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Rotationally resolved photoelectron spectra in resonance enhanced multiphoton ionization of H₂O via the C^1B₁ Rydberg state

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In this paper, we extend a previous formulation of molecular resonance enhanced multiphoton ionization (REMPI) photoelectron spectra of diatomic molecules to treat rotationally resolved photoionization of nonlinear polyatomic molecules. Useful parity selection rules, which govern changes of angular momenta \( \Delta K_a \) and \( \Delta K_r \), are also derived. As an example, we use this formulation to study rotational branching ratios and photoelectron angular distributions resulting from \((3+1')\) REMPI of H₂O via the C^1B₁ (3pa₁) Rydberg state. Cooper minima are predicted to occur in the \( d \) wave \((I=2)\) of the \( k \alpha_1 \) \((I=0)\) and \( k \beta_1 \) \((I=1)\) photoelectron continua. The effects of these Cooper minima on rotationally resolved photoelectron spectra are also investigated.

I. INTRODUCTION

Resonance enhanced multiphoton ionization coupled with high-resolution photoelectron spectroscopy (REMPI-PES) provides a useful probe of molecular excited states and the photoionization dynamics of these states. In REMPI, a single rotational level of the resonant state is selected and therefore only a small number of rotational levels of the ion are generally accessed. This results in substantial simplification in the photoelectron spectra, making such spectra particularly useful in investigating the photoionization dynamics of nonlinear molecules. Such rotationally resolved ion spectra of nonlinear molecules (NH₃, C₆H₆, H₂S, para-difluorobenzene, phenol-H₂O, and pyrazine) have been studied by zero-kineti-energy (ZEKE) photoelectron spectroscopy. For ZEKE detection, the spectral resolution is about the laser bandwidth (\( \sim 0.1 \) cm\(^{-1} \)) which readily provides for rotational resolution in molecular ions.

We have previously given a formulation for REMPI photoelectron spectra of diatomic molecules which explicitly used multiplet-specific final-state wave functions for the photoionized system. With the aid of parity selection rules such as \( \Delta N+I=odd \), \( \Delta N \) and \( I \) are the rotational quantum numbers of the ionic and intermediate states, respectively, and \( \Delta N \) is the net angular momentum component of the photoelectron, we have exploited this formulation to quantitatively account for ion rotational distributions and the effects of Cooper minima on such distributions resulting from REMPI of Rydberg states of diatomic molecules (NO, CH, H₂S, and OH). Here this formulation is extended to characterize rotationally resolved REMPI spectra of nonlinear molecules. In this paper, emphasis is placed on molecules of C₂ᵥ symmetry. Useful formulas and associated parity selection rules are obtained. This formulation has been used recently to interpret successfully the dynamical origins of type a transitions seen in the experiments of Tonkyn et al. in photoionization of jet-cooled water with coherent vacuum ultraviolet (VUV) radiation.

Our formulation is used here to study REMPI spectra resulting from \((3+1')\) REMPI of the C^1B₁ Rydberg state of H₂O. We choose this specific example for the following reasons: Recently, Kuge and Kleinermanns have studied the rotational predissociation of H₂O by \((3+1')\) REMPI of the C^1B₁ (3pa₁) Rydberg state in a supersonic jet. However, the REMPI ion spectra for ionization of a specific rotational level of the resonant C^1B₁ state were not rotationally resolved and, hence, the associated photoionization dynamics and ion rotational propensity rules were not transparent. Meanwhile, Tonkyn et al. have investigated the rotationally resolved single-photon VUV ZEKE photoelectron spectra of jet-cooled water by pulsed field ionization of extremely high-\( n \) Rydberg states. Both type a and type c transitions were observed in these ion spectra in contrast to the prediction of type c transitions only by Child and Jungen. Lee et al. have accounted successfully for these type a transitions as arising from nonatomic-like behavior of the molecular photoelectron continua.

Of particular interest here is to examine related behavior which may be also associated with REMPI spectra of the C^1B₁ Rydberg state of H₂O.

Results of theoretical studies of ion rotational distributions and associated photoelectron angular distributions are presented here for \((3+1')\) REMPI via the C^1B₁ (3pa₁) Rydberg state of H₂O. Examination of angular momentum components of photoelectron matrix elements reveal that Cooper minima are associated with these photoionization continua. Cooper minima have been shown previously to have pronounced effects on ion rotational distributions. For example, they give rise to an-

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expected $\Delta N=0$ peak in REMPI spectra of the $D^2\Sigma^+ (3\sigma)$ Rydberg state of NO, the $D^2\Sigma^- (3\sigma)$ state of OH, and the $f^1\Pi (3\sigma)$ state of NH. These effects of Cooper minima on rotationally resolved photoelectron spectra of nonlinear molecules are also studied here at various kinetic energies. To our knowledge, Cooper minima in the photoionization of excited states of nonlinear molecules have not been reported previously.

