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Cross sections and photoelectron asymmetry parameters for photoionization of H$_2$O

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The iterative Schwinger variational method is used to obtain cross sections and photoelectron asymmetry parameters for photoionization of the three outermost valence orbitals (1b$_1$, 3a$_1$, and 1b$_2$) of H$_2$O for photon energies from near threshold to 50 eV. A comparison of these calculated results with available experimental data is encouraging.

I. INTRODUCTION

The increasing availability of tunable radiation from synchrotron sources continues to provide new and interesting data on the photoionization cross sections and photoelectron angular distributions for a wide range of diatomic and polyatomic molecules. Such experimental studies have stimulated the development of several theoretical approaches for studying these cross sections and photoelectron asymmetry parameters and for understanding their dynamical content. These approaches include the continuum-multiple-scattering method (CMM) which assumes a model potential so as to simplify the solution of the scattering equations, the Stieltjes–Tchebycheff moment theory (STMT) method which extracts cross sections from the results of diagonalization of the Hamiltonian in a discrete basis thereby avoiding the explicit construction of molecular continuum orbitals, and those more elaborate procedures which use single-center expansions and other numerical techniques to solve the photoelectron equations with a full nonspherical, nonlocal molecular ion potential.

In this paper we present the results of applications of one of these numerical techniques—the iterative Schwinger variational method—to obtain the cross sections and photoelectron asymmetry parameters for photoionization of the three outermost valence orbitals of H$_2$O. This procedure, which is based on an iterative extension of the original Schwinger variational principle, has been extensively used to study photoionization cross sections for diatomic and linear polyatomic molecules at the static-exchange (Hartree–Fock), fixed-nuclei level of approximation. More recently, it has also been applied to the nonlinear polyatomic molecule CH$_4$ (Ref. 17). This method utilizes discrete basis functions, e.g., Cartesian Gaussians, which are known to represent wave functions in the “near-molecular” region very effectively, in an iterative procedure for obtaining converged solutions of the Lippmann–Schwinger equation for the photoelectron wave function. These static-exchange photoelectron wave functions provide accurate estimates of single-particle features in the cross sections such as those arising from shape resonances, and furthermore serve as a starting point in quantitative studies of multielectron aspects of photoelectron spectra such as autoionization.

An outline of the paper is as follows. In the next section we discuss some essential features of the extension of our method to nonlinear (C$_2$H$_6$) molecular targets. Many of these were not included, for sake of brevity, in our earlier paper on CH$_4$ (Ref. 17). In Sec. III we discuss some numerical aspects of our calculations. In Sec. IV we present our calculated cross sections and asymmetry parameters along with comparisons with other available theoretical results and experimental data.

II. METHOD

The essential quantities in the calculation of molecular photoionization cross section are the length and velocity forms of the dipole transition matrix elements

$$I_{k,h}^L = (k)^{1/2} \langle \Psi_l | \vec{r} \cdot \hat{n} | \Psi_k^{(-)} \rangle$$

and

$$I_{k,h}^V = \frac{(k)^{1/2}}{E} \langle \Psi_l | \vec{k} \cdot \hat{n} | \Psi_k^{(-)} \rangle ,$$

respectively. In Eqs. (1) $\Psi_l$ is the target ground state wave function, $\Psi_k^{(-)}$ is the final state wave function for the system (ion plus photoelectron), $E$ is the photon energy, $k$ is the photoelectron momentum, and $\hat{n}$ is a unit vector in the direction of polarization of the radiation. In these studies we use a Hartree–Fock wave function for $\Psi_l$, and for $\Psi_k^{(-)}$ we assume the frozen-core Hartree–Fock approximation. In this approximation the final state is described by a single electronic configuration in which the ionic core orbitals are constrained to be identical to those of the initial ground state and the photoelectron orbital is a solution of the one-electron Schrödinger equation

$$\left[ -\frac{1}{2} \nabla^2 + V_{N=1} (\vec{r}, \vec{R}) + \frac{k^2}{2} \right] \phi_\xi (\vec{r}) = 0 .$$

