

Low Energy Elastic Scattering of Electrons by Water Molecules

Luiz M. Brescansin and Marco A. P. Lima

*Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas
Caixa Postal 6165, Campinas, 13081, São Paulo, Brasil*

Luiz E. Machado

*Departamento de Física, Universidade Federal de São Carlos
Caixa Postal 676, São Carlos, 13560, São Paulo, Brasil*

Lee Mu-Tao

*Departamento de Química, Universidade Federal de São Carlos
Caixa Postal 676, São Carlos, 13560, São Paulo, Brasil*

Received May 11, 1992

We report calculated elastic differential cross sections for electrons scattering by H_2O at 15, 20 and 30 eV, using the iterative Schwinger variational method in a fixed-nuclei static-exchange approximation. Our results compare very favorably with recent experimental and theoretical results at all angles above 30 degrees. Nevertheless, as used here, this approximation can not describe correctly the differential cross sections in the forward direction, whose behavior is associated with the dipolar nature of the molecular potential.

I. Introduction

Despite its relevancy to several fields of research¹, mainly biology, atmospheric physics and astrophysics, only recently low-energy electron scattering by water vapour has been more extensively studied. Early measurements include total² and differential³ elastic scattering cross sections. This latter is restricted in angular range and electron impact energies (E_0). Danjo and Nishimura⁴ have measured absolute elastic differential and momentum-transfer cross sections in the 10-120 degrees angular range, with E_0 ranging from 4 to 200 eV; Shyn and Cl.o⁵ reported measurements of absolute vibrationally elastic differential and momentum-transfer cross sections, extending the angular range to 15-165 degrees, for impact energies from 2.2 to 20 eV; Shyn *et al.*⁶ have reported vibrationally inelastic cross sections for $e^- - H_2O$ collisions and, finally, Johnstone and Newell⁷ have measured vibrationally elastic differential, integral and momentum-transfer cross sections in the 6-50 eV energy range. Additional experimental results of total cross sections have been reported by Sokolov and Sokolova⁸, Sueoka *et al.*⁹, Szmytkowski *et al.*¹⁰ and Zecca *et al.*¹¹. Theoretically, elastic differential and momentum-transfer cross sections have been calculated by Fujita *et al.*¹² using Glauber approximation for $E_0 \geq 50$ eV, by Gianturco and Thompson¹³ us-

ing a local exchange and model polarization potentials, by Brescansin *et al.*¹⁴ using a static-exchange approximation in a multichannel extension of the Schwinger variational method and recently by Gianturco¹⁵ using a parameter-free model interaction.

A reliable theoretical study of the $e^- - H_2O$ collision requires accurate descriptions for both short- and long-range potentials. A fixed-nuclei treatment of electron scattering by polar molecules is known to lead to divergent differential cross sections (DCS) in the forward direction, due to the slow falloff of the partial-wave T-matrix elements for large l ¹⁶. This is an essential property of the potential associated with the polar nature of the target. This divergence can be removed only by the introduction of the nuclear motion in the Hamiltonian. However, most of the calculations performed in the fixed-nuclei approximation are usually truncated at a given l_m although the description of that divergent would require the inclusion of hundreds of partial waves¹⁷. Even so, the low partial wave fixed-nuclei description is directly useful, since it can provide good DCS at large scattering angles. Furthermore, these low-partial-wave cross sections can then be adequately corrected by laboratory-frame Born calculations¹⁸.

In this paper we report calculated differential cross sections for elastic scattering of electrons by H_2O , for

incident energies of 15, 20 and 30 eV. We used the fixed-nuclei and static-exchange approximations to obtain scattering amplitudes via the iterative Schwinger variational method¹⁹. In this energy range, the static-exchange potential can be expected to describe well these low-partial-wave collisions.

The details of this method are presented in Section II. In Section III some aspects of the calculations are presented, while our results along with some recent data available for comparison are shown in Section IV.