II. THEORY AND NUMERICAL DETAILS

A. Rotationally resolved $(n+1')$ REMPI theory

$(n+1')$ REMPI processes via a resonant intermediate state of any molecule can be viewed as a two-step process of $n$-photon absorption from an unaligned initial (or ground) state (all $M_{J_i}$ sublevels are equally populated) to the resonant intermediate state, followed by subsequent one-photon ionization of the aligned intermediate state. The photon energies of the excitation and ionization steps of REMPI may differ from each other in a two-color experiment. Under collision-free conditions, each $M_J$ channel can be treated as an independent ionization channel for linearly polarized light. The differential cross section for photoionization of the resonant state by the final photon can then be written as

$$
\frac{d\sigma}{d\Omega} \propto \sum_{M_{J_i}M_{J+}} \rho_{M_{J_i}M_{J+}} |\Gamma_{M_{J_i}M_{J+}}|^2
$$

where $\sigma$ is the total cross section, $\rho_{M_{J_i}M_{J+}}$ is an asymmetry parameter, $|\Gamma_{M_{J_i}M_{J+}}|^2$ is the ionization probability out of the $M_{J_i}$ magnetic sublevel of the intermediate state leading to the $M_{J+}$ sublevel of the ion, $\rho_{M_{J_i}M_{J+}}$ is the population of the $M_{J_i}$ sublevel induced by the $n$-photon excitation, and $J_i$ and $J_+$ are the total angular momenta of the intermediate and ionic states in the laboratory frame, respectively. Note that subscripts $i$ and $+$ denote the quantum numbers for the intermediate and ionic states, respectively. The evaluation of $\rho_{M_{J_i}M_{J+}}$ usually requires a summation over all dipole-allowed virtual states and possible paths. However, in many cases, explicit evaluation of these summations is not necessary if one is interested only in the relative population (the alignment) of the different $M_{J_i}$ sublevels of the intermediate state. Under these circumstances, $\rho_{M_{J_i}M_{J+}}$ has the simple form

$$
\rho_{M_{J_i}M_{J+}} = \left( \begin{array}{c c c}
J_i & J_0 & 0 \\
-1 & M_{J_i} & M_{J+} \\
0 & 0 & M_{J_i} \\
\end{array} \right) B
$$

with $B$ the rotational line strength (which is just an overall multiplicative factor) and $J_0$ the rotational quantum number of the initial state.

We now examine the matrix element for photoionization of an $M_{J_i}$ sublevel of the resonant state leading to an $M_{J_+}$ sublevel of the final continuum state. The following formulation is generally derived for asymmetric top molecules. However, the application of this formulation to a symmetric top is straightforward. The bound–free transition moment $\Gamma_{M_{J_i}M_{J+}}$ can be written as

$$
\Gamma_{M_{J_i}M_{J+}} = \sum_{\Lambda} \langle \phi_e | (\Lambda \Sigma_f) \langle \Lambda \Sigma_f | D_{pq} | i \rangle, \quad (3)
$$

where

$$
D_{pq} = \sqrt{\frac{4\pi}{3}} \sum_{\mu} (-1)^{\mu_0-\mu} |_{\mu \text{lad}} Y_{\mu \text{lad}}(\hat{r})
$$

with $D_{pq}$ the dipole moment operator in the laboratory frame and $|_{\mu \text{lad}}$ rotational matrices in Edmonds' notation. In Eq. (3), the total final-state continuum wave function (ion–photoelectron)

$$
|f\rangle = \sum_{\Lambda \Sigma} |\Lambda \Sigma_f \rangle \langle \Lambda \Sigma_f | f\rangle
$$

is used where $|\Lambda \Sigma_f \rangle$ is a dipole-allowed multiplet-specific final-state wave function.