In Eq. (2), $V_{N=1}$ is the static-exchange potential of the molecular ion and $\phi_\xi (\vec{r})$ satisfies the appropriate boundary conditions. To proceed, we work with the Lippmann–
Schwinger equation, the integral equation form of Eq. (2),
\[ \phi^{(-)}_{\mathbf{k}}(r) = \Phi_{\mathbf{k}}^{(+)} + G^{(+)} V \phi^{(-)}_{\mathbf{k}}(r), \tag{3} \]
where \( V = V_N + (1/r) \), i.e., the short-range part of \( V_{N-1} \), \( \Phi^{(+)}_{\mathbf{k}} \) is the pure Coulomb scattering function, and \( G^{(+)} \) is the incoming-wave Coulomb Green's function. The incoming-wave solution \( \phi^{(-)}_{\mathbf{k}} \) correctly incorporates the boundary condition for photoionization.

To take advantage of the possible symmetry of a nonlinear target, we work with symmetry-adapted functions, as incoming-wave solution where boundary condition for photoionization. Schwinger equation, the integral equation form of Eq. (2), can be written in terms of the spherical harmonics as
\[ X_{lm}(\hat{r}) = \sum_{\mathbf{m}} b_{lm} \phi_{lm}(\hat{r}), \tag{4} \]
where \( \rho \) is one of the irreducible representations (IR) of the molecular point group, \( \mu \) is a component of this representation, and \( h \) distinguishes between different bases for the same IR corresponding to the same value of \( L \). The functions \( X_{lm}(\hat{r}) \) satisfy well-known orthogonality conditions which lead to useful relations between the coefficients \( b_{lm} \). Details can be found in Burke et al. For the \( C_{2v} \) point group of interest here, tables of these coefficients are given in Ref. 19.

Expansion of the photoelectron wave function in these symmetry-adapted functions
\[ \phi^{(-)}_{\mathbf{k}}(\hat{r}) = \left[ \frac{2}{\pi} \right]^{1/2} \sum_{\mathbf{m}} \hat{\mathbf{m}} \phi^{(-)\mathbf{m}}_{\mathbf{k}}(\hat{k}) X_{\mathbf{m}}^{\mathbf{k}}(\hat{r}), \tag{5} \]
and use of this expansion in the bilinear form of the Schwinger variational expression for the \( T \) matrix, i.e.,
\[ \tilde{T}_{\mathbf{h},\mathbf{k}}^{(-)} = \langle \Phi^{(+)}_{\mathbf{h}}(r)|V|\phi^{(-)\mathbf{m}}_{\mathbf{k}}(r) \rangle + \langle \Phi^{(+)}_{\mathbf{h}}(r)|V|\phi^{(+)}_{\mathbf{k}}(r) \rangle - \langle \Phi^{(+)}_{\mathbf{k}}(r)|V|\phi^{(-)\mathbf{m}}_{\mathbf{h}}(r) \rangle - \langle \Phi^{(+)}_{\mathbf{k}}(r)|V|\phi^{(+)}_{\mathbf{h}}(r) \rangle, \tag{6} \]
with a trial function \( \phi_{\mathbf{k}}^{(+)} \), gives the partial-wave variational expression for \( T \);
\[ \tilde{T}_{\mathbf{h},\mathbf{k}}^{(+)} = \langle \Phi^{(+)}_{\mathbf{h}}(r)|V|\phi^{(+\mathbf{m}}_{\mathbf{k}}(r) \rangle + \langle \Phi^{(+)}_{\mathbf{h}}(r)|V|\phi^{(+\mathbf{m}}_{\mathbf{k}}(r) \rangle - \langle \Phi^{(+)}_{\mathbf{k}}(r)|V|\phi^{(+\mathbf{m}}_{\mathbf{h}}(r) \rangle - \langle \Phi^{(+)}_{\mathbf{k}}(r)|V|\phi^{(+\mathbf{m}}_{\mathbf{h}}(r) \rangle. \tag{7} \]
In going from Eq. (6) to Eq. (7) we assume a partial-wave expansion of \( \Phi_{\mathbf{k}}^{(+)} \) (Ref. 8). Expansion of the partial-wave scattering function \( \phi^{(+\mathbf{m}}_{\mathbf{h}}(r) \) in a basis \( \alpha_{\mathbf{t}} \),
\[ \hat{\mathbf{m}} = \frac{3}{5} \sum_{\rho \mu 
abla \mu} \frac{1}{(1002)} \sum_{\mu 
abla \mu} \sum_{\mu 
abla \mu} (11 - m_{\mathbf{t}} m_{\mathbf{e}})|2M'\rangle (l'10020) (l'1 - m_{\mathbf{t}} m_{\mathbf{e}})|2 - M'\rangle, \tag{13} \]
where \( I_{\rho 
abla \mu}^{(L,\nu)} \) are the partial-wave components of the dynamical coefficients \( I_{\rho 
abla \mu}^{(L,\nu)} \),
\[ I_{\rho 
abla \mu}^{(L,\nu)} = \left( \frac{4\pi}{3} \right)^{1/2} \sum_{\mu 
abla \mu} I_{\rho 
abla \mu}^{(L,\nu)} X_{lm}(\hat{k}) X_{lm}^{-1}(\hat{h}), \tag{14} \]
with \( \rho \otimes \rho \otimes \rho \otimes \rho = I_{\mathbf{t}} \), the totally symmetric IR of the symmetry group of the molecule. In Eq. (11), \( \alpha_{\mathbf{t}}^{(L,\nu)} \) and \( \beta_{\mathbf{t}}^{(L,\nu)} \) are the integral cross section and the photoelectron asymmetry parameter, respectively. In Eq. (12) \( c \) is the speed of light, while in Eq. (13) \( (l, l_{\mathbf{e}} m_{\mathbf{e}}, l_{\mathbf{t}} m_{\mathbf{t}}) \) is the usual Clebsch-Gordan coefficient.
III. COMPUTATIONAL DETAILS

