Superelastic cross sections in e^--H$_2$ scattering

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We present superelastic cross sections of H$_2$ by electron impact. Our results, obtained with the Schwinger multichannel method, include cross sections for the c $^3\Pi_u \rightarrow$ X $^1\Sigma_g^{(+)}$, c $^3\Pi_u \rightarrow$ b $^3\Sigma_u^{(+)}$, c $^3\Pi_u \rightarrow$ a $^3\Sigma_g^{(+)}$, and elastic c $^3\Pi_u \rightarrow$ c $^3\Pi_u$ transitions. The calculated cross sections are very large, indicating their importance in the modeling of discharge environments. We also investigate the dependence of these cross sections on the internuclear separation of the H atoms and on different approximations of the target wave function. To assess the role of the exchange potential in these processes, we also present the corresponding polarization fractions. [S1050-2947(97)01304-8]

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The collision process of electrons with molecules in excited states is a very interesting problem for basic science and has important applications [1–3]. Despite this importance, almost all studies [4] are related to experimental or theoretical aspects of the dissociative attachment processes of H$_2$ and CO. In addition to those, there is one study on the superelastic collision of electrons with vibrationally excited N$_2$ [5] and another on the $a\,^1\Delta_g \rightarrow b\,^1\Sigma_g^+$ electronic transition in O$_2$ [6]. Even for atoms, the number of studies involving collisions of electrons with electronically excited targets is small [7]. Despite that, cross sections for such collisions are required for the understanding and modeling of discharge environments (cold plasmas), planetary atmospheres, and molecular lasers. These environments have some features that make collisions between electrons and excited molecules very important for understanding their properties [8]. The energy difference between excited states is usually much smaller than the difference between one excited state and the ground state. As a consequence, for a given free-electron distribution, the fraction of electrons with enough energy to produce an inelastic transition from an excited state is much larger than the fraction capable of producing excitations from the ground state. In the case of elastic or superelastic transitions this fraction approaches one. In addition, these cross sections can also be very large. The combination of these two features may allow a small percentage of excited molecules to give rise to important effects.

In this brief report we use the Schwinger multichannel method (SMC) [9] to calculate integrated and differential cross sections for the following transitions of the H$_2$ molecule: c $^3\Pi_u \rightarrow$ X $^1\Sigma_g^{(+)}$, c $^3\Pi_u \rightarrow$ b $^3\Sigma_u^{(+)}$, c $^3\Pi_u \rightarrow$ a $^3\Sigma_g^{(+)}$, and c $^3\Pi_u \rightarrow$ c $^3\Pi_u$. We also calculate spin-flip cross sections for transitions between triplet states.

The majority of the low-lying excited states of the H$_2$ molecule are short-lived states. The exception is the c $^3\Pi_u$ ($v=0$) state, located 291 cm^{-1} below the a $^3\Sigma_g^{(+)}$ [10], with a lifetime of 1 ms. This longer lifetime increases the importance of this excited species on the medium properties and may allow experimental studies, as in the case of O$_2$ [6]. For other states, theory may become the only way of obtaining the cross sections.

In the last few years, the *R* Matrix [11], the Schwinger multichannel (SMC) [9], and the complex Kohn [12] have been established as reliable methods to describe the electron-molecule collision processes. In all these approaches the many-body character of the electronic system is kept in the description of the wave function. Such a property has allowed studies of electronic excitations of molecular targets by low-energy electron impact.

Details of the SMC method applied to open-shell systems have been given previously [13,14]. For transitions between triplet states the expressions are the same as in the case of O$_2$ [13]. For completeness, we present here just a summary of the dependence of these expressions on the doublet $[f^{(2)}]$ and quartet $[f^{(4)}]$ scattering amplitudes. The differential cross section for scattering of an unpolarized electron beam is given by

$$\frac{d\sigma}{d\Omega} = \frac{1}{3}\frac{k_f}{k_i}\{2|f^{(4)}|^2 + |f^{(2)}|^2\}. \tag{1}$$

