PHYSICAL REVIEW A VOLUME 60, NUMBER 1 JULY 1999

Intermediate-energy electron-impact ionization of molecules

A. L. Monzani and L. E. Machado
Departamento de Física, UFSCar, 13565-905 São Carlos, SP, Brazil

M.-T. Lee
Departamento de Química, UFSCar, 13565-905 São Carlos, SP, Brazil

A. M. Machado
Instituto de Física de São Carlos, USP, 13560-970 São Carlos, SP, Brazil

(Received 11 February 1999)

The distorted-wave approximation is used to calculate doubly and triply differential cross sections for the electron-impact ionization of hydrogen molecules for incident energies of 100 and 250 eV. In the present model, the wave function of the incoming electron is calculated in the static-exchange (SE) potential field generated by a neutral H_2 molecule, whereas those of the two outgoing electrons are calculated in the SE field of the H_2^+ ion. The Schwinger variational iterative method was used in the calculation of these distorted waves. Comparison of the present calculated results with experimental data available in the literature is encouraging. [S1050-2947(99)50807-X]

PACS number(s): 34.80.Gs

I. INTRODUCTION

Despite the extensive investigation on low- and intermediate-energy (e,2e) processes in atoms carried out over the last decades [1–3], the corresponding processes for molecular targets have been comparatively much less studied. Experimentally, doubly differential cross sections (DDCS) were measured for H_2 and N_2 [4–8]. Pioneering measurements of triple differential cross sections (TDCS) for electron-impact ionization were performed, for molecular hydrogen and nitrogen, by Jung *et al.* [9] (at 100 and 250 eV) and for the CO molecule by Dey *et al.* [10] (at 400 and 1200 eV). Absolute TDCS for asymmetric (e,2e) experiments were also reported by Avaldi *et al.* [11] for the ionization of the $3\sigma_g$ orbital of nitrogen. More recently, relative TDCS were reported for 100-eV ionization of the $3\sigma_g$ and $1\pi_u$ orbitals of nitrogen by Doering and Yang [12]. Also, Rioual, Nguyen, and Pochat [13] reported relative TDCS for coplanar symmetric ionization of several valence orbitals of N_2 and CO in the 90–400-eV incident-energy range.

On the theoretical side, the disparity between atomic and molecular investigations is even more pronounced. For atoms, some earlier studies based on the Born [14,15] and distorted-wave [16–18] approximations have been widely used for ionization of rare-gas targets. Several more elaborated theoretical models were recently applied for electron-impact ionization of atoms. These methods include, among others, the R-matrix method [19], the semiclassical description of the postcollision effects [20], and the converged-close-coupling method [21]. For molecules, however, the only theoretical model currently in use is the plane-wave impulse approximation (PWIA) extensively exploited by McCarthy and Weigold [22]. Although the PWIA has been applied with relative success to ionization studies on H_2 [23], N_2 [13,24], and CO [10,13] for incident energies of 400 eV and above, it is expected that this method would not provide reliable TDCS for lower energies.

In this Rapid Communication, we report calculations based on the distorted-wave approximation (DWA) for electron-impact ionization of hydrogen molecule at incident energies of 100 and 250 eV. Despite its simplicity, the DWA has been widely applied with relative success to studies of electron-impact atomic excitation [25–27] and ionization processes [16–18,28] in the low- and intermediate-energy range. It has also been applied to a lesser extent to molecular excitation processes [29,30]. We expect that the present study would provide insights into dynamics involved in the electron-impact ionization of molecules.

II. THEORY AND CALCULATION

Since the (e,2e) process of H_2 results in three spin-1/2 systems, two partial-spin-specific collisional dynamics, namely the singlet and the triplet couplings, must be considered. In the present work, we use the Born-Oppenheimer approximation and assume that the vibrational and rotational levels of the target are essentially degenerate. Thus, applying the closure relation over final-state rotational and vibrational levels, the laboratory-frame (LF) TDCS expanded in a j_t basis [31] can be written as

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 dE} = (2\pi)^4 \frac{2k_1k_2}{k_0} \sum_{j_t m_t m_t'} \frac{1}{(2j_t+1)} \left[\frac{1}{4} |B^{j_t S}_{m_t m_t'}|^2 + \frac{3}{4} |B^{j_t T}_{m_t m_t'}|^2 \right], \tag{1}$$

where Ω_1 and Ω_2 are LF solid angles of the two outgoing electrons with linear momenta $\vec{k}_1$ and $\vec{k}_2$, respectively, $\vec{k}_0$ is the linear momentum of the incident electron, E is the energy of one of the outgoing electrons, and $\vec{j}_t = \vec{l}_0 - \vec{l}_1 - \vec{l}_2$ is the angular momentum transferred during the collision with projections m_t', m_t along the laboratory and molecular axes, respectively. Also, DDCS can be obtained by integrating the TDCS over the angular variables of one of the outgoing electrons.

