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Electronic excitation of H_2O by low-energy electron impact

H. P. Pritchard and V. McKoy
Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

M. A. P. Lima
Instituto de Física "Gleb Wataghin," Universidad Estadual de Campinas,
Caixa Postal 6165, 13081 Campinas, São Paulo, Brazil

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Cross sections for electronic excitation of H_2O by low-energy electrons have been studied using the Schwinger multichannel method. Differential and integral cross sections for excitation of the $(3a_1 \rightarrow 3sa_1)\,{}^3A_1$ dissociative state are reported for impact energies of 12, 15, and 20 eV. A comparison of the calculated integral cross sections with emission measurements for OH $(A\,{}^2\Sigma^+)$ produced via dissociative electron-impact excitation of H_2O in this energy range is encouraging.

I. INTRODUCTION

Electronic excitation of water by electron impact and the dissociation dynamics subsequent to such excitations are of considerable interest in studies of radiation chemistry and physics and space sciences.[1-3] However, although there have been several experimental studies of the cross sections for elastic scattering, as well as for rotational and vibrational excitation of water by low-energy electrons,[4,5] relatively little cross-section data are available for electronic excitation of this molecule. Available cross sections for various excitation processes have been reviewed by Trajmar, Register, and Chutjian,[6] and more recently by Hayashi[7] and Shimamura.[8] Electron-impact excitation at low scattering angles and at kinetic energies between 30 and 60 eV has been studied by Skerbele, Dillon, and Lassettre.[9] Sanche and Schulz[10] have also investigated resonances associated with excitation of the highest occupied orbital $(1b_1)$ of the water molecule. Trajmar *et al.* have measured relative differential cross sections for several singlet and triplet states at 15-, 20-, and 53-eV impact energies in the 0°–90° angular range.[11] The electron scattering spectrum of water has also been interpreted by Claydon, Segal, and Taylor on the basis of semiempirical electronic structure calculations of the molecule and its anion.[12]

Ab initio studies of electronic excitation of molecules by low-energy electrons have generally been limited to diatomic targets.[13-17] For example, the Schwinger multichannel (SMC) method has been used to study the electronic excitation of H_2, N_2, and CO. This method[18] is a multichannel extension of Schwinger's original variational principle[19] which preserves the important feature of the original Schwinger principle of allowing for a completely L^2 expansion of the scattering wave function. Furthermore, if a Cartesian Gaussian basis is chosen for this expansion, all matrix elements arising in the variational expression, with one important exception, can be evaluated analytically for a general polyatomic target. This feature can obviously be useful in practical applications of the method.

In this Rapid Communication, we report the first results of applications of the SMC method to obtain cross sections for electronic excitation of a polyatomic target. The electronic transition of interest here is the triplet excitation of the $3a_1$ orbital to the $3sa_1$ Rydberg level. This excitation is dissociative, its principal products being OH $(A\,{}^2\Sigma^+)$ and ground-state H atoms. These dissociative products, as well as those arising from the $\tilde{A}\,{}^{1,3}B_1$ excited states, have been studied via fluorescence measurements, laser-induced fluorescence, and mass spectrometry.[20-24] For electron-impact excitation of the $\tilde{B}\,{}^{1,3}A_1$ state, in particular, non-Boltzman rotational distributions of product OH have been observed. These rotational distributions have been interpreted as arising from dissociation via both singlet and triplet excited states of the molecule.[21,23] Such emission measurements only provide indirect evidence of cross sections for excitation of the ground state. Furthermore, their interpretation in terms of excitation cross sections for specific states can be ambiguous due to cascading and other complicating effects. However, they are useful in indicating the dependence of the singlet and triplet contributions to the cross section on impact energy through a deconvolution of the measured fluorescence excitation function.[21]

In the following, we discuss some of the computational aspects of the study, followed by comparison of our results with available data including unnormalized emission cross sections of Becker, Stompf, and Schulz.[21]

II. PROCEDURE

Details of both the formulation and application of the SMC method have been given elsewhere[16-18] and need not be repeated here. The present calculations were carried out with essentially the same procedure used in previous studies of elastic electron scattering by the water molecule.[25] Here, however, the principal value, as well as residue contributions to the matrix elements of the $VG_P^{(+)}V$ term arising in the variational expression are evaluated by numerical quadrature.[26] This approach has proven to be more reliable than earlier methods which relied on an insertion basis of L^2 functions to evaluate these principal-value terms.[26]