To evaluate $\Gamma_{M_{J_i}M_{J+}}$, explicit forms for wave functions of the intermediate state $|i\rangle$, ionic state $|f^+\rangle$, and photoelectron $|\phi_e\rangle$ are necessary. They have the forms

$$
|i\rangle = \psi \chi_{\alpha}(0,\mathbf{r}) \chi_{\gamma}(\mathbf{r}) \chi_{\delta}(\mathbf{r})
$$

and

$$
|\phi_e\rangle = \left( \frac{2}{\pi} \right)^{1/2} \left[ \begin{array}{c}
1 \\
0 \\
1 \\
\end{array} \right] m_{\sigma} \sum_{\mathbf{q}_{\text{hid}}} \hat{\phi}_{\mathbf{q}_{\text{hid}}}^{(\text{vdw})(\mathbf{r})} \chi_{\mathbf{h}\text{lad}}^{(\text{vdw})(\mathbf{k})}
$$

where $\hat{\phi}_{\mathbf{q}_{\text{hid}}}^{(\text{vdw})(\mathbf{r})}$ is the spin eigenfunction of the photoelectron, $\mathbf{k}$ defines the photoelectron kinetic energy, $\gamma$ is one of the irreducible representations (IR) of the molecular point group, $q$ is a component of this representation, $h$ distinguishes between different bases for the same IR corresponding to the same value of $l$, $\phi_{\mathbf{q}_{\text{hid}}}^{(\text{vdw})(\mathbf{r})}$ is a partial wave component of the photoelectron orbital, $X_{\mathbf{h}\text{lad}}^{(\text{vdw})(\mathbf{k})}$ is a generalized harmonic, and $\psi_i$ and $\chi_i$ are the electronic and vibrational wave functions of the state $|i\rangle$, respectively. Note that Hund's case (b) coupling scheme is chosen to represent both the intermediate and ionic states [see Eqs. (6) and (7)]. The rotational levels of both intermediate and ionic states are described by the asymmetric top wave function

$$
|NMKA_{\alpha}K_{\gamma}\rangle = \sum_{K} a_{K} S(NMKA_{\alpha}K_{\gamma}P_{\rho})
$$

where $a_{K}$ is the rotational wavefunction of the ion.
where $\tau = K_a - K_c$ with $K_a$ and $K_c$ the projections of the total angular momentum along the $a$ and $c$ axes, respectively, and the coefficients $a_{\nu K}$ are determined by diagonalizing the rigid rotor Hamiltonian

$$H_r = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z}$$

(10)

in the basis of the symmetric top eigenfunctions. In Eq. (9), $S(NM_N\nu Kp)$ is a linear combination of symmetric top functions and has the form

$$S(NM_N\nu Kp) = \frac{1}{\sqrt{2}} \left[ |NM_NK\rangle + (-1)^p |NM_N-K\rangle \right]$$

(11)

for $K > 0$ with $p$ the parity index having the value of 0 or 1, and

$$S(NM_N00) = |NM_N00\rangle$$

(12)

for $K = 0$. The symmetric top wave functions $|NM_NK\rangle$ in Eqs. (11) and (12) are given by

$$|NM_NK\rangle = \left(\frac{2N+1}{8\pi^2}\right)^{1/2} (-1)^{K-M_N} \Omega^N_{N\nu K}. \quad (13)$$

Note that the $S(NM_N\nu Kp)$ functions adopted in Eq. (9) instead of symmetric top eigenfunctions $|NM_NK\rangle$ fulfill the symmetry requirements of the $V_4$ group. In Eq. (8), we use the generalized harmonics $X_{\nu K}^{\mu}(\hat{k})$ as bases for the IR of the molecular point group. These symmetry-adapted angular functions satisfy well-known orthonormality relations and can be expressed in terms of the usual spherical harmonics

$$X_{\nu K}^{\mu}(\hat{k}) = b_{\nu K}^{\mu} Y_{\nu K}^{\mu}(\hat{k}) + b_{\nu -K}^{\mu} Y_{\nu -K}^{\mu}(\hat{k})$$

(14)

in the body-fixed frame. The coefficients $b_{\nu K}^{\mu}$ for the $C_{2v}$ and $O_h$ symmetries have been given by Burke et al. They $Y_{\nu K}^{\mu}(\hat{k})$ can be further written in terms of the spherical harmonics $Y_{\nu m}(\hat{k'})$ in the laboratory frame as

$$Y_{\nu K}^{\mu}(\hat{k}) = \sum_m (-1)^{\lambda-m} \Omega_{km}^{\nu m} Y_{\nu m}(\hat{k'}). \quad (15)$$