In Eq. (1) the $B^{j_t{}^{(S,T)}}_{m_t m_t'}$ are the singlet-coupling (S) and triplet-coupling (T) j_t-basis expansion coefficients that can be expressed as

$$B^{j_t{}^{(S,T)}}_{m_t m_t'} = (-1)^{m_t' + m_t}\left(\frac{2}{\pi}\right)^{3/2}$$
$$\times \sum_{\substack{l_0 m_0 l_1 m_1 m_1' \\ l_2 m_2 m_2' l m m'}} (-1)^{m_2+m_2'} i^{l_0-l_1-l_2} e^{i(\sigma_{l_1}+\sigma_{l_2})}$$
$$\times \frac{2l+1}{2l_2+1}\sqrt{\frac{2l_0+1}{4\pi}}(lm'l_0 0|j_t m_t')$$
$$\times (lml_0 - m_0|j_t m_t)(l-m'l_1 m_1'|l_2 - m_2')$$
$$\times (l-ml_1 m_1|l_2 - m_2) T^{(S,T)}_{l_0 m_0 l_1 m_1 l_2 m_2}$$
$$\times Y_{l_1 m_1'}(\hat{k}_1') Y_{l_2 m_2'}(\hat{k}_2'), \tag{2}$$

where σ_{l_1} and σ_{l_2} are the Coulomb phase shifts of the two outgoing electrons and $T^{(S,T)}_{l_0 m_0 l_1 m_1 l_2 m_2}$ are the corresponding partial-wave components of the electronic portion of the T matrix that can be expressed as

$$T^{(S)} = \frac{1}{\sqrt{2}}[2f - g] \tag{3}$$

and

$$T^{(T)} = -\sqrt{\frac{3}{2}}g \tag{4}$$

for the singlet and the triplet couplings, respectively. In Eqs. (3) and (4), f and g are the direct- and exchange-scattering contributions to the T matrix, given by

$$f = \left\langle \chi^-_{\vec{k}_1}\chi^-_{\vec{k}_2}\left|\frac{1}{r_{12}}\right|\varphi_0 \chi^+_{\vec{k}_0}\right\rangle \tag{5}$$

and

$$g = \left\langle \chi^-_{\vec{k}_2}\chi^-_{\vec{k}_1}\left|\frac{1}{r_{12}}\right|\varphi_0 \chi^+_{\vec{k}_0}\right\rangle, \tag{6}$$

where φ_0 is the active bound orbital of the ground-state target, $\chi^+_{\vec{k}_0}$ is the continuum wave function of the incident electron, and $\chi^-_{\vec{k}_1}$ and $\chi^-_{\vec{k}_2}$ are the wave functions of the two outgoing electrons, calculated using the appropriate spin couplings.

In our study, both the incoming- and outgoing-electron wave functions are approximated by the DWA. These distorted wave functions are calculated using the Schwinger variational iterative method (SVIM) [32]. Particularly, $\chi^+_{\vec{k}_0}$ is obtained in the static-exchange potential field generated by a neutral H_2 molecule, whereas $\chi^-_{\vec{k}_1}$ and $\chi^-_{\vec{k}_2}$ are obtained in the SE potential field of the $H_2{}^+$ ion constructed assuming the frozen-core approximation. In the SVIM calculations, the continuum wave functions are single-center expanded as

$$\chi^{\pm}_{\vec{k}}(\vec{r}) = \left(\frac{2}{\pi}\right)^{1/2} \sum_{lm} i^l e^{\pm i\sigma_l} \chi^{\pm}_{klm}(\vec{r}) Y_{lm}(\hat{k}), \tag{7}$$

where σ_l equals to zero for the initial-neutral distorted wave functions.