II. The Method

The Schrodinger equation for the continuum scattering orbitals can be written (in atomic units) as:

$$[-\nabla^2 + U(\vec{r}) - k^2]\Psi_{\vec{k}}(\vec{r}) = 0, \quad (1)$$

where $U(\vec{r}) = 2V(\vec{r})$ and $V(\vec{r})$ is the interaction potential between the target and the scattering electron. It is equivalent to work with the Lippman-Schwinger equations¹⁹

$$\Psi_{\vec{k}}(\pm) = \Phi_{\vec{k}} + G_0^{(\pm)}U\Psi_{\vec{k}}(\pm), \quad (2)$$

with $G_0^{(\pm)}$ being the free-particle Green's operator with outgoing ($G_0^{(+)}$) or incoming ($G_0^{(-)}$) wave boundary conditions. In order to take advantage of the C_{2v} symmetry of the target, symmetry adapted functions $X_{lh}^{p\mu}(\vec{r})$ are used. These functions can be expanded²⁰ in terms of the $Y_{lm}(\vec{r})$ as:

$$X_{lh}^{p\mu}(\vec{r}) = \sum_m b_{lhm}^{p\mu} Y_{lm}(\vec{r}). \quad (3)$$

Here p is an irreducible representation (IR) of the molecular point group, μ is a component of this representation and h distinguishes between different bases of the same IR corresponding to the same value of l . The coefficients $b_{lhm}^{p\mu}$ satisfy important orthogonality conditions and are tabulated in Ref. 20. Using these symmetry adapted functions, $\Psi_{\vec{k}}(\pm)(\vec{r})$ can be expanded as^{21,22}:

$$\Psi_{\vec{k}}(\pm)(\vec{r}) = \left[\frac{2}{\pi}\right]^{\frac{1}{2}} \frac{1}{k} \sum_{p\mu lh} i^l \Psi_{k,lh}^{(\pm)p\mu}(\vec{r}) X_{lh}^{p\mu}(\hat{k}). \quad (4)$$

The Schwinger variational expression for the T-matrix can be written in the bilinear form as:

$$\begin{aligned} T_{\vec{k},\vec{k}'}^{(\pm)} &= \langle \Phi_{\vec{k}'}^{(\mp)} | U | \tilde{\Psi}_{\vec{k}}^{(\pm)} \rangle + \\ &\langle \tilde{\Psi}_{\vec{k}'}^{(\mp)} | U | \Phi_{\vec{k}}^{(\pm)} \rangle - \\ &\langle \tilde{\Psi}_{\vec{k}'}^{(\mp)} | U - UG_0^{(\pm)}U | \tilde{\Psi}_{\vec{k}}^{(\pm)} \rangle \end{aligned} \quad (5)$$

with $\tilde{\Psi}_{\vec{k}}(\pm)$ denoting trial scattering wave vectors. Using a partial-wave expansion similar to (4) for both

$\tilde{\Psi}_{\vec{k}}(\pm)$ and the free-particle wave vector $\Phi_{\vec{k}}(\pm)$, a partial wave on-shell T-matrix (diagonal in both p and μ) is obtained:

$$\begin{aligned} T_{k,lh;l'h'}^{(\pm)p\mu} &= \langle \Phi_{k,l'h'}^{(\mp)p\mu} | U | \tilde{\Psi}_{k,lh}^{(\pm)p\mu} \rangle + \\ &\langle \tilde{\Psi}_{k,l'h'}^{(\mp)p\mu} | U | \Phi_{k,lh}^{(\pm)p\mu} \rangle - \\ &\langle \tilde{\Psi}_{k,l'h'}^{(\mp)p\mu} | U - UG_0^{(\pm)}U | \tilde{\Psi}_{k,lh}^{(\pm)p\mu} \rangle, \end{aligned} \quad (6)$$

where $k = |\vec{k}| = |\vec{k}'|$ for the elastic process.

The initial scattering wave functions can be expanded in a set R_0 of L^2 basis functions $\alpha_i(\vec{r}) = \langle \vec{r} | \alpha_i \rangle$:

$$\tilde{\Psi}_{k,lh}^{(\pm)p\mu}(\vec{r}) = \sum_{i=1}^N a_{i,lh}^{(\pm)p\mu}(k) \alpha_i(\vec{r}). \quad (7)$$

