sum_{m'_s} (-1)^{s+m'_s} [A_{ji}|\Omega = \frac{1}{2}\rangle |sm'_s\rangle F_{k\lambda, m'_s+1/2}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s-m'_s k, m'_s + \frac{1}{2} |skj \frac{1}{2}) \right. \\
+ B_{ji}|\Omega = -\frac{1}{2}\rangle |sm'_s\rangle F_{k\lambda, m'_s-1/2}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s-m'_s k, m'_s - \frac{1}{2} |skj -\frac{1}{2}) \\
+ C_{ji}|\Omega = \frac{3}{2}\rangle |sm'_s\rangle F_{k\lambda, m'_s+3/2}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s-m'_s k, m'_s + \frac{3}{2} |skj \frac{3}{2}) \\
\left. + D_{ji}|\Omega = -\frac{3}{2}\rangle |sm'_s\rangle F_{k\lambda, m'_s-3/2}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s-m'_s k, m'_s - \frac{3}{2} |skj -\frac{3}{2}) \right\} (Jkl0|J\lambda k - \lambda), \quad (11)
\end{aligned}$$

where the identity

$$(2l+1)^{1/2} (k\lambda l0|klJ\lambda) = (-1)^{k-\lambda} (2J+1)^{1/2} (Jkl0|J\lambda k - \lambda)$$

[see Edmonds⁴² Eq. (3.5.16) has been used]. The channel functions which are to be used to expand the scattering wave function in the H₂O body-fixed axis system may now be defined:

$$\begin{aligned}
G_{k\lambda ji}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) = \sum_{m'_s} (-1)^{s+m'_s} [A_{ji}|\Omega = \frac{1}{2}\rangle |sm'_s\rangle F_{k\lambda, m'_s+1/2}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s-m'_s k, m'_s + \frac{1}{2} |skj \frac{1}{2}) \\
+ B_{ji}|\Omega = -\frac{1}{2}\rangle |sm'_s\rangle F_{k\lambda, m'_s-1/2}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s-m'_s k, m'_s - \frac{1}{2} |skj -\frac{1}{2}) \\
+ C_{ji}|\Omega = \frac{3}{2}\rangle |sm'_s\rangle F_{k\lambda, m'_s+3/2}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s-m'_s k, m'_s + \frac{3}{2} |skj \frac{3}{2}) \\
+ D_{ji}|\Omega = -\frac{3}{2}\rangle |sm'_s\rangle F_{k\lambda, m'_s-3/2}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s-m'_s k, m'_s - \frac{3}{2} |skj -\frac{3}{2})]. \quad (12)
\end{aligned}$$

The functions $G_{k\lambda ji}^{JMp}$ defined above are analogous to the $\Theta_{j\lambda}^{JMp}$ functions of our previous paper.²¹ The extra complexity arises from the proper consideration afforded here to the electronic spin and orbital angular momenta. Substituting Eq. (12) into Eq. (11), we obtain

$$|JMp;klji\rangle = \sum_{\lambda} (-1)^{k-\lambda} 2t_{\lambda} (Jkl0|J\lambda k - \lambda) G_{k\lambda ji}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}). \quad (13)$$

This equation is completely analogous to Eq. (B10) of our previous paper.²¹

IV. EXPANSION OF THE CONTINUUM WAVE FUNCTION

The continuum wave function has the asymptotic form:

$$\begin{aligned}
\Psi_f(\hat{\mathbf{k}}E, vjmi, m_s) \underset{R \rightarrow \infty}{\sim} [\mu k_{vj} c / \hbar (2\pi)^2]^{1/2} \\
\times \left\{ \exp(i\mathbf{k}_{vj} \cdot \mathbf{R}) \chi_{vj}(r) |jmi\rangle |sm_s\rangle \right. \\
+ \sum_{v'f m' i' m'_s} \int_{v'f m' i' m'_s} (\hat{\mathbf{k}}, \hat{\mathbf{R}}) \exp(-i\mathbf{k}_{v'f} \cdot \mathbf{R}) \\
\left. \times \chi_{v'f}(r) |j' m' i'\rangle |sm'_s\rangle \cdot \frac{1}{R} \right\}, \quad (14)
\end{aligned}$$

where the coordinates used are illustrated in Fig. 1 and $\hat{\mathbf{k}}$ represents the direction in the space-fixed axes into which the fragments are expelled. Using the identity

$$\exp[i\mathbf{k}_{vj} \cdot \mathbf{R}] = 4\pi \sum_{lm_i} i^l Y_{lm_i}^*(\hat{\mathbf{k}}) Y_{lm_i}(\hat{\mathbf{R}}) j_l(k_{vj} R) \quad (15)$$

and the inverses of the transformations of Eqs. (3) and (8),

$$\begin{aligned}
|jmi\rangle |sm_s\rangle Y_{lm_i}(\hat{\mathbf{R}}) = \sum_{JMp} \sum_{km_k} |JMp;klji\rangle \\
\times (jskm_k | jmsm_s) (klJM | km_k lm_i), \quad (16)
\end{aligned}$$

the plane wave part of the continuum wave function may be rewritten as:

$$\begin{aligned}
\exp[i\mathbf{k}_{vj} \cdot \mathbf{R}] \chi_{vj}(r) |jmi\rangle |sm_s\rangle \\
= 4\pi \sum_{lm_i} i^l Y_{lm_i}^*(\hat{\mathbf{k}}) \sum_{JMp} \sum_{km_k} |JMp;klji\rangle \\
\times (jskm_k | jmsm_s) (klJM | km_k lm_i) \chi_{vj}(r) j_l(k_{vj} R). \quad (17)
\end{aligned}$$

The entire continuum wave function may therefore be expanded in the form

$$\begin{aligned}
\Psi_f^-(\hat{\mathbf{k}}E, vjmi, m_s) = 2 \left(\frac{\mu k_{vj} c}{\hbar} \right)^{1/2} \sum_{lm_i} \sum_{JMp} \sum_{km_k} i^l Y_{lm_i}^*(\hat{\mathbf{k}}) \\
\times (jskm_k | jmsm_s) (klJM | km_k lm_i) \\
\times \sum_{v'k'l'j'i'} |JMp;k'l'j'i'\rangle \chi_{v'f}(r) F_{v'k'l'j'i'}^{-(Jvklji)}(R)/R, \quad (18)
\end{aligned}$$

where the radial wave function obeys the boundary conditions:

$$\begin{aligned}
F_{v'k'l'j'i'}^{-(Jvklji)}(R) \underset{R \rightarrow 0}{\sim} 0 \\
\underset{R \rightarrow \infty}{\sim} \frac{1}{2ik_{vj}} \left\{ \exp[i(k_{vj} R - l\pi/2)] \delta_{vv'} \delta_{kk'} \delta_{ll'} \delta_{jj'} \delta_{ii'} - S_{v'k'l'j'i', vklji}^* \left(\frac{k_{vj}}{k_{v'f}} \right)^{1/2} \exp[-i(k_{v'f} R - l'\pi/2)] \right\}. \quad (19)
\end{aligned}$$

The radial wave functions in Eqs. (18) and (19) are referred to a space fixed axis system. By substituting Eq. (13) into Eq.