By substituting Eqs. (4) and (6)–(8) into Eq. (3) and making use of the properties of $3j$ symbols, Eq. (3) can be rewritten as

$$\Gamma_{M_j M_{j+}} = \sum_{\nu m} C_{\nu m} |M_j M_{j+}\rangle Y_{\nu m}(\hat{k'}), \quad (16)$$

where

$$Q = \Delta \nu + \Delta M_j - S_l + S_l - \mu_0 - \mu + M_{N_+} + K_l - 1/2, \quad (18)$$

and

$$\bar{P}_{\mu\nu}(\Lambda_j \Sigma_f) = \langle \gamma_{+} + \gamma_{-}\Omega_\nu | \Lambda_f \rangle \times \langle \Lambda_j | \Sigma_f \rangle Y_{\mu\nu}^{\gamma_{-}}(\Lambda_j \Sigma_f), \quad (19)$$

and

$$P_{\mu\nu}(\Lambda_j \Sigma_f) = \frac{\sqrt{2}}{\pi} \frac{(-i)^l}{k} \int dr dr' \psi^*_\nu(r,R) \chi^*_\mu(R) \times \varphi^*_{\mu\nu}(r,R') Y_{\mu\nu}(r,R), \quad (20)$$

with $\Delta \nu = p_+ - p_0$, $\Delta M_j = M_{J+} - M_{J-}$, and the summation in Eq. (17) goes over all possible indices. Substituting Eq. (16) into Eq. (1), it is easy to verify that

$$\sigma = \sum_{\nu m} |C_{\nu m}|^2 \rho_{M_j M_{j+}}, \quad (21)$$

and

$$\beta_{2L} = \frac{4L+1}{\sigma} \sum_{\nu m} (-1)^m (2l+1)(2l'+1)$$

$$\times \rho_{M_j M_{j+}} C_{\nu m} (M_j M_{j+}) C_{\nu m}^* (M_j M_{j+})$$

$$\times \left(\begin{array}{ccc} m & -m & 0 \\
-2L & 0 & 0 \
0 & 0 & 0 \end{array} \right). \quad (22)$$

Furthermore, for the branching ratios of interest here, the constant implied in Eqs. (1) and (21) is unimportant and
will be suppressed. Equations (21) and (22) are also suitable for photoionization of symmetric top molecules except that $a_{N,K}$ of Eq. (17) becomes unity for both the intermediate and ionic states.

B. Parity selection rule

Equation (17) yields the general parity selection rule

$$\Delta N + \Delta p + l = \text{odd},$$

(23)

which has the same form as for diatomic molecules for Hund's case (b) coupling.\(^5\)-\(^8\) However, this selection rule is not particularly transparent since the parity indices $p,$ and $p_\perp$ are defined with respect to the $S(NM_KP_\perp)$ functions used to expand the asymmetric top wave functions [see Eq. (11)]. Equation (23) should be modified to reveal explicitly its dependence on the angular momentum changes $\Delta K_a$ and $\Delta K_c.$

Here we choose a left-handed coordinate system for the molecular internal $x,$ $y,$ and $z$ axes with the molecular $z$ axis as the symmetry axis. With the symmetry properties of the asymmetric top,\(^23\) it can be shown that $\Delta K_a$ is even (odd) when $\Delta N + \Delta p$ is even (odd), where $\eta$ is the principal axis lying along the molecular $x$ axis and $K_a$ is the projection of the total angular momentum along this axis. The parity selection rule of Eq. (23) then reduces to

$$\Delta K_\eta + l = \text{odd}.$$  

(24)

The selection rules also depend on which principal axis coincides with the molecular $z$ axis. With the properties of 3-$j$ symbols, Eq. (17) provides additional selection rules\(^23\)

$$\mu + \lambda = \left\{ \begin{array}{ll}
\Delta K_a, & \text{if } a//z// \text{ the symmetry axis} \\
\Delta K_{bo}, & \text{if } b//z// \text{ the symmetry axis} \\
\Delta K_c, & \text{if } c//z// \text{ the symmetry axis}
\end{array} \right.$$

(25)

To relate the selection rules of Eqs. (24) and (25), a relationship among $\Delta K_a,$ $\Delta K_{bo}$ and $\Delta K_c$ is essential. This relationship, which can be obtained from the symmetry properties of asymmetric top,\(^23\) is

$$\Delta K_a + \Delta K_c = \text{even (odd)} \leftrightarrow \Delta K_{bo} = \text{even (odd)}.$$  

(26)

For example, if the molecular axes $x,$ $y,$ and $z$ coincide with the $b,$ $c,$ and $a$ axes, respectively, the selection rules of Eqs. (24) and (25) become $\Delta K_a + l = \text{odd}$ and $\mu + \lambda = \Delta K_{bo}$ respectively. Determination of $\mu + \lambda$ now becomes a critical step in the application of these selection rules. Whereas Eqs. (24)-(26) are suitable for any nonlinear polyatomic molecule, $\mu + \lambda$ must be determined specifically for a given molecular symmetry.