Using (6) and (7), variational $T_{k,lh;l'h'}^{(\pm)p\mu}$ matrix elements can be derived as:

$$\begin{aligned} T_{k,lh;l'h'}^{(\pm)p\mu} &= \sum_{i,j=1}^N \langle \Phi_{k,l'h'}^{(\mp)p\mu} | U | \alpha_i \rangle \\ &[D^{(\pm)}]_{ij}^{-1} \langle \alpha_j | U | \Phi_{k,lh}^{(\pm)p\mu} \rangle, \end{aligned} \quad (8)$$

where

$$D_{ij}^{(\pm)} = \langle \alpha_i | U - UG_0^{(\pm)}U | \alpha_j \rangle, \quad (9)$$

and the corresponding approximate scattering solution with outgoing wave boundary condition becomes:

$$\begin{aligned} \Psi_{k,lh}^{(+p\mu(S_0))}(\vec{r}) &= \Phi_{k,lh}^{p\mu}(\vec{r}) + \sum_{i,j=1}^M \langle \vec{r} | G_0^{(+)}U | \alpha_i \rangle \\ &[D^{(+)}]_{ij}^{-1} \langle \alpha_j | U | \Phi_{k,lh}^{p\mu} \rangle. \end{aligned} \quad (10)$$

As in the case of linear molecules¹⁸, converged solutions of (10) can be obtained via an iterative procedure. The method consists in augmenting the basis set R_0 by the set

$$S_0 = \{\Psi_{k,l_1h_1}^{(-)p\mu(S_0)}(\vec{r}), \Psi_{k,l_2h_2}^{(-)p\mu(S_0)}(\vec{r}), \dots, \Psi_{k,l_ch_c}^{(-)p\mu(S_0)}(\vec{r})\} \quad (11)$$

where l_c is the maximum value of l for which the expansion of the scattering solution (4) is truncated, and $h, \leq l_c$. A new set of partial wave scattering solutions can now be obtained from:

$$\begin{aligned} \Psi_{k,lh}^{(+p\mu(S_1))}(\vec{r}) &= \Phi_{k,lh}^{p\mu}(\vec{r}) + \sum_{i,j=1}^M \langle \vec{r} | G^{(+)}U | \eta_i^{(S_0)} \rangle \\ &[D^{(+)}]_{ij}^{-1} \langle \eta_j^{(S_0)} | U | \Phi_{k,lh}^{p\mu} \rangle \end{aligned} \quad (12)$$

where $\eta_i^{(S_0)}(\vec{r})$ is any function in the set $R_1 = R_0 \cup S_0$ and M is the number of functions in R_1 . This iterative procedure continues until a converged $\Psi_{k,lh}^{(+p\mu(S_n))}(\vec{r})$ is

achieved. In an actual calculation we compute the converged partial wave K-matrix elements, $K_{k,lh;l'h'}^{p\mu(S_n)}$. Since no boundary conditions are needed to be imposed on the trial scattering functions in the Schwinger variational iterative method, these K-matrix elements can be obtained by replacing $D^{(P)}$ for $D^{(+)}$ in (9), where

$$D_{ij}^{(P)} = \langle \alpha_i | U - UG_0^{(P)}U | \alpha_j \rangle, \quad (13)$$

with $G_0^{(P)}$ denoting the principal value free particle Green's function. Hence, the corresponding partial-wave T-matrix elements can be calculated from

$$T_{k,lh;l'h'}^{p\mu(S_n)} = - \left[\frac{2}{\pi} \right] \sum_{l''h''} [1 - iK^{(S_n)}]_{k,lh;l''h''}^{p\mu} K_{k,l''h'';l'h'}^{p\mu(S_n)} \quad (14)$$

Finally, after squaring the laboratory-frame (LF) scattering amplitudes and averaging over all molecular orientations with respect to the incident beam, the DCS can be written as:

$$\frac{d\sigma}{d\theta} = \sum_L A_L(k) P_L(\cos\theta), \quad (15)$$

where θ is the scattering angle. The coefficients $A_L(k)$ in (15) are given by the formula

$$A_L(k) = \frac{1}{2} \frac{1}{2L+1} \sum_{\substack{p\mu lh'l'm'm' \\ p_1\mu_1 l_1 h_1 l'_1 h'_1 m_1 m'_1}} (-1)^{m'-m} \sqrt{(2l+1)(2l_1+1)} \times \\ b_{l'_1 h'_1 m'_1}^{p_1\mu_1} b_{l_1 h_1 m_1}^{p_1\mu_1} b_{l'h'm'}^{p\mu} b_{lhm}^{p\mu} a_{l_1 h_1 l'_1 h'_1}^{p_1\mu_1} a_{lh;l'h'}^{p\mu}(k) \times \\ (l_1 0 l_0 | l_1 0 l'_0 | L 0) (l_1 - m_1 l m | L - M) \\ (l'_1 m'_1 l' m' | LM), \quad (16)$$