These calculations were carried out at the two-state level in the fixed-nuclei approximation. The experimental molecular geometry was assumed.[25] The target and scattering wave functions were expanded in the Cartesian Gaussian basis shown in Table I. In our previous studies of H_2O, uncontracted basis sets were used to provide greater flexibility in the insertion basis needed in evaluating the $VG_P^{(+)}V$ term. Such large, uncontracted basis sets are not essential here, since the entire $VG_P^{(+)}V$ term is evaluated numerically. The contraction coefficients are those of Dunning.[27] This basis gives a ground-state Hartree-Fock energy of -76.0524 a.u. and a dipole moment of 1.98 D. The experimental value is 1.86. The excited-state wave function was obtained in the improved-virtual-orbital (IVO) approximation.[28] This approximation gives an excitation energy of 10.28 eV for the $(3a_1 \rightarrow 3sa_1)$ triplet transition of interest. If the IVO orbital energy is used along with the experimental value of the ionization potential of the $3a_1$ orbital, a vertical transition energy of 9.14 eV is obtained. Goddard and Hunt[28] reported a value of 9.04 eV for the excitation energy for this transition. This compares with 9.34 eV for the reported best value.[29] In this study, the 10.28-eV threshold was used. The expectation values of $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ for the $3sa_1$ orbital used here are $4.350a_0^2$, $6.660a_0^2$, and $7.215a_0^2$, respectively. In their work on water,[28] Goddard and Hunt found these expectation values to be $4.280a_0^2$, $6.982a_0^2$, and $7.624a_0^2$.

Finally, the scattering amplitudes were calculated in the body frame, expanded in spherical harmonics up to $l = 7$, and subsequently transformed to the laboratory frame. In this study, polarization effects were neglected.

TABLE I. Basis sets used in the expansion of Eq. (10).

Continuum symmetry	Center	Cartesian Gaussian function[a]	Exponents (α)
a_1	O	s	16.0, 8.0, 4.0, 2.0, 1.0, 0.5
		z	4.0, 2.0, 1.0, 0.5
		x^2	1.0, 0.5
		y^2	1.0, 0.5
		z^2	1.0, 0.5
	H	s	2.0, 1.0, 0.5
b_1	O	y	8.0, 4.0, 2.0, 1.0, 0.5
		yz	2.0, 1.0, 0.5, 0.1
b_2	O	x	8.0, 4.0, 2.0, 1.0, 0.5
		xz	2.0, 1.0, 0.5, 0.1
	H	s	2.0, 1.0, 0.5
a_2	O	xy	4.0, 2.0, 1.0, 0.5, 0.1

[a] Cartesian Gaussian basis functions are defined as $\phi^{\alpha,l,m,nA}(\mathbf{r}) = N(x-A_x)^l(y-A_y)^m(z-A_z)^n\exp(-\alpha|\mathbf{r}-\mathbf{A}|^2)$, and are centered on the nuclei.

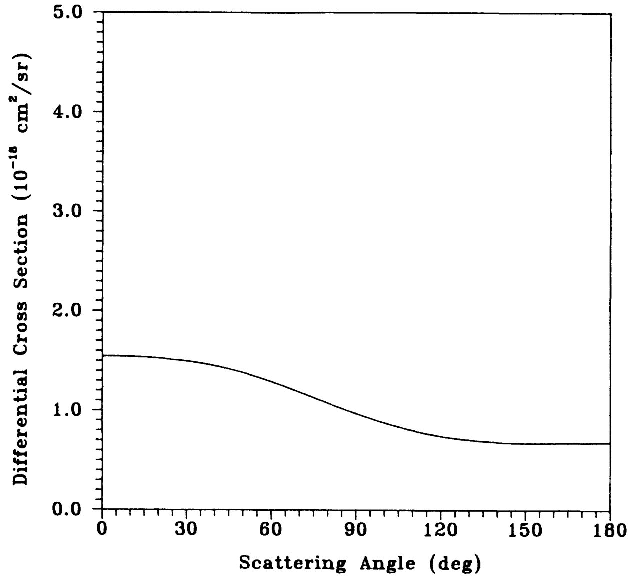

FIG. 1. Inelastic differential cross section for electron-impact excitation of $\tilde{X}\,^1A_1 \rightarrow (3a_1 \rightarrow 3a_1)\,^3A_1$ transition in H_2O at 12 eV.