(18) a body-fixed radial wave function $\Phi_{v'k'\lambda'j'f'}^{-(Jvkljip)}(R)$ may be defined. The total continuum wave function may be written in terms of body-fixed functions as

$$\Psi_f^-(\hat{\mathbf{k}}E, vjmi, m_s) = 2 \left(\frac{\mu k_{vj} c}{\hbar} \right)^{1/2} \sum_{lm_i} \sum_{JM_p} \sum_{km_k} Y_{lm_i}^*(\hat{\mathbf{k}}) (jskm_k | jmsm_s) (klJM_i | km_k lm_i) \\ \times \sum_{\lambda} (Jkl0 | J\lambda k - \lambda) \sum_{v'k'\lambda'j'f'} G_{k'\lambda'j'f'}^{JM_p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \chi_{v'f'}(r) \Phi_{v'k'\lambda'j'f'}^{-(Jvkljip)}(R)/R, \quad (20)$$

where

$$\Phi_{v'k'\lambda'j'f'}^{-(Jvkljip)}(R) = \sum_{l'l'} i^{l'} (-1)^{k-\lambda'} (J\lambda k - \lambda | Jkl'0) F_{v'k'\lambda'j'f'}^{-(Jvkl'ji)}(R) (Jk'l'0 | J\lambda'k' - \lambda') \left(\frac{4t_{\lambda'}}{1 + \delta_{\lambda 0}} \right) \quad (21)$$

[see Ref. 21 Eqs. (B11) to (B15)].

The body-fixed radial wave function obeys the boundary conditions:

$$\Phi_{v'k'\lambda'j'f'}^{-(Jvkljip)}(R) \underset{R \rightarrow \infty}{\sim} \left(\frac{4t_{\lambda}}{1 + \delta_{\lambda 0}} \right) \cdot \frac{1}{2ik_{vj}} (-1)^{k+\lambda} \\ \times \left\{ \exp(ik_{vj}R) \delta_{vv'} \delta_{kk'} \delta_{jj'} \delta_{ll'} \delta_{\lambda\lambda'} - S_{v'k'\lambda'j'f', vklji}^{Jp*} \left(\frac{k_{vj}}{k_{v'f'}} \right)^{1/2} \exp(-ik_{v'f'}R) \right\}. \quad (22)$$

[See Ref. 23 Eq. (3a)].

V. FINAL STATE INTERACTION AND DIFFERENTIAL EQUATIONS FOR RADIAL CONTINUUM WAVE FUNCTION

The major difference between the present work and previous theories of photodissociation processes is the inclusion of the electronic and spin degrees of freedom in the channel wave functions. This is totally unavoidable if it is desired to properly describe the dissociation of the system into individual Λ -doublet states of $\text{OH}_A(X^2\Pi)$. In the theory which follows we only treat the three $2p - \pi$ electrons of OH_A and the one electron of the departing hydrogen atom (H_B), explicitly. The other electrons on OH are assumed to form a "frozen core" which is chemically inactive. The model of the electronic structure of the system, used below, is not intended for use in actual computations. Its purpose is to account correctly for all the symmetry aspects of the problem and to show how the results of accurate electronic structure calculations, of the Born–Oppenheimer potential energy surfaces, may be utilized in the calculation of the photofragmentation dynamics. The treatment of $\text{H} + \text{OH}(^2\Pi)$ collisions given by Shapiro and Kaplan³² is very similar to the present one for the photodissociation process. It differs in that they use a one-electron picture of the electronic structure of $\text{OH}(^2\Pi)$ as compared to the three-electron picture used here. They, however, take approximate account of the participation of the $\text{OH}(^2\Sigma)$ state, which is purposely omitted in the present treatment.

In most nuclear geometries the H_2O system has C_s symmetry. The electronic wave functions may therefore belong to either A' or A'' irreducible representations. These are, respectively, even and odd with respect to reflection in the molecular plane. In the model of the electronic structure an OH_A body-fixed system is used, with the $\text{H}_A\text{--O}$ bond forming the z axis. The electronic structure of the molecule is described using a valence-bond approach.

The valence-bond structures are constructed from p_x and p_y atomic orbitals on the oxygen atom and from the $1s_B$ orbital on the departing hydrogen atom (hydrogen atom B). This picture of the electronic structure is not intended to be

in any way accurate. With the minimal basis set used, there is only one valence-bond structure for each "symmetry" type, and the model of the electronic structure is used only to find a transformation between the molecular states in the " $p_x, p_y, 1s_B$ " basis and the basis constructed from the direct product of the proper Λ -doublet OH_A wave functions with the electron of hydrogen atom B in the $1s_B$ orbital.

There are eight molecular electronic wave functions of symmetries $^3A'$, $^1A'$, $^3A''$, and $^1A''$. This basis of molecular valence-bond structures may be written in the form

$$\begin{aligned} \phi_1^M &= |^3A', 1\rangle = |p_x p_y \bar{p}_y 1s_B|, \\ \phi_2^M &= |^3A', 2\rangle = (1/\sqrt{2})\{|p_x p_y \bar{p}_y \bar{1s}_B| + |\bar{p}_x p_y \bar{p}_y 1s_B|\}, \\ \phi_3^M &= |^3A', 3\rangle = |\bar{p}_x p_y \bar{p}_y \bar{1s}_B|, \\ \phi_4^M &= |^1A'\rangle = (1/\sqrt{2})\{|p_x p_y \bar{p}_y \bar{1s}_B| - |\bar{p}_x p_y \bar{p}_y 1s_B|\}, \\ \phi_5^M &= |^3A'', 1\rangle = |p_x \bar{p}_x p_y 1s_B|, \\ \phi_6^M &= |^3A'', 2\rangle = (1/\sqrt{2})\{|p_x \bar{p}_x p_y \bar{1s}_B| + |p_x \bar{p}_x \bar{p}_y 1s_B|\}, \\ \phi_7^M &= |^3A'', 3\rangle = |p_x \bar{p}_x \bar{p}_y \bar{1s}_B|, \\ \phi_8^M &= |^1A''\rangle = (1/\sqrt{2})\{|p_x \bar{p}_x p_y \bar{1s}_B| - |p_x \bar{p}_x \bar{p}_y 1s_B|\}, \end{aligned} \quad (23)$$

where, for example, $|p_x p_y \bar{p}_y 1s_B|$ represents a Slater determinant and orbitals p_x, p_y , and $1s_B$ are associated with spin $m_s = \frac{1}{2}$ and \bar{p}_y indicates that the p_y orbital is associated with spin $m_s = -\frac{1}{2}$. The spin-orbital coupled basis functions for OH_A corresponding to Hund's case A are best written in terms of atomic orbitals p_{-1} , p_0 , and p_{+1} . These are related to the p_x, p_y , and p_z orbitals by

$$\begin{aligned} p_{-1} &= (1/\sqrt{2})(p_x - ip_y), \\ p_0 &= p_z, \\ p_{+1} &= -(1/\sqrt{2})(p_x + ip_y). \end{aligned} \quad (24)$$