where $(j_1 m_1 j_2 m_2 | j_3 m_3)$ are the usual Clebsch-Gordan coefficients and the auxiliary amplitudes $a_{lh;l'h'}^{p\mu}(k)$ are defined as

$$a_{lh;l'h'}^{p\mu}(k) = - \frac{\sqrt{\pi^3}}{k} i^{l'-l} \sqrt{2l'+1} T_{k,lh;l'h'}^{p\mu(S_n)}, \quad (17)$$

III. Numerical procedure

The static-exchange potential used in (2) is constructed from an SCF wave function of the ground state of H_2O . For this SCF calculation we used the standard [3s2p,2s] contracted Gaussian basis of Dunning and Hay²³ augmented by one uncontracted d function

(exponent 0.34) on the Oxygen nucleus and one uncontracted p function (exponent 0.13) on the Hydrogen nuclei. At the experimental equilibrium geometry of $R(O-H) = 1.81a_0$ and $\Theta(H-O-H) = 104.5$ deg (Ref. 24), this basis gives an SCF total energy of -76.0199 a.u. and an electric dipole moment of 0.761 a.u., compared with the Hartree-Fock (HF) limit of -76.0632 a.u.²⁵ and the experimental dipole moment of 0.724 a.u.²⁶, respectively. The orbital energies for $1a_1$, $2a_1$, $3a_1$, $1b_2$ and $1b_1$ orbitals are -20.563, -1.358, -0.582, -0.717 and -0.512 a.u., respectively. In our method, all the \vec{r} -dependent functions appearing in eqs. (4-9) are expanded as in (4). All partial-wave expansions were truncated at $l = 10$ and all possible values of $h \leq l$ were retained for a given l . The resulting orbital normalizations were better than 0.9999 for all bound orbitals. In Table I we show the basis set corresponding to R_0 . Our results shown below were all converged within four iterations.

IV. Results and discussion

In Figures 1-3 we show our calculated elastic DCS for incident electron energies of 15, 20 and 30 eV, along with the published experimental values of Danjo and Nishimura⁴, Shyn and Cho⁵ and Johnstone and Newell⁷ and theoretical results of Brescansin et al.¹⁴ and Gianturco¹⁵. General good agreement with the experimental results is observed in the entire angular range for all incident energies. Comparison with the theoretical results of Brescansin et al.¹⁴ shows a good agreement for scattering angles above 35 degrees. However, the present iterative method provides a better description than the Schwinger multichannel (SMC) method¹⁴ in the small angle region, where an enhancement of the DCS due to the long-range dipole potential of the target is expected. On the other hand, although the theoretical results of Gianturco¹⁵ seem to reproduce the experimental data at small scattering angles his method clearly underestimates the DCS at larger scattering angles.

The present method was also applied to lower impact energies (2.2 - 10 eV). Our DCS curves for these lower energies (results not shown) exhibit some oscillations which can be attributed to the non-fully converged partial-wave expansions resulting from the truncation to $l = 10$. According to Jain and Thompson¹⁷, full convergence in such cases can be reached possibly only after hundreds of partial wave components have been taken into account. This is obviously impossible to be done, for the moment, in our method. A possible way to surpass this difficulty is to replace the high- l scattering amplitudes by the corresponding first Born approximation partial wave scattering amplitudes. This method has already been successfully applied for elastic electron scattering by C_2H_2 (Ref. 18). Its extension for $e^- - H_2O$ scattering is under way.