The spin-polarization fraction P' to P (the ratio between the final and the initial spin polarization of the electronic beam) is

$$\frac{P'}{P} = 1 - 2\frac{\left(\dfrac{d\sigma_{sf}}{d\Omega}\right)}{\left(\dfrac{d\sigma}{d\Omega}\right)}, \tag{2}$$

where the $(d\sigma_{sf}/d\Omega)$ is the spin-flip cross sections, written as

$$\frac{d\sigma_{sf}}{d\Omega} = \frac{4}{27}\frac{k_f}{k_i}|f^{(4)} - f^{(2)}|^2. \tag{3}$$

Our calculations have been carried out within the framework of the fixed-nuclei and Frank-Condon approximations. To assess the influence of internuclear separation on the cross sections we have used two different internuclear distances for the calculations: the equilibrium separation of the c $^3\Pi_u$ state, 1.96 a_0, and the equilibrium separation of the X $^1\Sigma_g^{(+)}$ state, 1.4 a_0. We used a set of $6s6p1d$ [15] Cartesian Gaussian function on each atom. In both cases, for all
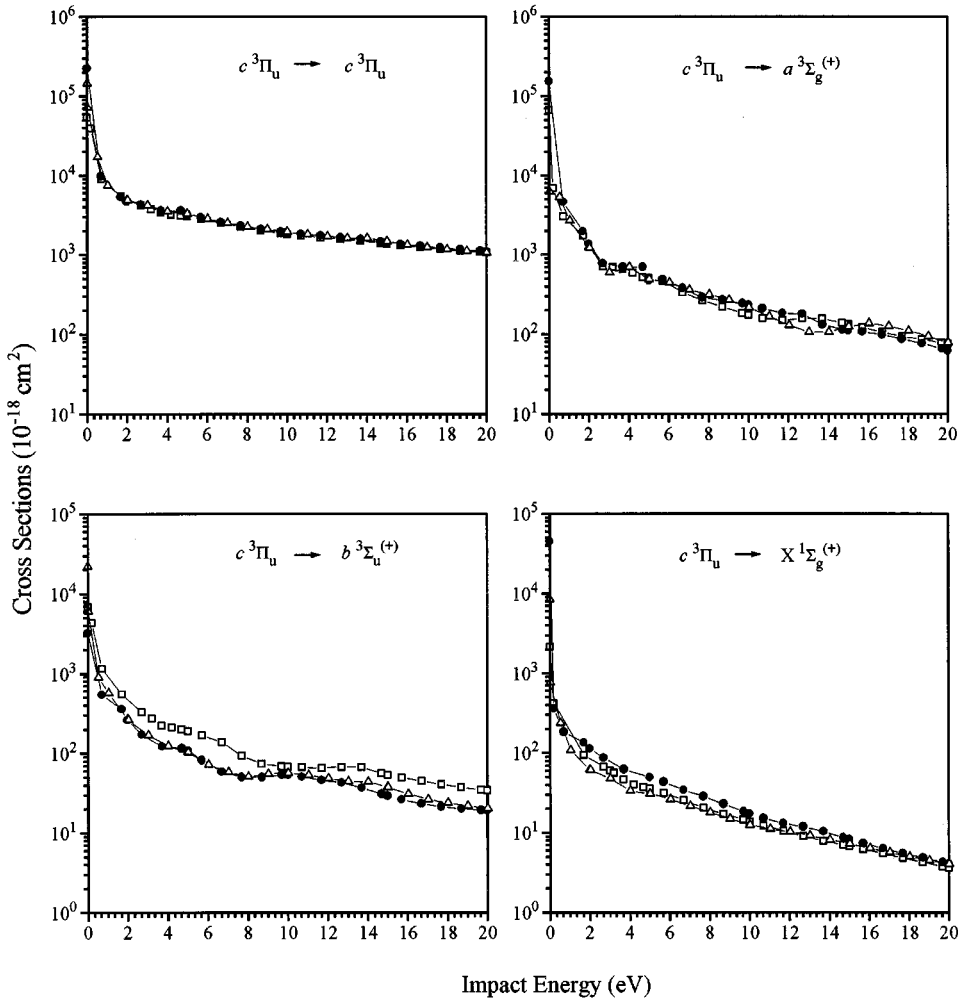
FIG. 1. Electronic transition cross sections of an excited H_2 molecule for the $c\,^3\Pi_u \rightarrow c\,^3\Pi_u$, $c\,^3\Pi_u \rightarrow a\,^3\Sigma_g^{(+)}$, $c\,^3\Pi_u \rightarrow b\,^3\Sigma_u^{(+)}$, and $c\,^3\Pi_u \rightarrow X\,^1\Sigma_g^{(+)}$ transitions. Open triangles: target description of type 1 for $R_{H-H} = 1.4a_0$; closed circles: target description of type 1 for $R_{H-H} = 1.96a_0$; open squares: target description of type 2 for $R_{H-H} = 1.96a_0$. For target descriptions, see text.