The direct products of the spin-orbit coupled OH_A basis functions with the electron of the other hydrogen atom may then be written as

$$\begin{aligned}
\phi_1^\Omega &= |\Omega = \frac{3}{2}\rangle |m_s = \frac{1}{2}\rangle = -(1/\sqrt{2})\{|^3A', 1\rangle + i|^3A'', 1\rangle\}, \\
\phi_2^\Omega &= |\Omega = \frac{1}{2}\rangle |m_s = \frac{1}{2}\rangle \\
&= -\frac{1}{2}\{(|^3A', 2\rangle - |^1A'\rangle) + i(|^3A'', 2\rangle - |^1A''\rangle)\}, \\
\phi_3^\Omega &= |\Omega = -\frac{1}{2}\rangle |m_s = \frac{1}{2}\rangle = (1/\sqrt{2})\{|^3A', 1\rangle - i|^3A'', 1\rangle\}, \\
\phi_4^\Omega &= |\Omega = -\frac{3}{2}\rangle |m_s = \frac{1}{2}\rangle \\
&= \frac{1}{2}\{(|^3A', 2\rangle - |^1A'\rangle) - i(|^3A'', 2\rangle - |^1A''\rangle)\}, \\
\end{aligned} \quad (25)$$

$$\begin{aligned}
\phi_5^\Omega &= |\Omega = \frac{3}{2}\rangle |m_s = -\frac{1}{2}\rangle \\
&= -\frac{1}{2}\{(|^3A', 2\rangle + |^1A'\rangle) + i(|^3A'', 2\rangle + |^1A''\rangle)\}, \\
\phi_6^\Omega &= |\Omega = \frac{1}{2}\rangle |m_s = -\frac{1}{2}\rangle \\
&= -(1/\sqrt{2})\{|^3A', 3\rangle + i|^3A'', 3\rangle\}, \\
\phi_7^\Omega &= |\Omega = -\frac{1}{2}\rangle |m_s = -\frac{1}{2}\rangle \\
&= \frac{1}{2}\{(|^3A', 2\rangle + |^1A'\rangle) - i(|^3A'', 2\rangle + |^1A''\rangle)\}, \\
\phi_8^\Omega &= |\Omega = -\frac{3}{2}\rangle |m_s = -\frac{1}{2}\rangle \\
&= (1/\sqrt{2})\{|^3A', 3\rangle - i|^3A'', 3\rangle\},
\end{aligned}$$

where Eq. (24) has been used in deriving the above relationships. The total Hamiltonian operator for the system may be decomposed in the form:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{el}} + \hat{\mathcal{H}}_{\text{nuc}} + \hat{\mathcal{H}}_{\text{spin orbit}} + \hat{\mathcal{H}}_{\text{nuc-el}}, \quad (26)$$

where $\hat{\mathcal{H}}_{\text{el}}$ is the electronic Born–Oppenheimer Hamiltonian with clamped nuclei and only electrostatic interactions. $\hat{\mathcal{H}}_{\text{nuc}}$ is the kinetic energy operator for the nuclear motion. $\hat{\mathcal{H}}_{\text{spin orbit}}$ is the Hamiltonian for the spin-orbit interaction. $\hat{\mathcal{H}}_{\text{nuc-el}}$ is the Hamiltonian for the non-Born–Oppenheimer interaction, coupling the nuclear motion and the electronic wave functions. In the region of asymptotically large $\text{H}_\text{B}-\text{OH}_\text{A}$ separations, this Hamiltonian is diagonal in the Λ -doublet basis constructed from the direct product of OH_A Λ -doublet states (labeled by “ ji ”) and the wave functions of hydrogen atom B (i.e., $|sm_s\rangle$). Our scattering problem must consequently be expanded in terms of this basis. At smaller internuclear separations the Born–Oppenheimer electronic Hamiltonian ($\hat{\mathcal{H}}_{\text{el}}$) is (within the present approximate model) diagonal in the molecular valence-bond basis ϕ_i^M . In the absence of better, more rigorously based, calculations we assume that the spin-orbit and nuclear–electronic interaction parts of the total Hamiltonian operator ($\hat{\mathcal{H}}_{\text{spin orbit}} + \hat{\mathcal{H}}_{\text{nuc-el}}$) are independent of the $\text{H}_\text{B}-\text{OH}_\text{A}$ separation, and are therefore always diagonal in the Λ -doublet basis. These diagonal matrix elements of the Hamiltonian are evaluated from experimental spectroscopic data. The matrix elements of $\hat{\mathcal{H}}_{\text{el}}$, which is not diagonal in the Λ -doublet basis, are evaluated by relating this basis to the molecular valence-bond basis (ϕ_i^M) through the use of Eq. (25).

The diagonal matrix elements of $\hat{\mathcal{H}}_{\text{el}}$ in the ϕ_k^M basis are denoted by V_k

$$\langle \phi_k^M | \hat{\mathcal{H}}_{\text{el}} | \phi_i^M \rangle = V_k(\mathbf{R}, \mathbf{r}) \delta_{ki}. \quad (27)$$

The V_k ’s are the four Born–Oppenheimer potential energy surfaces calculated in a standard electronic structure calcu-

lation (with a much more flexible set of basis functions than the ϕ_i^M ’s). The correspondence between the indices “ k ” and the four possible electronic potential energy surfaces is

$$\begin{aligned}
V_1 &= V_2 = V_3 = E(^3A'), \\
V_4 &= E(^1A'), \\
V_5 &= V_6 = V_7 = E(^3A''), \\
V_8 &= E(^1A'').
\end{aligned} \quad (28)$$

The relationship between the bases ϕ_i^M [Eq. (23)] and ϕ_i^Ω [Eq. (25)] may be written in matrix form as:

$$\phi^\Omega = \mathbf{T} \phi^M, \quad (29)$$

where the matrix \mathbf{T} may be read off directly from Eq. (25). In order to derive the coupled differential equations for the radial wave functions $\Phi_{\nu k j i}^{JM p}$, the matrix elements of the Hamiltonian between the channel basis functions $G_{k \lambda j i}^{JM p}(\mathbf{R}, \mathbf{r})$ must be evaluated. These functions are formed from individual Λ -doublet basis functions and therefore diagonalize the last two terms in the Hamiltonian of Eq. (26).