The photoelectron wave functions are obtained using a static-exchange potential for the $\text{H}_2\text{O}^+$ ion constructed from the SCF calculation of the neutral ground state. For this SCF calculation we used the standard $[4s3p2s]$ contracted Gaussian basis of Dunning and Hay, augmented by two uncontracted $d$ functions with exponents 1.0484 and 0.3105 on the oxygen nucleus so as to better describe the dipole moment. At the experimental equilibrium geometry of $R(\text{O}-\text{H}) = 1.81$ a.u. and $\theta(\text{O}-\text{H}=\text{O}) = 104.5^\circ$, this basis gives an SCF energy of $-76.015$ a.u. and a dipole moment of 1.964 D. This calculated value of the dipole moment compares well with the experimental value of 1.864 D. The orbital energies of this SCF calculation are $-20.558$, $-1.343$, $-0.715$, $-0.574$, and $-0.501$ a.u. for the $1a_1$, $2a_1$, $1b_2$, $3a_1$, and $1b_1$ orbitals, respectively. All matrix elements arising in these calculations were evaluated using a single-center expansion procedure such as in Eq. (5). For $C_{2v}$, the partial-wave expansions ($l$) run over all integers starting from 0 ($a_1$), 1 ($b_1$ and $b_2$), and 2 ($a_2$). The $h$ values must be even ($h > 0$ for $a_1$ and $h = 0$ for $a_2$) or odd for $b_1$ and $b_2$ ($h > 0$). Furthermore, $h < l$. All angular momentum expansions were truncated at $l = 7$ and all allowed values of $h$, for a given $l$, were retained. These expansions give orbital normalization integrals better than 0.99 for all bound orbitals. Increasing the maximum value of $l$ in these expansions did not lead to any significant change in the resulting cross sections. The basis sets used in the solution of Eq. (10) and in subsequent steps in the iterative procedure are given in Table I. All cross sections shown below were converged within three iterations.