Table I: Cartesian Gaussian^a basis sets used in separable potential

Scattering Symmetry	Center	Cartesian Gaussian Function ^a	Exponents
ka_1	O	s	2.0, 0.5, 0.1, 0.025
		z	2.0, 0.5, 0.05
		x^2, y^2, z^2	0.2, 0.05
	H	s	0.8, 0.2
		x,z	0.5, 0.1
ka_2	O	yz	4.0, 2.0, 1.0, 0.5, 0.1
	H	y	1.2, 0.4, 0.1
kb_1	O	y	8.0, 4.0, 2.0, 1.0, 0.5
		yz	2.0, 1.0, 0.5, 0.1
	H	y	2.0, 1.0, 0.5
kb_2	O	x	8.0, 4.0, 2.0, 1.0, 0.5
		xz	2.0, 1.0, 0.5, 0.1
	H	x	2.0, 1.0, 0.5

^a Cartesian Gaussian basis functions are defined as

$$\phi^{\alpha, \ell, m, n, \mathbf{A}}(\mathbf{r}) = N(x - \mathbf{A}_x)^\ell (y - \mathbf{A}_y)^m (z - \mathbf{A}_z)^n \exp(-\alpha |\mathbf{r} - \mathbf{A}|^2)$$

with N a normalization constant.

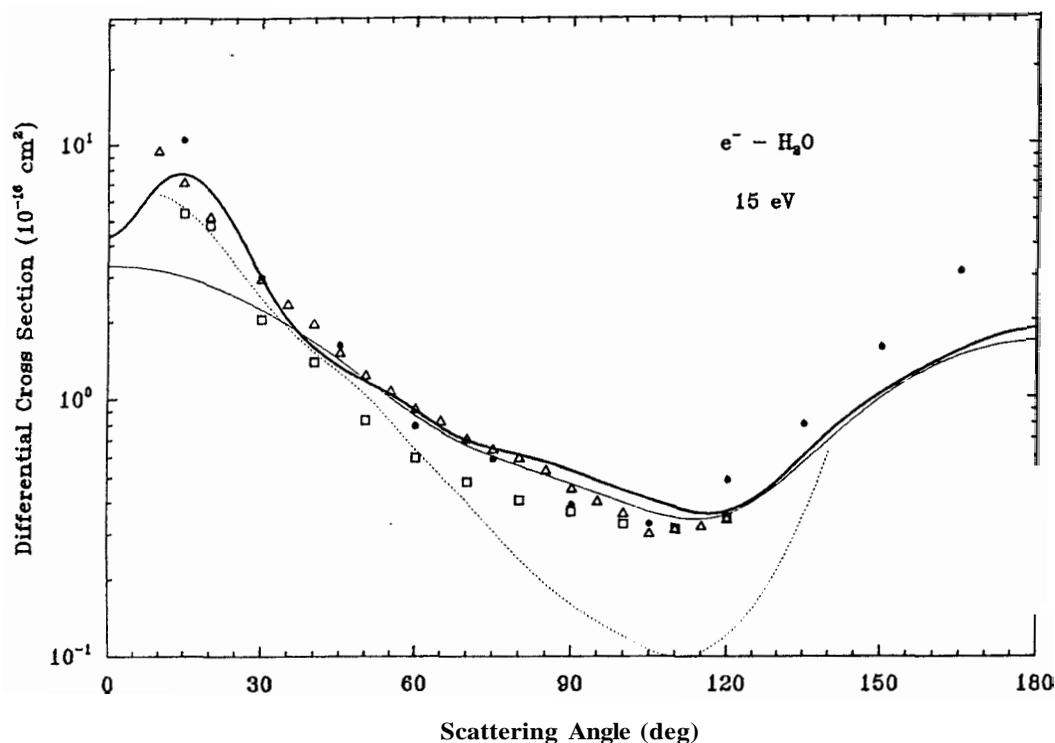


Figure 1.: (a) Differential cross sections for $E_0 = 15$ eV. Thick solid line, present results; thin solid line, theoretical results of Brescansin *et al.* (Ref. 14); thin dashed line, theoretical results of Gianturco (Ref. 15); solid circle, experimental results of Shyn and Cho (Ref. 5); triangles, experimental results of Johnston and Newell (Ref. 7); squares, experimental results of Danjo and Nishimura (Ref. 4).