III. RESULTS AND DISCUSSION

Although not reported here, our calculated elastic differential cross sections give values of 9.1, 8.4, and 7.1×10^{-16} cm^2 for the momentum transfer cross section at impact energies of 12, 15, and 20 eV, respectively. These can be compared with the recommended values of 9.2, 8.7, and 7.6×10^{-16} cm^2 of Hayashi[7] at these energies. Our inelastic differential cross sections at 12, 15, and 20 eV incident electron energies are shown in Figs. 1, 2, and 3, respectively. No measured differential cross sec-

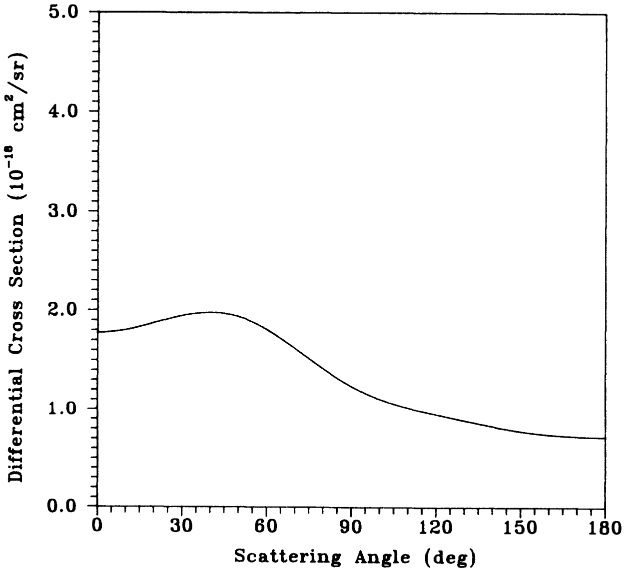

FIG. 2. Inelastic differential cross section for electron-impact excitation of the $\tilde{X}\,^1A_1 \rightarrow (3a_1 \rightarrow 3sa_1)\,^3A_1$ transition in H_2O at 15 eV.

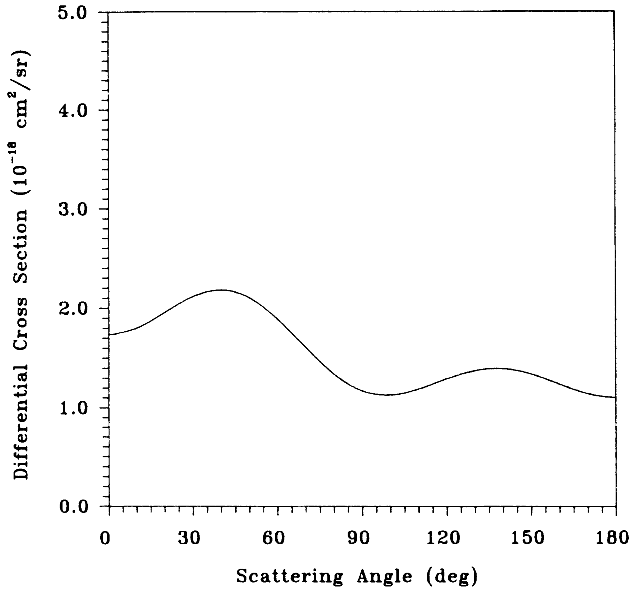

FIG. 3. Inelastic differential cross section for electron-impact excitation of the $\tilde{X}\,{}^1A_1 \rightarrow (3a_1 \rightarrow 3sa_1)\,{}^3A_1$ transition in H_2O at 20 eV.