IV. RESULTS AND DISCUSSION

Figures 1 to 3 show our calculated photoionization cross sections and photoelectron angular distributions for ionization of water leading to the $^2B_1(1b_1^{-1})$, $^2A_1(3a_2^{-1})$, and $^2B_2(1b_2^{-1})$ ionic states. The photon energies shown in these figures assume the experimental values of 12.61, 14.73, and 18.55 eV for the vertical ionization potentials of the $1b_1$, $3a_1$, and $1b_2$ levels, respectively.

Table I. Basis set used in the expansion of Eq. (10).

<table>
<thead>
<tr>
<th>Continuum symmetry</th>
<th>Center</th>
<th>Gaussian function</th>
<th>Exponents $(a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>$s$</td>
<td>$16.0,8.0,4.0,2.0,1.0,0.5$</td>
<td>$x$</td>
</tr>
<tr>
<td>$b_1$</td>
<td>$y$</td>
<td>$2.0,1.0,0.5$</td>
<td>$s$, $x$</td>
</tr>
<tr>
<td>$b_2$</td>
<td>$z$</td>
<td>$8.0,4.0,2.0,1.0,0.5$</td>
<td>$y$</td>
</tr>
<tr>
<td>$a_2$</td>
<td>$y$</td>
<td>$2.0,1.0,0.5$</td>
<td>$z$, $x$</td>
</tr>
</tbody>
</table>

*Defined as $\rho^{a l m n q}(r) = N(x - A_x)(y - A_y)^m(z - A_z)^n \times \exp(-\alpha|\vec{r} - \vec{A}|^2)$.

Figure 1(a) shows the calculated $1b_1$ photoionization cross sections along with those of Cacelli et al., and some selected experimental results obtained from $(e,2e)$ (Refs. 26 and 27) and synchrotron radiation studies. The agreement between the present results using converged solutions of Eq. (3) obtained with the iterative procedure outlined above and those of Cacelli et al., obtained via a $K$-matrix technique with an $L^2$ basis and a large number of special oscillating functions, is very encouraging. This is particularly so for the dipole–velocity results. Furthermore, both our cross sections and those of Cacelli et al. calculated with the velocity form of the dipole operator are in better agreement with the experimental data than those obtained with the length form, particularly above 20 eV. Differences as seen here between the dipole–length and velocity results are known to be generally due to neglect of electron correlation in the wave functions. Our calculated cross sections also show the same strong increase just above threshold as seen experimentally. However, they are significantly lower than the measured values of Brion and Carnovale below about 19 eV, where structure due to autoionizing states leading to higher thresholds can be expected. At the present level our formulation provides only the direct contribution to the photoionization cross sections and does not include any effects arising from autoionization. Also shown in Fig. 1(a) are the arithmetic averages of the dipole length and velocity cross sections for...
photoionization into the allowed continua, i.e., $1b_1 - ka_1$, $kb_1$, and $ka_2$. These arithmetic averages are shown solely for convenience and clarity in the figures. The near equivalence of the $kb_1$ and $ka_2$ cross sections has been noted previously and attributed to the atomic-like $p - d$ character of these transitions.

In Fig. 1(b) we compare our photoelectron asymmetry parameters (velocity) with the corresponding results of Cacelli et al. and the earlier Banna et al. Our calculated dipole-length and velocity photoelectron asymmetry parameters, as well as those of Cacelli et al. are essentially equal. Agreement between the calculated and experimental asymmetry parameters is, in general, good. However, the structure seen in the experimental values below 30 eV and which may be due to autoionization is not reproduced by the calculations.

Figure 2(a) shows our calculated cross sections for photoionization of the $3a_1$ orbital along with the results of Cacelli et al. and the experimental synchrotron data of Ref. 28. The results of similar calculations for photoionization of the $1b_2$ orbital are shown in Figs. 3(a) and 3(b). Below 25 eV the calculated cross sections, including those of Cacelli et al., are significantly larger and rise more steeply than the experimental data. Possible reasons for these differences in this region are not immediately obvious. In Fig. 3(b) we compare our photoelectron asymmetry parameters with the experimental data. The agreement between the calculated and measured photoelectron asymmetry parameters at low energies is particularly encouraging.

ACKNOWLEDGMENTS

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