To illustrate these selection rules, $3 + 1'$ REMPI via the $C_1^1 B_1 \ (3p_{a_1})$ Rydberg state of H\(_2\)O is taken as an example. The molecular $x,$ $y,$ and $z$ axes are chosen to coincide with the $a,$ $c,$ and $b$ axes, respectively, for H\(_2\)O and H\(_2\)O\(^+\). Therefore, the selection rules of Eqs. (24) and (25) become

$$\Delta K_a + l = \text{odd}$$  

(27)

and

$$\mu + \lambda = \Delta K_{bo}$$  

(28)

respectively. For the $C_{2v}$ symmetry of H\(_2\)O and H\(_2\)O\(^+\), the $x,$ $y,$ and $z$ components of the dipole moment operator belong to the $b_{2v},$ $b_{1v},$ and $a_{1v}$ irreducible representations, respectively. There are three corresponding dipole-allowed continuum channels $kb_2,$ $kb_1,$ and $ka_1$ for photoionization from the $3p_{a_1}$ orbital of the $C_1^1 B_1$ Rydberg state leading to the $X^2 B_1$ ground state of the ion. In this case, odd $\lambda$ and $\mu$ are associated with the $kb_2$ and $kb_1$ channels, whereas even $\lambda$ and $\mu$ are associated with the $ka_1$ channel. Therefore $\lambda + \mu$ is always even for all allowed transitions. Thus, from Eq. (28), we have $\Delta K_b = \text{even}$. Based on the relationship of Eq. (26), we have

$$\Delta K_a + \Delta K_c = \text{even}.$$  

(29)

Equations (27) and (29) show that only type $b$ transitions are allowed. These transitions with $\Delta K_a = \text{odd}$ and $\Delta K_c = \text{odd}$ are associated with even $l$ partial waves of the photoelectron matrix elements and those of $\Delta K_a = \text{even}$ and $\Delta K_c = \text{even}$ with even $l$ partial waves. However, type $a$ ($\Delta K_a = \text{even}$ and $\Delta K_c = \text{odd}$) and type $c$ ($\Delta K_a = \text{odd}$ and $\Delta K_c = \text{even}$) transitions are forbidden.

C. $(3 + 1')$ REMPI via the $C_1^1 B_1$ Rydberg state of H\(_2\)O

There are three dipole-allowed transition channels for photoionization of the $3p_{a_1}$ orbital of the $C_1^1 B_1$ Rydberg state. The corresponding multiplet-specific final-state wave functions $|\varphi, \xi_f\rangle$ of Eq. (5) are given by

$$\Psi(1B_1) = \frac{1}{\sqrt{2}} \left[ \left| (\text{core}) 1b_1ka_1 \right| - \left| (\text{core}) 1b_1ka_1 \right| \right],$$  

(30a)

$$\Psi(1A_1) = \frac{1}{\sqrt{2}} \left[ \left| (\text{core}) 1b_1kb_1 \right| - \left| (\text{core}) 1b_1kb_1 \right| \right],$$  

(30b)

and

$$\Psi(1A_2) = \frac{1}{\sqrt{2}} \left[ \left| (\text{core}) 1b_1kb_2 \right| - \left| (\text{core}) 1b_1kb_2 \right| \right],$$  

(30c)

where $(\text{core}) = 1a_{1v}^22a_{2v}^33a_{1v}^21b_{2v}^2.$ Within the frozen-core Hartree–Fock model for the final state, the photoelectron orbital $\phi_f$ can be shown to be a solution of the one-electron Schrödinger equation of the form\(^25\),\(^26\)

$$P(f + \sum_{i=\text{core}} (2J_i-K_i) + a_\sigma J_n + b_\sigma K_n - \epsilon)P|\phi_f\rangle = 0,$$  