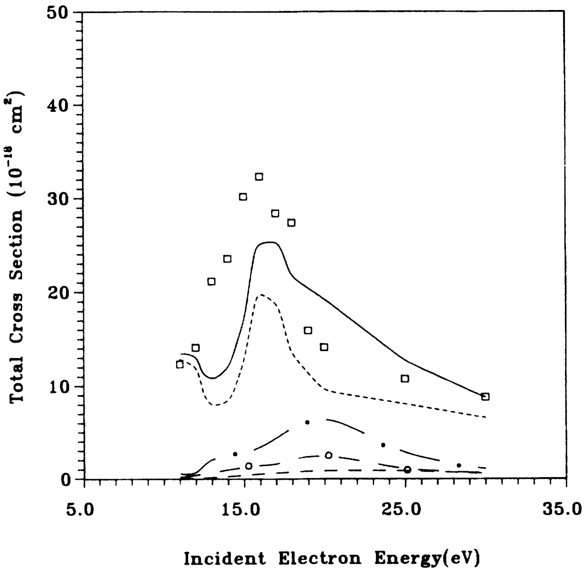

FIG. 4. Integral cross section for electron-impact excitation of the $\tilde{X}\,{}^1A_1 \rightarrow (3a_1 \rightarrow 3sa_1)\,{}^3A_1$ transition in H_2O: ——, total calculated cross section; ---, the ${}^2A_1$ component of the cross section; -○-, the ${}^2B_2$ component; -●-, the ${}^2B_1$ component; ---, the ${}^2A_2$ component. (□) relative emission measurements of Ref. 21 normalized to calculated cross sections at 30 eV. Note that the threshold assumed in the calculated cross sections is 10.24 eV. The threshold for dissociative electron-impact excitation leading to OH emission in the measurements of Ref. 21 is about 9.3 eV. See text for further discussion.

tions are available with which to directly compare these results. It is worth noting, however, that the 9.81-eV energy-loss feature observed by Trajmar, Williams, and Kupperman[11] and ascribed to a triplet excitation, exhibits qualitatively very similar behavior to our results at 20 eV over the scattering angles reported, 0°-90°. The calculated integral cross section for this excitation is given in Fig. 4, along with the contributions from the ${}^2A_1$, ${}^2B_1$, ${}^2B_2$, and ${}^2A_2$ symmetry components of the scattering wave function. Such symmetry contributions to the cross sections can provide useful insight into the underlying dynamics of the excitation.

In ${}^2A_1$ symmetry, the s-wave contribution to the scattering amplitudes decreases rapidly with increasing incident electron energy. The only other significant terms in the expansion of this symmetry's contribution to the scattering amplitude are the $|m|=1$ terms. At the peak in the cross section observed at 17 eV, the ${}^2A_1$ cross section consists almost entirely of this same component. The $|m|=2$ and $|m|=3$ partial-wave contributions are small at all energies of interest in this study. The ${}^2B_1$ component of the integral cross section consists primarily of waves with $|m|=2$ and 3 while the ${}^2B_2$ contribution is predominantly $|m|=1$ throughout the collision energies of interest, even near threshold. As expected, the ${}^2A_2$ symmetry is principally $|m|=1$ in character, given the orientation of the molecular symmetry axis along the y axis. This symmetry makes only a small contribution to the total-excitation cross section at all energies.

Also shown in Fig. 4 are relative emission cross-section measurements by Becker *et al.*[21] for OH $(A\,{}^2\Sigma^+)$ produced via dissociative electron-impact excitation of water with a threshold energy of 9.3 ± 0.25 eV. They obtained fluorescence intensities from both highly rotationally excited [$P_1(27)$ branch] and rotationally cool [$Q_1(3)$ branch] OH species. Making use of the fact that the former are generated mainly by excitation of a singlet state, probably the $\tilde{B}\,{}^1A_1(3a_1 \rightarrow 3sa_1)$, and assuming the known high-energy behavior of triplet excitation cross sections relative to those of singlets, they estimated the contribution from triplet states to the fluorescence observed in the Q branch. Their resulting relative intensities for "triplet" excitation are shown in Fig. 4 where they have been normalized to our calculated cross section at 30 eV. It is important to stress that although the triplet state or states contributing to dissociation in these experiments[21] have not been explicitly identified, it is reasonable to assume that the behavior of these cross sections with energy should be characteristic of triplet states in water. Both the emission cross sections and the calculated excitation cross sections exhibit a similar energy dependence above 16 eV, although the measured intensities decrease somewhat more rapidly with electron energy. This direct comparison of the calculated cross sections and measured emission results may be also be complicated by cascading effects from higher excited states of the molecule. The assumption that the energy dependence of the singlet excitation is the same for both rotational branches may introduce some error in determining the triplet contribution to the cross section at a given energy.[21] Furthermore, inclusion of additional open and closed channels can also be expected to lead to changes in the calculated cross sections.

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