The calculation of $\chi_{\vec{k}}(\vec{r})$ starts with the expansion of trial functions $\tilde{\chi}_{k,lm}(\vec{r})$ in a set R_0 of L^2 basis functions $\alpha_i(\vec{r})$ as follows:

$$\tilde{\chi}_{k,lm}(\vec{r}) = \sum_{i=1}^{N} a_{i,lm}(k)\alpha_i(\vec{r}). \tag{8}$$

Using this basis set, the reactance K-matrix elements can be derived as

$$K^{(R_0)}_{k,ll'm} = \sum_{i,j=1}^{N} \langle \Phi_{k,l'm}|U|\alpha_i\rangle [D^{-1}]_{ij} \langle \alpha_j|U|\Phi_{k,lm}\rangle, \tag{9}$$

where $\Phi_{k,lm}$ are the partial-wave free-particle (Coulomb) wave functions for the neutral (ionic) case and

$$D_{ij} = \langle \alpha_i | U - UG^{(P)}U | \alpha_j \rangle. \tag{10}$$

Here $G^{(P)}$ is the principal value of the free-particle (Coulomb) Green's operator, and the zeroth-iteration wave function $\chi^{R_0}_{k,lm}$ is calculated using Eq. (8) with appropriately calculated coefficients $a_{i,lm}$. As demonstrated by Lucchese *et al.* [32], the converged scattering solutions can be obtained via an iterative procedure. This procedure consists in augmenting the basis set R_0 by the set

$$S_0 = \{\chi^{(P)^{(R_0)}}_{k,l_1 m_1}(\vec{r}), \chi^{(P)^{(R_0)}}_{k,l_2 m_2}(\vec{r}), \ldots \chi^{(P)^{(R_0)}}_{k,l_c m_c}(\vec{r})\}, \tag{11}$$

where l_c is the maximum value of l for which the expansion of the scattering solution (7) is truncated, and $m_c \leqslant l_c$. A new set of partial-wave scattering solutions can now be obtained from

$$\chi^{(P)^{(R_1)}}_{k,lm}(\vec{r}) = \Phi_{k,lm}(\vec{r}) + \sum_{i,j=1}^{M} \langle \vec{r}|G^{(P)}U_1|\eta_i^{(R_1)}\rangle$$
$$\times [D^{-1}]_{ij} \langle \eta_j^{(R_1)}|U_1|\Phi_{k,lm}\rangle, \tag{12}$$

where $\eta_i^{(R_1)}(\vec{r})$ 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 $\chi^{(P)^{(R_n)}}_{k,lm}(\vec{r})$ is achieved.

The self-consistent-field (SCF) wave function for ground-state H_2 is constructed with a $5s/3p$ uncontracted Cartesian Gaussian basis set of Huzinaga [33] augmented by three s ($\alpha = 0.04$, 0.015, and 0.003) and three p ($\alpha = 0.06$, 0.03, and 0.01) uncontracted functions. With this basis set, the calculated SCF energy in the equilibrium internuclear distance ($1.4006a_0$) is $-1.133\,026$ a.u., to be compared with the Hartree-Fock limit [34] of -1.1336 a.u. The quadrupole moment given by this function is 0.486 a.u. The electronic wave function of the ground-state $H_2{}^+$ is assumed to be identical to the $1\sigma_g$ orbital of H_2.

In the scattering calculations, the partial-wave expansion of the bound orbital is truncated at $l_{max} = 10$, whereas the

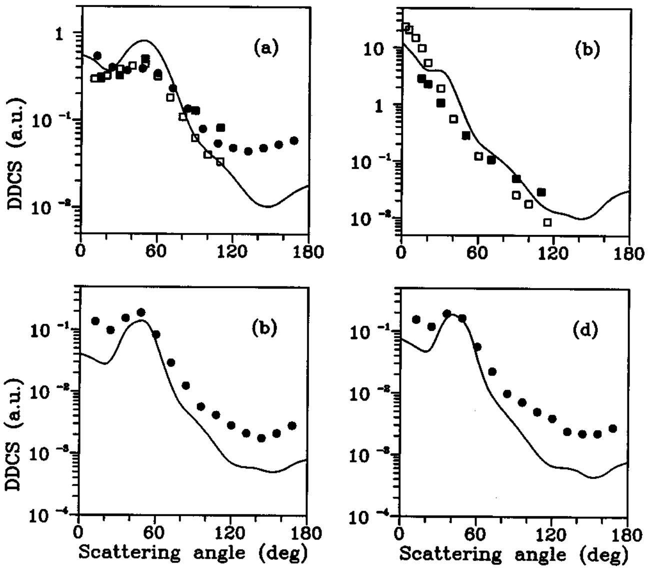

FIG. 1. DDCS for electron-impact ionization of H_2. (a) $E_0 = 100$ eV and $E_b = 30$ eV; (b) $E_0 = 100$ eV and $E_b = 60$ eV; (c) $E_0 = 250$ eV and $E_b = 100$ eV; (d) $E_0 = 250$ eV and $E_b = 117.3$ eV, where E_0 is the energy of the incoming electron and E_b is the energy of one of the outgoing electrons. Solid line, present DWA results; full squares, experimental results of DuBois and Rudd [5]; full circles, experimental results of Shyn, Sharp, and Kim [6]; open squares, experimental results of Al-Nasir *et al.* [8].

truncation parameters used for the expansion of the continuum orbitals, as well as all the matrix elements, are $l_{max} = 16$ and $m_{max} = 4$. Some test runs were also performed using $l_{max} = 16$ and $m_{max} = 6$, in order to verify the convergence. No significant differences have been noticed in the TDCS calculated with these two cutoff parameters, showing that the calculated results have already been converged. The SVIM calculations were converged within two iterations.