(31)

where $J_i$ and $K_i$ are the Coulomb and exchange operators, respectively, and $P$ is a projection operator which enforces orthogonality of the continuum orbital to the occupied orbitals.\(^25\),\(^26\) The photoelectron kinetic energy is given by $\epsilon = \frac{1}{2}k^2.$ The one-electron operator $f$ in Eq. (31) is

$$f = \frac{-1}{2} \nabla_i^2 - \sum_{a} \frac{Z_a}{r_a},$$  

(32)

where $Z_a$ is a nuclear charge. Using the wave functions of Eq. (30), the coefficients $a_\sigma$ and $b_\sigma$ associated with $1b_1$ orbital assume the value of 1.
For the wave function of the $C^1B_1(1b_1 \rightarrow 3p_{a1})$ resonant state, we use the improved virtual orbital (IVO) method in which the core orbitals are taken to be those of the fully relaxed $^2B_1$ ion. The orbital basis used in these calculations consists of a (6s4p) contraction of the (10s6p) primitive Cartesian Gaussian functions of Dunning augmented by three $s$ ($\alpha=0.065, 0.016,$ and $0.004$), three $p$ ($\alpha=0.065, 0.012,$ and $0.003$), and four $d$ ($\alpha=1.322, 0.3916, 0.09,$ and $0.02$) functions on the oxygen atom. On the hydrogen, we use a (3s) contraction of the (4s) primitive Cartesian Gaussian functions of Dunning augmented by three $s$ ($\alpha=0.072, 0.018,$ and $0.0045$) and four $p$ ($\alpha=1.12, 0.1296, 0.03,$ and $0.006$) functions. With this basis and choice of wave functions, we obtain a total energy of $-75.745$ 462 a.u. for the $C^1B_1$ Rydberg state at the known equilibrium geometry ($R_{O-H}=1.8085$ a.u. and $\theta_{H-O-H}=104.5^\circ$). The single-center expansion of the $3p_{a1}$ orbital around the center of mass shows $12.97\%$, $77.96\%$, $8.65\%$, and $0.41\%$ $d$, $s$, $p$, and $f$ character, respectively.

To obtain the photoelectron orbital $\phi_3$, we have used an iterative procedure, based on the Schwinger variational principle, to solve the Lippmann–Schwinger equation associated with Eq. (31). This procedure begins by approximating the static-exchange potential of the relaxed ionic core by a separable form

$$U(r,r') = \sum_{ij} \langle r | U_{ij} | r' \rangle,$$

where the matrix $U$ is the inverse of the matrix with the elements $U_{ij} = \langle \alpha_i | U | \alpha_j \rangle$ and the $\alpha$'s are discrete basis functions such as Cartesian or spherical Gaussian functions. $U$ is twice the static-exchange potential in Eq. (31) with the long-term Coulomb potential removed. The Lippmann–Schwinger equation with this separable potential $U(r,r')$ can be readily solved and provides an approximate photoelectron orbital $\phi_3^{(0)}$. These $\phi_3^{(0)}$ can be iteratively improved to yield converged solutions to the Lippmann–Schwinger equation containing the full static-exchange potential. In this study, four iterations provided converged solutions of Eq. (31). The scattering basis sets used in the separable expansion of Eq. (33) are listed in Table I.

All matrix elements arising in the solution of the Lippmann–Schwinger equation and elsewhere were evaluated by using single-center expansions about the center of mass. For converged results, the maximum partial wave used in the expansions of bound orbitals, potentials, and photoelectron continuum orbital was seven. For the electron nuclear potential, 14 partial waves were used. Runs with larger partial wave expansions showed that our calculated cross sections are converged. The radial integration grid extended to 73 a.u. and contained 600 points. The integration step sizes ranged from 0.005 to 0.16 up to 9 a.u. and up to 0.32 a.u. beyond this point.

### III. RESULTS AND DISCUSSION

In Fig. 1, we show the total cross sections and the asymmetry parameter $\beta$ as a function of photon energy for photoionization of the $C^1B_1(3p_{a1})$ Rydberg state of H$_2$O leading to the $X^2B_1$ ionic ground state. The partial cross sections associated with the $3p_{a1} \rightarrow ka_1$, $3p_{a1} \rightarrow kb_1$, and $3p_{a1} \rightarrow kb_2$ channels are also shown in Fig. 1(a). The total cross section and partial cross sections of the $ka_1$ and $kb_1$ channels decrease sharply near threshold. A minimum