It is useful, at this stage, to define the eight functions

$$\begin{aligned}
g_1^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= -C_{ji} F_{k \lambda 2}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s - \frac{1}{2}k2 |skj \frac{3}{2}), \\
g_2^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= -A_{ji} F_{k \lambda 1}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s - \frac{1}{2}k1 |skj \frac{1}{2}), \\
g_3^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= -B_{ji} F_{k \lambda 0}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s - \frac{1}{2}k0 |skj - \frac{1}{2}), \\
g_4^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= -D_{ji} F_{k \lambda -1}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s - \frac{1}{2}k - 1 |skj - \frac{3}{2}), \\
\end{aligned} \quad (30)$$

$$\begin{aligned}
g_5^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= C_{ji} F_{k \lambda 1}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s \frac{1}{2}k1 |skj \frac{3}{2}), \\
g_6^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= A_{ji} F_{k \lambda 0}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s \frac{1}{2}k0 |skj \frac{1}{2}), \\
g_7^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= B_{ji} F_{k \lambda -1}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s \frac{1}{2}k - 1 |skj - \frac{1}{2}), \\
g_8^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= D_{ji} F_{k \lambda -2}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s \frac{1}{2}k - 2 |skj - \frac{3}{2}).
\end{aligned}$$

Using the above definition, together with Eqs. (12) and (25) we may rewrite the channel basis functions in the form

$$G_{k \lambda j i}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) = \sum_n g_n^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \phi_n^\Omega. \quad (31)$$

The matrix elements of the electronic Born–Oppenheimer Hamiltonian between the channel basis functions may then be evaluated through the use of Eqs. (27) and (29):

$$\begin{aligned}
V_{k' \lambda' j' i', k \lambda j i}^{JM p}(\mathbf{R}, \mathbf{r}) &= \langle G_{k' \lambda' j' i'}^{JM p} | \hat{\mathcal{H}}_{\text{el}} | G_{k \lambda j i}^{JM p} \rangle \\
&= \sum_n \sum_{n'} \sum_q T_{n'q} T_{nq} \langle g_{n'}^{JM p, k' \lambda' j' i'} | V_q | g_n^{JM p, k \lambda j i} \rangle \delta_{\lambda \lambda'}, \quad (32)
\end{aligned}$$

where the brackets $\langle \rangle$ imply integration over all the coordinates of the functions $G_{k \lambda j i}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}})$ (i.e., all electronic plus all angular coordinates). The angular functions $g_n^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}})$ of Eq. (30), may be rewritten in the form

$$g_n^{JM p, k \lambda j i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) = q_{k j i n} F_{k \lambda \nu(n)}^{JM p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}), \quad (33)$$

where $\nu(1) = 2$, $\nu(2) = 1$, $\nu(3) = 0$, $\nu(4) = -1$, $\nu(5) = 1$, $\nu(6) = 0$, $\nu(7) = -1$, $\nu(8) = -2$, and the numerical coefficients $q_{k j i n}$ may be read off from Eq. (30).

Using Eqs. (10), (30), and (33) and Eqs. (4.2.5) and (4.6.1) of Edmonds,⁴² the angular integrals in Eq. (32) can be written as

$$\langle g_n^{JM_p, k' \lambda' j' i} | V_q | g_n^{JM_p, k \lambda j i} \rangle = q_{k' j' i n'} q_{k j i n} V_{q, k' \lambda' \nu'(n'), k \lambda \nu(n)}(R, r), \quad (34)$$

where the matrix elements $V_{q, k' \lambda' \nu'(n'), k \lambda \nu(n)}(R, r)$ must be evaluated numerically from the calculated Born-Oppenheimer potential energy surface and are defined by

$$V_{q, k' \lambda' \nu'(n'), k \lambda \nu(n)}(R, r) = \frac{1}{2}[(2k' + 1)(2k + 1)]^{1/2} \times \int d\gamma d_{\nu'(n'), \lambda'}^k(\gamma) V_q(R, r, \gamma) d_{\nu(n), \lambda}^k(\gamma) \sin \gamma d\gamma. \quad (35)$$

In the coupled differential equations for the radial continuum functions, the matrix elements of this potential between vibrational OH_A basis functions will be required. These matrix elements are

$$V_{q, v' f' k' \lambda' \nu'(n'), v f k \lambda \nu(n)}(R) = \int \chi_{v' f'}(r) V_{q, k' \lambda' \nu'(n'), k \lambda \nu(n)}(R, r) \chi_{v f}(r) r^2 dr. \quad (36)$$

The coupled differential equations for the radial continuum wave function may now be written as^{21,23}

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + (\epsilon_{v' f' i} - E) + L_{\lambda', \lambda'}^{Jk' p}(R) + V_{v' k' \lambda' j' i, v' k' \lambda' j' i}^J(R) \right\} \Phi_{v' k' \lambda' j' i}^{-(Jv k \lambda j i p)}(R) + \sum_{\lambda''} L_{\lambda', \lambda''}^{Jk' p}(R) \Phi_{v' k' \lambda'' j' i}^{-(Jv k \lambda j i p)}(R) + \sum_{v'' k'' \lambda'' j'' i''} V_{v' k' \lambda' j' i, v'' k'' \lambda'' j'' i''}^J(R) \Phi_{v'' k'' \lambda'' j'' i''}^{-(Jv k \lambda j i p)}(R) = 0, \quad (37)$$

where $\epsilon_{v' f' i}$ are the energies of the individual A-doublet states in particular vibrational levels, the two summations do not include any diagonal terms,

$$L_{\lambda', \lambda'}^{Jk' p}(R) = \langle G_{k' \lambda' j' i}^{JM_p} | (\hat{J} - \hat{k})^2 | G_{k' \lambda' j' i}^{JM_p} \rangle = [J(J+1) + k(k+1) - 2\lambda^2]/R^2, \quad (38)$$

$$\hat{k} = \hat{j} + \hat{s}, \quad (39)$$

$$L_{\lambda', \lambda'}^{Jk' p} = C_{\lambda', \lambda'+1}^{Jk'} \delta_{\lambda', \lambda'+1} + C_{\lambda', \lambda'-1}^{Jk'} \delta_{\lambda', \lambda'-1}, \\ L_{\lambda', \lambda'+1}^{Jk' p} = C_{\lambda', \lambda'+1}^{Jk'} \quad \text{if } \lambda' > 0, \\ L_{\lambda', \lambda'-1}^{Jk' p} = C_{\lambda', \lambda'-1}^{Jk'} \quad \text{if } \lambda' > 1, \quad (40)$$

$$L_{0,1}^{Jk' p} = 2^{1/2} C_{0,1}^{Jk'} \quad \text{if } p = 1, \\ L_{1,0}^{Jk' p} = 2^{1/2} C_{1,0}^{Jk'} \quad \text{if } p = 1, \\ L_{0,1}^{Jk' p} = L_{1,0}^{Jk' p} = 0 \quad \text{if } p = -1, \\ C_{\lambda, \lambda \pm 1}^{Jk} = -[J(J+1) - \lambda(\lambda \pm 1)]^{1/2} \\ \times [k(k+1) - \lambda(\lambda \pm 1)]^{1/2} R^{-2}, \quad (41)$$

$$V_{v' k' \lambda' j' i, v'' k'' \lambda'' j'' i''}^J(R) = \sum_{n' n''} \sum_q T_{n' q} T_{n'' q} q_{k' j' i n'} \times q_{k'' j'' i n''} V_{q, v' f' k' \lambda' \nu'(n'), v'' f'' k'' \lambda'' \nu''(n'')} (R) \\ [\text{see Eqs. (29) and (31)-(35)}]. \quad (42)$$