III. RESULTS AND DISCUSSION

In Figs. 1(a)–1(d) we show our calculated DDCS for electron-impact ionization of H_2 for some selected energies of incident and outgoing electrons. Our results are compared to the available absolute experimental results of DuBois and Rudd [5], Shyn, Sharp, and Kim [6] and Al-Nasir *et al.* [8]. In general, there is a good qualitative agreement between the calculated and experimental data. Particularly, the positions of the main structures in the experimental DDCS are appropriately predicted by our theory. Quantitatively the agreement between the theory and experiments is also satisfactory. Specifically, at an incident energy of 100 eV [Figs. 1(a) and 1(b)], our calculated DDCS generally agree well with the measured data, particularly with those of Al-Nasir *et al.* [8]. Nevertheless, at 250 eV [Figs. 1(c) and 1(d)] our calculation underestimates the only absolute DDCS reported by Shyn, Sharp, and Kim [6] at small and large scattering angles. These discrepancies are probably due to the neglect of multichannel effects [21] and also of postcollisional correlation between the two outgoing electrons in our distorted-wave treatment.

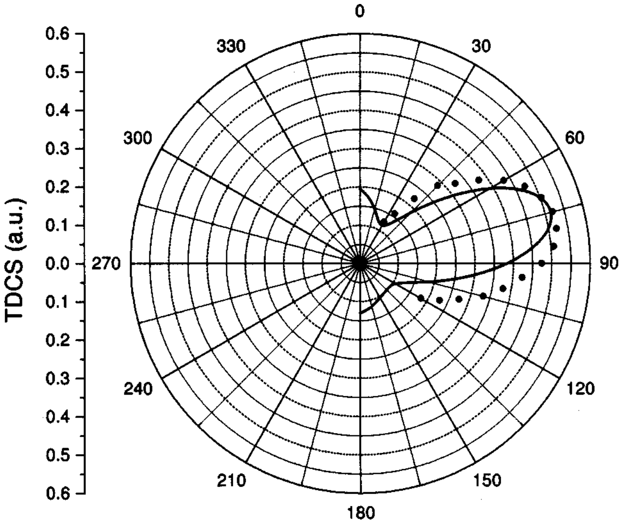

FIG. 2. TDCS for electron-impact ionization of H_2 at $E_0 = 250$ eV and $E_b = 9$ eV, where E_0 is the energy of the incoming electron and E_b is the energy of the slow outgoing electron. The detection angle of the fast outgoing electron is fixed at $-8°$. Solid line, present DWA results; full circles, experimental results of Jung *et al.* [9].

In Fig. 2 we present our calculated TDCS for electron-impact ionization of H_2 at 250-eV incident energy. The experimental results of Jung *et al.* [9] in arbitrary units, normalized to our calculated TDCS at the maximum, are also shown for comparison. In this figure, the angular variable defines the direction of the slow outgoing electron, relative to the direction of the incident electron, whereas the direction of the fast outgoing electron is fixed at $-8°$, and the radial variable indicates the magnitude of the TDCS. In addition, the energy of the slow outgoing electron was fixed at 9 eV. A good qualitative agreement between the calculated and measured TDCS is seen. Particularly, our calculation predicts the position of the maximum of the TDCS, in quite good agreement with the experimental data.

In summary, the present work reports a distorted-wave treatment for the electron-impact ionization of H_2 at 100- and 250-eV incident energies. Despite its simplicity, the application of the DWA to studies of such processes is very encouraging. Our theory was able to provide DDCS and TDCS that are in good qualitative and in some cases also quantitative agreement with available experimental data. Major discrepancies, in particular, those seen in the DDCS at small and large scattering angles, are probably due to the neglect of multichannel effects [21] as well as postcollisional interaction between the two outgoing electrons in our distorted-wave treatment. Inclusion of such effects in theoretical studies of electron-impact ionization of molecules is presently a difficult task [13]. Nevertheless, some improvements on our DWA, e.g., incorporation of core relaxation and/or effective charges, can be made. Investigations in this direction, including other molecular targets, are underway.