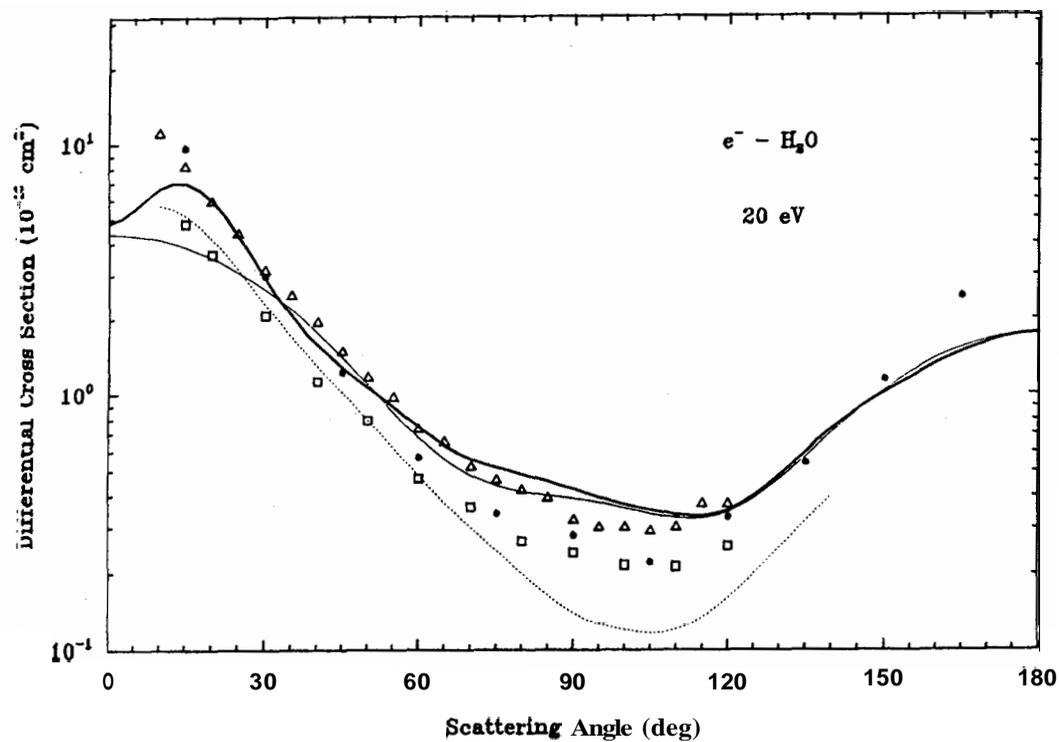


Figure 2.: Same as Fig. 1 for $E_0 = 20 \text{ eV}$

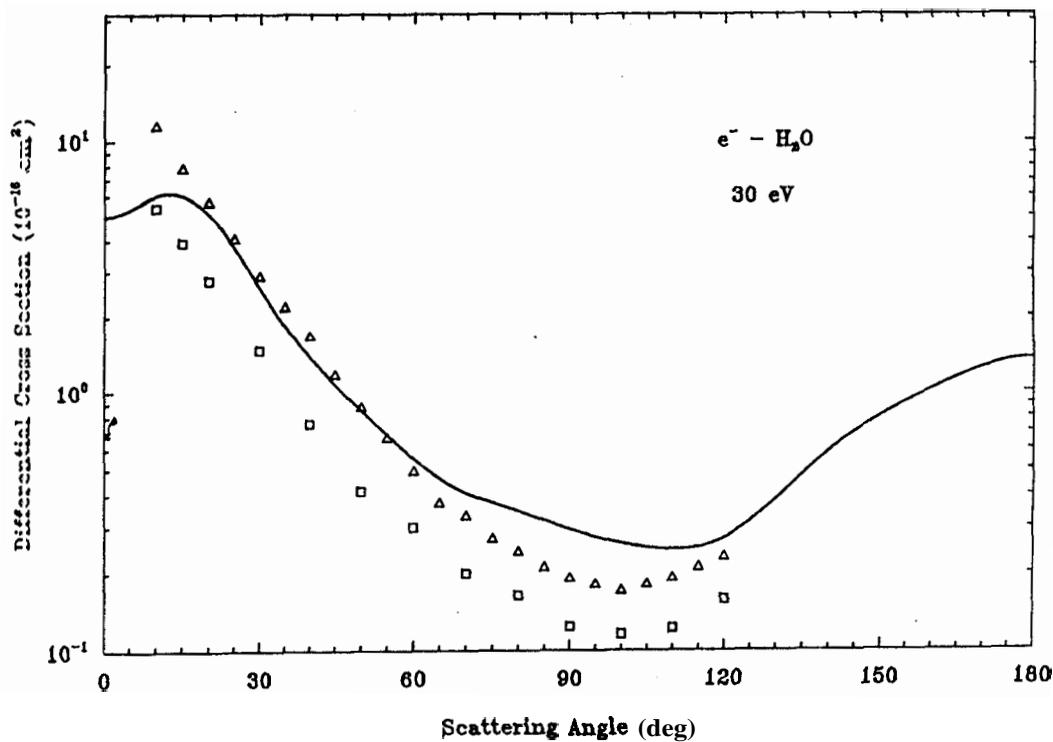


Figure 3.: Same as Fig. 1 for $E_0 = 30 \text{ eV}$.