VI. THE PHOTOFRAGMENTATION T MATRIX AND THE DETAILED DIFFERENTIAL PHOTOFRAGMENTATION CROSS SECTION

The detailed photofragmentation cross section may be written in terms of a photofragmentation amplitude

$$f(\hat{k}E, v j m_i, m_s | E_i J_i M_i p_i); \sigma(\hat{k}E, v j m_i, m_s | E_i J_i M_i p_i) = \left(\frac{8\pi^3 \nu}{hc} \right) |f(\hat{k}E, v j m_i, m_s | E_i J_i M_i p_i)|^2, \quad (43)$$

where

$$f(\hat{k}E, v j m_i, m_s | E_i J_i M_i p_i) = \langle \Psi_f^- (\hat{k}E, v j m_i, m_s) | \hat{\epsilon} \cdot \hat{\mu} | \Psi_i (E_i J_i M_i p_i) \rangle \quad (44)$$

and is just the bound-continuum integral of Eq. (1). Using Eq. (20) to expand the continuum wave function, the photofragmentation amplitude may be written in terms of a photofragmentation T matrix^{21,22} $t(E J v k \lambda j i | E_i J_i p_i)$:

$$f(\hat{k}E, v j m_i, m_s | E_i J_i M_i p_i) = 2 \left(\frac{\mu k_{v j i} c}{\hbar} \right)^{1/2} \sum_{J M \lambda} \sum_{k m_k} (j s k m_k | j m s m_s) \times \sum_{l m_l} Y_{l m_l}^*(\hat{k}) (k l J M_i | k m_k l m_l) (J k l 0 | J \lambda k - \lambda) t(E J v k \lambda j i | E_i J_i p_i) (-1)^{-M_i} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix}, \quad (45)$$

where the photofragmentation T matrix is defined as

$$t(E J v k \lambda j i | E_i J_i p_i) = \sum_{v' k' \lambda' j' i'} \langle G_{k' \lambda' j' i'}^{JM_p}(\hat{R}, \hat{r}) \chi_{v' f'}(r) \Phi_{v' k' \lambda' j' i'}^{-(Jv k \lambda j i p)}(R) R^{-1} | \hat{\epsilon} \cdot \hat{\mu} | \Psi_i(E_i J_i M_i p_i) \rangle (-1)^{M_i} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix}^{-1}. \quad (46)$$

Using Eq. (33) of Ref. 21,

$$\sum_{l m_l} Y_{l m_l}(\hat{k}) (k l J M_i | k m_k l m_l) (J k l 0 | J \lambda k - \lambda) = \left(\frac{2J+1}{4\pi} \right)^{1/2} (-1)^{k-m_k} D_{\lambda M_i}^J(\phi_k \theta_k 0) D_{-\lambda-m_k}^k(\phi_k \theta_k 0). \quad (47)$$

Equation (45) can be rewritten as

$$f(\hat{k}E, v j m_i, m_s | E_i J_i M_i p_i) = \left(\frac{\mu k_{v j i} c}{\pi \hbar} \right)^{1/2} \sum_{k m_k} (j s k m_k | j m s m_s) (-1)^{M_i + k - m_k} \times \sum_{J \lambda} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} (2J+1)^{1/2} D_{\lambda M_i}^J(\phi_k \theta_k 0) D_{-\lambda-m_k}^k(\phi_k \theta_k 0) t(E J v k \lambda j i | E_i J_i p_i). \quad (48)$$

Substituting this expression into Eq. (43), yields an expression for the *detailed differential photofragmentation cross section*:

$$\sigma(\hat{k}E, vjmi, m_s | E_i J_i M_i p_i) = \frac{4\pi\nu\mu k_{vji}}{\hbar^2} \left| \sum_{k m_k} (j k m_k | j m s m_s) (-1)^{k-m_k} \right. \\ \left. \times \sum_{J \lambda} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} (2J+1)^{1/2} D_{\lambda M_i}^J(\phi_k \theta_k 0) D_{-\lambda-m_k}^k(\phi_k \theta_k 0) t(EJv k \lambda j i | E_i J_i p_i) \right|^2. \quad (49)$$

The *differential cross section, summed over all final fragment magnetic quantum numbers, m and m_s* , may readily be shown to be

$$\bar{\sigma}(\hat{k}E v j i | E_i J_i M_i p_i) = \sum_{m m_s} \sigma(\hat{k}E, vjmi, m_s | E_i J_i M_i p_i) \\ = \frac{4\pi\nu\mu k_{vji}}{\hbar^2} \sum_k \sum_{J' \lambda} [(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J' & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \\ \times D_{\lambda M_i}^J(\phi_k \theta_k 0) D_{\lambda M_i}^{J'*}(\phi_k \theta_k 0) t(EJv k \lambda j i | E_i J_i p_i) t^*(EJ'v k \lambda j i | E_i J_i p_i). \quad (50)$$

In deriving Eq. (50) from Eq. (49) the following relationships have been used:

$$\sum_{m m_s} (j k m_k | j m s m_s) (j k' m'_k | j m s m_s) = \delta_{k k'} \delta_{m_k m'_k} \delta(j s k) \quad (51)$$

[see Edmonds⁴² Eq. (3.5.4)] and

$$\sum_{m_k} D_{-\lambda-m_k}^k(\phi_k \theta_k 0) D_{-\lambda'-m_k}^{k*}(\phi_k \theta_k 0) \\ = \sum_{m_k} D_{-\lambda-m_k}^k(\phi_k \theta_k 0) D_{-m_k-\lambda'}^k(0-\theta_k-\phi_k) = D_{-\lambda-\lambda'}^k(\phi_k 0-\phi_k) = \delta_{\lambda \lambda'}. \quad (52)$$

[see Edmonds⁴² Eqs. (4.1.12), (4.2.2), (4.2.4), and (4.2.1)].