### TABLE I. Basis sets used in the separable potential of Eq. (33).

<table>
<thead>
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<th>Symmetry</th>
<th>Center</th>
<th>Cartesian Gaussian function*</th>
<th>Exponents ($\alpha$)</th>
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<td>$a_1$</td>
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<td>$s$</td>
<td>16.0, 8.0, 4.0, 2.0, 1.0, 0.5, 0.25, 0.1</td>
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<td>$yx$</td>
<td>1.0, 0.1</td>
</tr>
<tr>
<td>$b_2$</td>
<td>O</td>
<td>$x$</td>
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<tr>
<td></td>
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<td>$xz$</td>
<td>2.0, 1.0, 0.5, 0.1</td>
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<tr>
<td></td>
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<td>$x^2$</td>
<td>1.0, 0.5, 0.1</td>
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<tr>
<td>$H$</td>
<td>s</td>
<td></td>
<td>2.0, 1.0, 0.5, 0.1</td>
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<tr>
<td></td>
<td></td>
<td>$x$</td>
<td>2.0, 1.0, 0.5, 0.1</td>
</tr>
</tbody>
</table>

*Defined as $\phi^{(lmnA)}(r) = \mathcal{N}(x - A_3)(y - A_2)(z - A_1)^\alpha \exp(-\alpha |r - A|^2)$ with $\mathcal{N}$ a normalization constant.
is clearly seen in the asymmetry parameter [Fig. 1(b)] around 4 eV. To identify the physical origin of this minimum, Fig. 2 shows the magnitude \( |D_\mu^{-1}| \) of the incoming-wave normalized partial wave dipole amplitude as a function of kinetic energy for the (a) \( 3p\alpha_1 \rightarrow ka_1 \); (b) \( 3p\alpha_1 \rightarrow kb_1 \); and (c) \( 3p\alpha_1 \rightarrow kb_2 \) channels for the \( C^1\text{B}_1 \) Rydberg state. \( (\lambda,\alpha) \) denotes each component of \( |D_\mu^{-1}| \). The insets show the principal-value dipole amplitude \( D_\alpha \) for the \( l=2 \) component.

Note also that \( (J,\lambda) \) is used to label components of \( |D_\mu^{-1}| \) in Fig. 2. Minima are clearly seen in the (2,0) component of the \( ka_1 \) channel and (2,1) component of the \( kb_1 \) channel. Examining the principal-value dipole amplitude \( D_\mu^{-1} \) (standing-wave normalized) shown in the insets of Figs. 2(a) and 2(b), a sign change is seen in the \( d \) wave of the \( ka_1(\lambda = 0) \) and \( kb_1(\lambda = 1) \) channels. This indicates the presence of Cooper minima which are responsible for the minimum in the asymmetry parameter \( \beta \) of Fig. 1(b). No minimum is seen in the cross sections [Fig. 1(a)], since other components such as (2,2) in the \( ka_1 \) channel and the (3,1) component in the \( kb_1 \) channel are predominant in the vicinity of Cooper minima in \( |D_\mu^{-1}| \). These Cooper minima are essentially similar to those found in photoionization of atoms, ground state of molecules, and Rydberg state of diatomic molecules, except that these minima also depend on \( \lambda \). Cooper minima have been shown to have pronounced effects on photoelectron spectra for photoionization of Rydberg states of diatomic molecules. It is clearly of interest to see what role these \( \lambda \)-dependent Cooper minima may play in the rotationally resolved photoionization dynamics.

Figure 3 shows the calculated ion rotational distributions resulting from (3 + 1) REMPI via the \( 3\Sigma^+ \) [Fig. 3(a)] and \( 3\Sigma^+ \) [Fig. 3(b)] rotational levels of the \( C^1\text{B}_1 \) Rydberg state. Here the rotational level is denoted by \( N_{KB} \). Both rotational levels originate from the \( 0_{00} \) rotational level of para water via three-photon excitation, i.e., the \( T(0) \) rotational branch. Since the rotational line strength \( B \) of Eq. (2) is just an overall constant here, the alignment of the \( 3\Sigma^+ \) and \( 3\Sigma^+ \) rotational levels can be determined individually from the \( 3-j \) symbols of Eq. (2). The photoelectron kinetic energy is about 0.72 eV. The calculated spectra are convoluted with a Gaussian detection function having a full width at half-maximum (FWHM) of 1.5 meV. Dominant rotational levels in the ion spectra are labeled. Note that both rotational levels of the \( C^1\text{B}_1 \) state have the same \( N \) quantum number and alignment \( \mu \). Interesting features of these ion rotational distributions include: (i) strong \( \Delta K_a = \text{odd} \) and \( \Delta K_c = \text{odd} \) transitions expected on the basis of the dominant (even) partial-wave components of the photoelectron matrix element, arising from the \( p \) character of the \( 3p\alpha_1 \) orbital of the \( C^1\text{B}_1 \) state; (ii) strong
Angular momentum changes are different for different rotational levels of the $C^1B_1$ Rydberg state. The photoelectron kinetic energy is about 0.72 eV. Each transition is convoluted with a Gaussian detection function with a FWHM of 1.5 meV. The highest intensity has been normalized to unity.