ACKNOWLEDGMENTS

The present work was partially supported by the Brazilian agencies FAPESP, CNPq, and FINEP-PADCT.

[1] U. Amaldi, Jr., A. Egidi, R. Marconero, and G. Pizzella, Rev. Sci. Instrum. **40**, 1001 (1969); H. Ehrhardt, M. Schulz, T. Tekaat, and K. Willmann, Phys. Rev. Lett. **22**, 89 (1969).

[2] M. Inokuti, Rev. Mod. Phys. **43**, 297 (1971).

[3] A. Lahmam-Bennani, J. Phys. B **24**, 2401 (1991).

[4] C. B. Opal, E. C. Beaty, and W. K. Peterson, At. Data **4**, 209 (1972).

[5] R. D. DuBois and M. E. Rudd, Phys. Rev. A **17**, 843 (1978).

[6] T. W. Shyn, W. E. Sharp, and Y.-K. Kim, Phys. Rev. A **24**, 79 (1981).

[7] M. E. Rudd, K. W. Hollman, J. K. Lewis, D. L. Johnson, R. R. Porter, and E. L. Fagerquist, Phys. Rev. A **47**, 1866 (1993).

[8] A. H. Al-Nasir, M. A. Chaudhry, A. J. Duncan, R. Hippler, and H. Kleinpoppen, Phys. Rev. A **47**, 2922 (1993).

[9] K. Jung, E. Schubert, D. A. L. Paul, and H. Ehrhardt, J. Phys. B **8**, 1330 (1975).

[10] S. Dey, A. J. Dixon, K. R. Lassey, I. E. McCarthy, P. J. O. Teubner, E. Weigold, P. S. Bagus, and E. K. Viinikka, Phys. Rev. A **15**, 102 (1977).

[11] L. Avaldi, R. Camilloni, E. Fainelli, and G. Stefani, J. Phys. B **25**, 3551 (1992).

[12] J. P. Doering and J. Yang, Phys. Rev. A **54**, 3977 (1996).

[13] S. Rioual, G. Nguyen Vien, and A. Pochat, Phys. Rev. A **54**, 4968 (1996).

[14] A. Salin, J. Phys. B **6**, L34 (1973).

[15] F. Mota Furtado and P. F. O'Mahony, J. Phys. B **22**, 3925 (1989).

[16] D. H. Madison, R. V. Calhoun, and W. N. Shelton, Phys. Rev. A **16**, 552 (1977).

[17] I. E. McCarthy and X. Zhang, J. Phys. B **22**, 2189 (1989).

[18] X. Zhang, C. T. Whelan, and H. R. J. Walters, J. Phys. B **23**, L509 (1990).

[19] R. Schwienhorst, A. Raeker, R. H. G. Reid, and K. Bartschat, J. Phys. B **28**, 4651 (1995).

[20] M. Nicolas, R. J. Tweed, and O. Robaux, J. Phys. B **29**, 791 (1996).

[21] I. Bray, D. V. Fursa, J. Röder, and H. Ehrhardt, J. Phys. B **30**, L101 (1997).

[22] I. E. McCarthy and E. Weigold, Rep. Prog. Phys. **51**, 299 (1988).

[23] M. Chérid, A. Lahmam-Bennani, A. Duguet, R. W. Zurales, R. R. Lucchese, M. C. Dal Cappello, and C. Dal Cappello, J. Phys. B **22**, 3483 (1989).

[24] L. Avaldi, R. Camilloni, E. Fainelli, and G. Stefani, J. Phys. B **20**, 4163 (1987).

[25] D. H. Madison and W. N. Shelton, Phys. Rev. A **7**, 499 (1977).

[26] L. D. Thomas, G. Csanak, H. S. Taylor, and B. S. Yarlagadda, J. Phys. B **7**, 1719 (1974).

[27] G. D. Meneses, C. B. Pagan, and L. E. Machado, Phys. Rev. A **41**, 4740 (1990).

[28] C. Pan and A. F. Starace, Phys. Rev. Lett. **67**, 185 (1991).

[29] G. D. Meneses, L. M. Brescansin, M.-T. Lee, S. E. Michelin, L. E. Machado, and G. Csanak, Phys. Rev. Lett. **71**, 1701 (1993).

[30] M.-T. Lee, A. M. Machado, M. M. Fujimoto, L. E. Machado, and L. M. Brescansin, J. Phys. B **29**, 4285 (1996).

[31] U. Fano and D. Dill, Phys. Rev. A **6**, 185 (1972).

[32] R. R. Lucchese, G. Raseev, and V. McKoy, Phys. Rev. A **25**, 2572 (1982).

[33] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

[34] W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).