The integral photodissociation cross section, summed over all final fragment magnetic quantum numbers may be obtained by integrating Eq. (50) over the angles ϕ_k and θ_k . This integration gives

$$\int D_{\lambda M_i}^J(\phi_k \theta_k 0) D_{\lambda M_i}^{J'*}(\phi_k \theta_k 0) \sin \theta_k d\theta_k d\phi_k = \frac{4\pi}{2J+1} \delta_{J J'}. \quad (53)$$

Using this together with Eq. (50) the *integral photodissociation cross section summed over all final fragment magnetic quantum numbers* may be written as

$$\bar{\sigma}(E v j i | E_i J_i M_i p_i) = \int \bar{\sigma}(\hat{k} v j i | E_i J_i M_i p_i) \sin \theta_k d\theta_k d\phi_k \\ = \frac{16\pi\nu\mu k_{vji}}{\hbar^2} \sum_k \sum_{J \lambda} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix}^2 |t(EJv k \lambda j i | E_i J_i p_i)|^2. \quad (54)$$

Finally the expression for the *integral photodissociation cross section averaged over all initial and summed over all final magnetic quantum numbers* may be written as

$$\bar{\bar{\sigma}}(E v j i | E_i J_i p_i) = \frac{1}{2J_i+1} \sum_{M_i} \bar{\sigma}(E v j i | E_i J_i M_i p_i) \\ = \frac{16\pi^2\nu\mu k_{vji}}{3\hbar^2} \cdot \frac{1}{2J_i+1} \sum_{J \lambda} \delta(J_i J 1) |t(EJv k \lambda j i | E_i J_i p_i)|^2, \quad (55)$$

where the relationship

$$\sum_{M_i} \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix}^2 = \sum_{M_i} \begin{pmatrix} J_i & J & 1 \\ M_i & -M_i & 0 \end{pmatrix}^2 = \frac{1}{3} \delta(J_i J 1) \quad (56)$$

[see Edmonds⁴² Eqs. (3.7.4) and (3.7.8) have been utilized].

Expressions for other types of differential and integral photofragmentation cross sections may be derived from the expression for the most detailed cross section, Eq. (49), using methods similar to those of Ref. 21.

VII. EVALUATION OF PHOTOFRAGMENTATION T MATRIX ELEMENTS

As always, the dynamics of the photofragmentation process is contained entirely in the photofragmentation T matrix.²² This T matrix is defined in Eq. (46) of the previous

subsection, as an integral over both nuclear and electronic coordinates. In this subsection the evaluation of this T matrix is considered in greater detail, and all integrations except for that over the radial coordinate R are performed analytically.

Contact between the present work and more standard treatments, which work entirely within the Born–Oppenheimer approximation,²¹ may best be established by inserting the identity operator in the electronic space, expanded in terms of molecular valence bond or any other suitable basis set of functions, into the bound-continuum integral of Eq. (46) to the left-hand side of the $\hat{\epsilon} \cdot \hat{\mu}$ term. For the present application, i.e., the photodissociation of water in its first absorption band ($\tilde{A}^1B_1 \leftarrow X^1A_1$), *this identity operator may, to a very good approximation, be expressed as a projection operator onto the \tilde{A}^1B_1 or \tilde{A}^1A'' electronic state.* Thus the expression for the photofragmentation T matrix may be written as:

$$t(EJ\nu k\lambda j i | E_i J_i p_i) = \sum_{\nu' k' \lambda' j' i'} \langle \chi_{\nu' j'}(r) \Phi_{\nu' k' \lambda' j' i'}^{-1(J\nu k\lambda j i p)}(R) R^{-1} \times \langle G_{k' \lambda' j' i'}^{J M p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) |^1 A'' \rangle_{\text{el}} \langle ^1 A'' | \hat{\epsilon} \cdot \hat{\mu} | \Psi_i(E_i J_i M_i p_i) \rangle_{\text{el}} \rangle, \quad (57)$$

where the electronic wave function $|^1 A''\rangle$ is written out more fully in Eq. (23), and the inner angular brackets denote integration over the electronic coordinates only.

The initial bound state wave function may be factored into nuclear and electronic parts using the Born–Oppenheimer approximation:

$$\Psi_i(E_i J_i M_i p_i) = \Psi_{i, \text{nuc}} \Psi_{i, \text{el}}. \quad (58)$$

The integration of the dipole moment operator between the two electronic wave functions then yields the transition dipole moment between the two electronic states involved. In the present case this transition dipole moment is directed perpendicular to the plane of the triatomic molecule, i.e., in the H₂O body-fixed y direction. The transformation of this body-fixed transition dipole moment function to the space-fixed axis system has been previously discussed.²¹ It should be noted, in particular, that $\hat{\epsilon}$ is a unit vector in the space-fixed z direction, and we therefore require the component of the transition dipole moment only in this direction. Based on

these considerations, the electronic integration over the dipole moment operator may be written as

$$\langle ^1 A'' | \hat{\epsilon} \cdot \hat{\mu} | \Psi_{i, \text{el}} \rangle_{\text{el}} = -(i/\sqrt{2}) \mu_y(R, r, \gamma) \times [D_{10}^1(\phi_R \theta_R \psi) + D_{-10}^1(\phi_R \theta_R \psi)]. \quad (59)$$

The nuclear part of the bound state wave function is expanded in terms of eigenfunctions of the total angular momentum and the parity

$$\Psi_{i, \text{nuc}}(\mathbf{R}, \mathbf{r}) = \sum_{\nu j \lambda} \chi_{\nu j}(r) \Theta_{j \lambda}^{J_i M_i p_i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \frac{\Phi_{\nu \lambda}^{J_i p_i}(R)}{R}. \quad (60)$$

This expansion is identical to that used in previous work.^{21,23} The angular momentum eigenfunctions are defined by [see Ref. 21, Eqs. (5) and (6)]

$$\Theta_{j \lambda}^{J_i M_i p_i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) = t_\lambda \left(\frac{2J_i + 1}{4\pi} \right)^{1/2} \times \{ D_{\lambda M_i}^{J_i}(\phi_R \theta_R \psi) Y_{j \lambda}(\gamma, 0) + p_i D_{-\lambda M_i}^{J_i}(\phi_R \theta_R \psi) Y_{j - \lambda}(\gamma, 0) \}. \quad (61)$$

It is now necessary to perform the integration $\langle G_{k' \lambda' j' i'}^{J M p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) |^1 A'' \rangle_{\text{el}}$ over the electronic coordinates in Eq. (57). For the purposes of such integrations the “atomic” orbitals used to construct the valence-bond structures of Eq. (23) are regarded as being mutually orthogonal. The main assumption of the present treatment is that the orthogonal orbitals used to represent the system at small internuclear separations should smoothly and adiabatically transform into the orthogonal fragment orbitals as the interfragment separation is increased. Assumptions, such as these, may only be removed if a more correct treatment of the electronic structure of the system is used, together with all the added complications which arise from this.