Acknowledgements

This research was partially supported by National Science Foundation, the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and FINEP. L.M.B., M.A.P.L., L.E.M. and L.M.-T. acknowledge financial support from CNPq.

References

1. S. Trajmar, D. F. Register and A. Cluitjian, *Phys. Rep.* **97**, 219 (1983).
2. E. Bruche, *Ann. Phys.* **1**, 93 (1929).
3. K. Jung, T. Antoni, R. Mueller, K. H. Kochen and H. Erhardt, *J. Phys. B* **91**, 3535 (1982).
4. A. Danjo and H. Nislimura, *J. Phys. Soc. Japan* **54**, 1224 (1985).
5. T. W. Shyn and S. Y. Cho, *Phys. Rev. A* **36**, 5138 (1987).
6. T. W. Sliyn, S. Y. Clio and T. A. Cravens, *Phys. Rev. A* **38**, 678 (1988).
7. W. M. Jolinstone and W. R. Newell, *J. Phys. B: At. Mol. Phys.* **24**, 3633 (1991).
8. V. F. Sokolov and Y. Sokolova, *Sov. Tech. Phys. Lett.* **7**, 268 (1981).
9. O. Sueoka, S. Mori and L. Katoyama, *J. Phys. B* **19**, L373 (1986).
10. C. Szymtkowski, *Cliem. Pliys. Lett.* **136**, 363 (1987).
11. A. Zecca, G. Karwasz, S. Oss, R. Grisenti and R. S. Brusa, *J. Phys. B* **20**, L133 (1987).
12. T. Fujita, K. Ogura and V. Watanabe, *J. Pliys. Soc. Japan* **52**, 811 (1982).
13. F. A. Gianturco and D. G. Thompson, *J. Pliys. B: At. Mol. Phys.* **13**, 613 (1980).
14. L. M. Bescansin, M. A. P. Lima, T. L. Gihson, V. McKoy and W. M. Huo, *J. Chern. Phys.* **85**, 1854 (1986).
15. F. A. Gianturco, *J. Phys. B: At. Mol. Opt. Phys.* **24**, 3837 (1991).
16. See, for example, D. W. Norcross and L. A. Collins, *Advances in Atomic and Molecular Physics (Acadernic, New York, 1982)* Vol. 18, p. 341.
17. A. Jain and D. G. Thompson, *J. Phys. B: At. Mol. Pliys.* **16**, 3077 (1983).
18. M.-T. Lee, L. M. Bescansin, M. A. P. Lima, L. E. Machado and E. P. Leal, *J. Phys. B: At. Mol. Opt. Phys.* **23**, 4331 (1990).
19. R. R. Lucchese, G. Raseev and V. McKoy, *Phys. Rev. A* **25**, 2572 (1982).
20. P. G. Burke, N. Chandra and F. A. Gianturco, *J. Phys. B: At. Mol. Phys. B* **5**, 2212 (1972).
21. M. Braunstein, V. McKoy, L. E. Machado, L. M. Bescansin and M. A. P. Lima, *J. Chem. Phys.* **89**, 2998 (1988).
22. L. E. Machado, L. M. Bescansin, M. A. P. Lima, M. Braustein and V. McKoy, *J. Chem. Phys.* **92**, 2362 (1990).
23. T. H. Dunning Jr. and J. P. Hay, in *Modern Theoretical Chemistry*, H. F. Schaeffer III, Ed. (Plenum, New York, 1977), Vol. **3**, p. 1.
24. See, for example, L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties* (Wiley, New York, 1972).
25. T. H. Dunning Jr., R. M. Pitzer and S. Aung, *J. Chem. Phys.* **57**, 5044 (1972).
26. See, for example, W. Meyer, in *Modern Theoretical Chemistry*, H. F. Schaeffer III, Ed. (Plenum, New York, 1977), Vol. **3**, p. 442.