The presence of these unexpected waves reflects angular momentum coupling induced by the strongly anisotropic molecular ion potential. This behavior is similar to that responsible for type $a$ transitions observed in the photoionization of ground state $H_2O$.^{1,13}

To illustrate the angular momentum composition of these photoelectron continua, Fig. 4 shows the photoelectron angular distributions associated with the ion spectra of Fig. 3. Terms up to $\beta_6$ of Eq. (1) are included. In these plots, we assume $\beta_0=1$ and $\theta=0^\circ$. Evidence of higher partial wave contributions are seen clearly especially for transitions with $\Delta N=-2$. Interface between partial waves of the photoelectron matrix element and between different ionization channels is important since these angular distributions are admixtures of various angular momentum components. These photoelectron angular distributions reflect the angular composition of the photoelectron upon ionization. Also, according to the selection rules of Eqs. (27)–(29), transitions with $\Delta K_a=\text{even}$ and $\Delta K_c=\text{odd}$ arise from odd partial waves and those with $\Delta K_a=\text{odd}$ and $\Delta K_c=\text{even}$ from even continuum waves.

Figures 5 and 6 show the calculated ion rotational distributions and associated photoelectron angular distributions, respectively, for $(3+1)$ REMPI via the (a) $4_{13}$ and (b) $4_{31}$ rotational levels of the $C^1B_1$ Rydberg state. Both rotational levels are populated by three-photon excitation from the ground rotational level $1_{01}$ of ortho water, i.e., the $T(1)$ rotational line. The calculated spectra are convoluted with a Gaussian detection function with a FWHM of 1.5 meV. Important features associated with photoionization of para water (Figs. 3 and 4) are also seen here except that the angular momentum changes ($\Delta N$, $\Delta K_a$, and $\Delta K_c$) as-
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FIG. 5. The same as in Fig. 3 except for (3 + 1) REMPI via the (a) 413 and (b) 431 rotational levels of the C state.

FIG. 6. Calculated photoelectron angular distributions for the rotational levels of Fig. 5. θ=0° is vertical.

FIG. 7. Calculated ionic rotational branching ratios resulting from (3 + 1') REMPI via the 413 rotational level of the C 1B1 Rydberg state at (a) 0.05; (b) 1.2; and (c) 3 eV of kinetic energies. The other notation is the same as in Fig. 3.

associated with the most intense peaks of Figs. 3(a) (312→321) and 3(b) (330→441) and Figs. 5(a) (413→322) and 5(b) (431→422) are different. It is interesting to note that the difference between the spectral profiles of Figs. 5(a) and 5(b) arises from the changes of the values of K_a and K_c in the C state.

Unexpected ΔN=even (especially ΔN=0) transitions have been observed in the ion spectra of NO, OH, and NH diatomic molecules in which Cooper minima play an important role. 10,11,20,21 These anomalous spectra arise primarily from the formation of Cooper minima in the d(l=2) continuum wave. The depletion of the d' wave contribution to the photoelectron matrix element in the vicinity of Cooper minima subsequently leads to an enhancement of the relative importance of the odd waves which make the dominant contributions to these unexpected ΔN=0 transitions. Cooper minima are also predicted to occur here (see Fig. 2). However, Figs. 3 and 5 do not show as strong an influence of these Cooper minima on the ion distributions as was seen for diatomic molecules, 10,11,20,21 even though the photoelectron kinetic energies lie in the vicinity of these Cooper minima. The main reason is due to the significant contributions from other even wave components such as the (2,2) component in the ka1 channel and (2,1) in the kb2 channel. In Fig. 7, we show the photoelectron spectra for (3 + 1') REMPI via the 413 [T(1) rotational branch] rotational level of the C 1B1 Rydberg state at several kinetic energies. The range of kinetic energies is chosen to span both Cooper minima (see Fig. 2). The ion rotational branching ratios depend on photoelectron kinetic energy due to the changes in the (l,l) partial wave composition of the matrix element D_{l0}^{l-l} around the Cooper minima. The effect of these Cooper minima are seen clearly from the photoelectron angular distributions shown in Fig. 8. Only...
selected ionic rotational levels are shown. These Cooper minima at low kinetic energies may be particularly useful in exploring the ionization dynamics of excited states of H$_2$O.

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