The electronic matrix elements $\langle G_{k' \lambda' j' i'}^{J M p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) |^1 A'' \rangle_{\text{el}}$ may readily be shown to be

$$\langle G_{k' \lambda' j' i'}^{J M p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) |^1 A'' \rangle_{\text{el}} = \frac{i}{2} \{ A_{j' i'} F_{k' \lambda' 1}^{J M p*}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s - \frac{1}{2} k' 1 | s k' j' \frac{1}{2}) + D_{j' i'} F_{k' \lambda' -1}^{J M p*}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s - \frac{1}{2} k' - 1 | s k' j' - \frac{3}{2}) + C_{j' i'} F_{k' \lambda' 1}^{J M p*}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s \frac{1}{2} k' 1 | s k' j' \frac{3}{2}) + B_{j' i'} F_{k' \lambda' -1}^{J M p*}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) (s \frac{1}{2} k' - 1 | s k' j' - \frac{1}{2}) \}, \quad (62)$$

through the use of Eqs. (23), (25), and (29)–(31).

The angular integrations over the nuclear coordinates in Eq. (57) will involve integration of the product of the right-hand sides of Eqs. (59), (61), and (62). The basic angular integral is therefore of the form

$$\langle F_{k' \lambda' j' i'}^{J M p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) | \mu_y(R, r, \gamma) [D_{10}^1(\phi_R \theta_R \psi) + D_{-10}^1(\phi_R \theta_R \psi)] | \Theta_{j \lambda}^{J_i M_i p_i}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \rangle = t_\lambda \cdot t_\lambda [(2J + 1)(2J_i + 1)(2k' + 1)]^{1/2} \pi^{1/2} \delta_{M M_i} (-1)^{\lambda' - M_i} \times \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \{ [J - \lambda' | J_i \lambda] \mu_y(k' \nu \lambda' | j \lambda) + p(-1)^\nu [J \lambda' | J_i \lambda] \mu_y(k' - \nu - \lambda' | j \lambda) \} + p_i [J - \lambda' | J_i - \lambda] \mu_y(k' \nu \lambda' | j - \lambda) + p p_i (-1)^\nu [J \lambda' | J_i - \lambda] \mu_y(k' - \nu - \lambda' | j - \lambda) \}, \quad (63)$$

where Eq. (4.6.2) of Edmonds⁴² has been used, together with the definitions;

$$[J \lambda' | J_i \lambda] = \begin{pmatrix} J & 1 & J_i \\ \lambda' & 1 & \lambda \end{pmatrix} + \begin{pmatrix} J & 1 & J_i \\ \lambda' & -1 & \lambda \end{pmatrix}, \quad (64)$$

$$\mu_y(k' \nu \lambda' | j \lambda) = \int_0^\pi d\nu_{\lambda'}(\gamma) \mu_y(R, r, \gamma) Y_{j \lambda}(\gamma, 0) \sin \gamma d\gamma, \quad (65)$$

where

$$\begin{pmatrix} J & 1 & J_i \\ \lambda' & 1 & \lambda \end{pmatrix}$$

is a 3- j symbol. Utilizing the symmetry properties

$$[J\lambda' | J_i \lambda] = (-1)^{J+1+J_i} [J-\lambda' | J_i -\lambda], \quad (66)$$

$$[J-\lambda' | J_i \lambda] = (-1)^{J+1+J_i} [J\lambda' | J_i \lambda],$$

$$\mu_y(k'\nu\lambda' | j\lambda) = (-1)^{\nu-\lambda'} \mu_y(k-\nu-\lambda' | j\lambda) = (-1)^\lambda \mu_y(k\nu\lambda' | j-\lambda) = (-1)^{\nu-\lambda'+\lambda} \mu_y(k-\nu-\lambda' | j-\lambda), \quad (67)$$

the basic angular integral may be rewritten in the form:

$$\begin{aligned} & \langle F_{k'\lambda'\nu}^{JM_p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) | \mu_y(R, r, \gamma) [D_{10}^1(\phi_R \theta_R \psi) + D_{-10}^1(\phi_R \theta_R \psi)] | \Theta_{j\lambda}^{JM_p}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \rangle \\ &= t_{\lambda'} t_{\lambda} [(2J+1)(2J_i+1)(2k'+1)]^{1/2} \delta_{MM_i} 2\pi^{1/2} (-1)^{\lambda'-M_i} \\ & \times \begin{pmatrix} J & 1 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \mu_y(k'\nu\lambda' | j\lambda) \{ [J-\lambda' | J_i \lambda] + p(-1)^{-\lambda'} [J\lambda' | J_i \lambda] \} \\ & \text{if } p_i p(-1)^{J+J_i} = 1 \text{ (i.e., if } F_{k'\lambda'\nu}^{JM_p} \text{ and } \Theta_{j\lambda}^{JM_p} \text{ have the same parity)} \\ &= 0 \text{ if } p_i p(-1)^{J+J_i} = -1. \end{aligned} \quad (68)$$

The angular integrals over the transition dipole moment function $\mu_y(R, r, \gamma)$ are still functions of R and r . In the final expression for the photofragmentation cross section these will appear as matrix elements between the fragment vibrational functions $\chi_{vj}(r)$. It is, therefore, useful to define the matrix elements as

$$\mu_y(v'j'k'\nu\lambda' | vj\lambda) = \int \chi_{v'j'}(r) \mu_y(k'\nu\lambda' | j\lambda) \chi_{vj}(r) r^2 dr. \quad (69)$$

Substituting Eqs. (59), (60), (62), (68), and (69) into the definition of the photofragmentation T matrix element, Eq. (57), the latter may be written in the more explicit form

$$\begin{aligned} t(EJ\nu k\lambda j | E_i J_i p_i) &= \sum_{v'k'\lambda'j'r'} \sum_{v''j''\lambda''} i\pi^{1/2} t_{\lambda'} t_{\lambda} [(2J+1)(2J_i+1)(2k'+1)]^{1/2} \{ [J-\lambda' | J_i \lambda''] (-1)^{\lambda'} + p [J\lambda' | J_i \lambda''] \} \\ & \times \{ [A_{j'r'}(s - \frac{1}{2}k'1 | sk'j' \frac{1}{2}) + C_{j'r'}(s \frac{1}{2}k'1 | sk'j' \frac{3}{2}) \} \langle \Phi_{v'k'\lambda'j'r'}^{-J\nu k\lambda jip}(R) R^{-1} | \mu_y(v'k'1\lambda' | v''j''\lambda'') \rangle \langle \Phi_{v''j''\lambda''}^{J_i p_i}(R) R^{-1} \rangle \\ & + [D_{j'r'}(s - \frac{1}{2}k' - 1 | sk'j' - \frac{3}{2}) + B_{j'r'}(s \frac{1}{2}k' - 1 | sk'j' - \frac{1}{2})] \\ & \times \langle \Phi_{v'k'\lambda'j'r'}^{-J\nu k\lambda jip}(R) R^{-1} | \mu_y(v'k' - 1\lambda' | v''j''\lambda'') \rangle \langle \Phi_{v''j''\lambda''}^{J_i p_i}(R) R^{-1} \rangle \}. \end{aligned} \quad (70)$$

This expression for the photofragmentation T matrix element contains, other than for the numerical integrations over R and r involving the transition dipole moment function, only analytic functions such as Clebsch-Gordan coefficients.

VIII. A SIMPLIFIED APPROXIMATE FORMULA FOR THE PRODUCT OH A-DOUBLET QUANTUM STATE DISTRIBUTION

If a sufficient number of simplifying assumptions are made concerning the nature of the transition dipole moment function and the dynamics of the nuclear motion, both on the ground and upper electronic state potential energy surfaces, it is possible to derive useful formulas for the final product quantum state distributions which depend only on a knowledge of the ground state wave function. Each of the simplifying assumptions which must be made are specified below.

Assumption 1. The transition dipole moment function is assumed to be a constant, independent of R and r . It is also assumed that the vibrational wave functions $\chi_{vj}(r)$ are identical for all j (i.e., vibration-rotation coupling in the OH fragments is ignored).

$$\begin{aligned} \mu(v'j'k'\nu\lambda' | v''j''\lambda'') &\approx \mu_y(k'\nu\lambda' | j''\lambda'') \delta_{v'v''} \\ &= \mu_y \delta_{v'v''} \int_{\gamma=0}^{\pi} d\gamma'_{\nu\lambda'}(\gamma) Y_{j''\lambda''}(\gamma, 0) \sin \gamma d\gamma. \end{aligned} \quad (71)$$

Assumption 2. There is no inelastic scattering in the final electronic state, and all final state (elastic) radial channel wave functions are identical:

$$\Phi_{v'k'\lambda'j'r'}^{-J\nu k\lambda jip}(R) = \Phi^{-}(R) \delta_{vv'} \delta_{kk'} \delta_{\lambda\lambda'} \delta_{jj'} \delta_{ir'}. \quad (72)$$

This assumption removes all the summations over final state quantum numbers in the expression for the photofragmentation T matrix [Eq. (70)].

Assumption 3. The ground state radial wave function is assumed to be independent of vibrational quantum number v'' , thus removing the summation over this quantum number in Eq. (70). This wave function is also assumed to be sharply peaked at $R = R_e$ (the equilibrium value of R) and is replaced by a delta function:

$$\Phi_{v''j''\lambda''}^{J_i p_i}(R) \approx C_{j''\lambda''}^{J_i p_i} \delta(R - R_e). \quad (73)$$

This final assumption of a delta function dependence on R is not essential for the derivation of the rotational distributions.

With these simplifying assumptions the expression for the photofragmentation T matrix reduces to

$$t(EJvk\lambda ji|E_i J_i p_i) \approx i\pi^{1/2} t_\lambda [(2J+1)(2J_i+1)(2k+1)]^{1/2} \Phi^-(R_e) \sum_{j''\lambda''} C_{j''\lambda''}^{J_i p_i} t_\lambda \cdot \\ \times \{ [J-\lambda | J_i \lambda''] (-1)^\lambda + p [J\lambda | J_i \lambda''] \} \{ [A_{ji}(s-\frac{1}{2}k1|skj\frac{1}{2}) + C_{ji}(s\frac{1}{2}k1|skj\frac{3}{2})] \mu(k1\lambda | j''\lambda'') \\ + [D_{ji}(s-\frac{1}{2}k-1|skj-\frac{3}{2}) + B_{ji}(s\frac{1}{2}k-1|skj-\frac{1}{2})] \mu(k-1\lambda | j''\lambda'') \}, \quad (74)$$

where the coefficients $C_{j''\lambda''}^{J_i p_i}$ may be obtained from an analysis of the ground state wave function, and all other quantities have either been explicitly specified or may be easily evaluated.

Using this expression for the photofragmentation T matrix the relative probability of producing different OH Λ -doublet states, each labeled by the quantum numbers ji , may be written as

$$P_{ji} = \sum_v \bar{\sigma}(Evji|E_i J_i p_i) \\ \propto \sum_{j''\lambda''} (2J+1)(2k+1) t_\lambda^2 \left| \sum_{j''\lambda''} C_{j''\lambda''}^{J_i p_i} t_\lambda \cdot \{ [J-\lambda | J_i \lambda''] (-1)^\lambda + p [J\lambda | J_i \lambda''] \} \right. \\ \times \{ [A_{ji}(s-\frac{1}{2}k1|skj\frac{1}{2}) + C_{ji}(s\frac{1}{2}k1|skj\frac{3}{2})] \mu(k1\lambda | j''\lambda'') \\ \left. + [D_{ji}(s-\frac{1}{2}k-1|skj-\frac{3}{2}) + B_{ji}(s\frac{1}{2}k-1|skj-\frac{1}{2})] \mu(k-1\lambda | j''\lambda'') \} \right|^2. \quad (75)$$

The assumptions made in deriving this formula are similar to those used by Beswick and Gelbart³³ and also by Morse and Freed.³⁴

IX. SUMMARY

In this work the theory for the photodissociation of H_2O in its first continuum has been derived. Expressions have been given for both differential equations (49) and (50) and integral equations (54) and (55) photofragmentation cross sections. In all cases these predict the probabilities of the photodissociation of water into specific OH product Λ -doublet states. The theory is built around a model of the electronic structure of both the ground and excited electronic states. Such a model is essential if the theory is not to become an order of magnitude more complex than that presented here. Nonetheless, the treatment presented here should give a sound starting point both for the generalization of the theory to a more exact treatment and for its generalization to more complex photodissociation processes. The theory is in many respects similar to that developed by Shapiro and Kaplan³² in their discussion of $H + OH(^2\Pi)$ collisional dynamics.

The coupled differential equations needed for the calculation of the radial channel wave functions, which occur in the expansion of the upper state continuum wave function, are derived. The potentials which occur in these equations are explicitly defined, and are related to the potential energy surfaces which may be obtained from high quality *ab initio* molecular electronic structure calculations. Four different electronic potential energy surfaces participate in governing the motion of the nuclei in the continuum state.

In Sec. VIII, an approximate "Franck-Condon" type of treatment is used to derive an explicit expression for the probability of producing specific OH product Λ -doublet states. The approximations needed to derive this expression are specified clearly. The formula assumes no final state interaction (i.e., no inelasticity during the motion on the upper electronic potential energy surface), and a constant transition dipole moment function. The formula should have useful predictive potential as it incorporates both the correct symmetry properties of the process and the correct angular momentum coupling. Indeed, applications of this formula

have predicted OH Λ -doublet state distributions in remarkable agreement with experimental observations.⁴⁵

There are two particularly significant omissions from the theory discussed in this paper. Firstly no account has been taken of the dissociative channels which lead to the production of $H_2(X^1\Sigma^+) + 0$, despite the fact that such channels are open at the energies of interest. Secondly the problem of antisymmetrization of the wave function with respect to exchange of hydrogen nuclei has not been addressed.²⁴ The former of these two omissions can only be overcome by an extension of the present theory, while the latter may be treated by the postantisymmetrization techniques described by Kuppermann, Schatz, and Baer⁴⁴ in relation to the reactive scattering problem.

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