transitions, we have used the theoretical vertical excitation energies. The target states were obtained in two different ways: type 1, by converging the self-consistent-field (SCF) wave function of the $X\,^1\Sigma_g^{(+)}$ and then diagonalizing the V_{N-1} potential to obtain the improved virtual orbitals (IVO) [16] to represent the excited states; type 2, by converging the SCF wave function of the $c\,^3\Pi_u$ state, and then calculating the triplet coupled IVO's with the $1\sigma_g$ orbital of the c state kept frozen. With this basis we reproduce the two-state excitation cross sections of Lima *et al.* [17] and observed multichannel effects qualitatively similar to those obtained by Parker *et al.* [18] by using the complex Kohn variational method.

In Fig. 1, we present results of integral cross sections for the four possible transitions from the $c\,^3\Pi_u$ state of H_2 using three different approximations for the target wave functions. We have used the type 1 description with the experimental equilibrium distances of the $X\,^1\Sigma_g^{(+)}$ and $c\,^3\Pi_u$ states, and type 2 with the equilibrium separation of the $c\,^3\Pi_u$ state. The results for most of the processes are quite similar except for the $c\,^3\Pi_u \rightarrow b\,^3\Sigma_u^{(+)}$ transition, which shows slightly higher sensitivity with respect to the choice of internuclear separation.

In Fig. 2 we show the integrated cross sections for some excitations from the $c\,^3\Pi_u$ state of H_2. These results were obtained at the experimental internuclear separation of the $c\,^3\Pi_u$ state, using type 1 description for the target wave func-
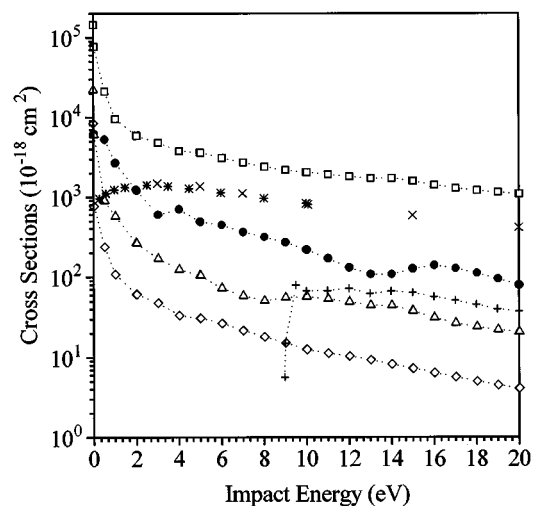

FIG. 2. Electronic transition cross sections of an excited H_2 molecule: open squares, $c\,^3\Pi_u \rightarrow c\,^3\Pi_u$; closed circles, $c\,^3\Pi_u \rightarrow a\,^3\Sigma_g^{(+)}$; open triangles, $c\,^3\Pi_u \rightarrow b\,^3\Sigma_u^{(+)}$; open diamonds, $c\,^3\Pi_u \rightarrow X\,^1\Sigma_g^{(+)}$; pluses, $X\,^1\Sigma_g^{(+)} \rightarrow c\,^3\Pi_u$; asterisks and crosses, experimental data of Refs. [19] and [20], respectively, for the $X\,^1\Sigma_g^{(+)} \rightarrow X\,^1\Sigma_g^{(+)}$ transition. We used target description (see text) of type 2 for $R_{H-H} = 1.96a_0$.
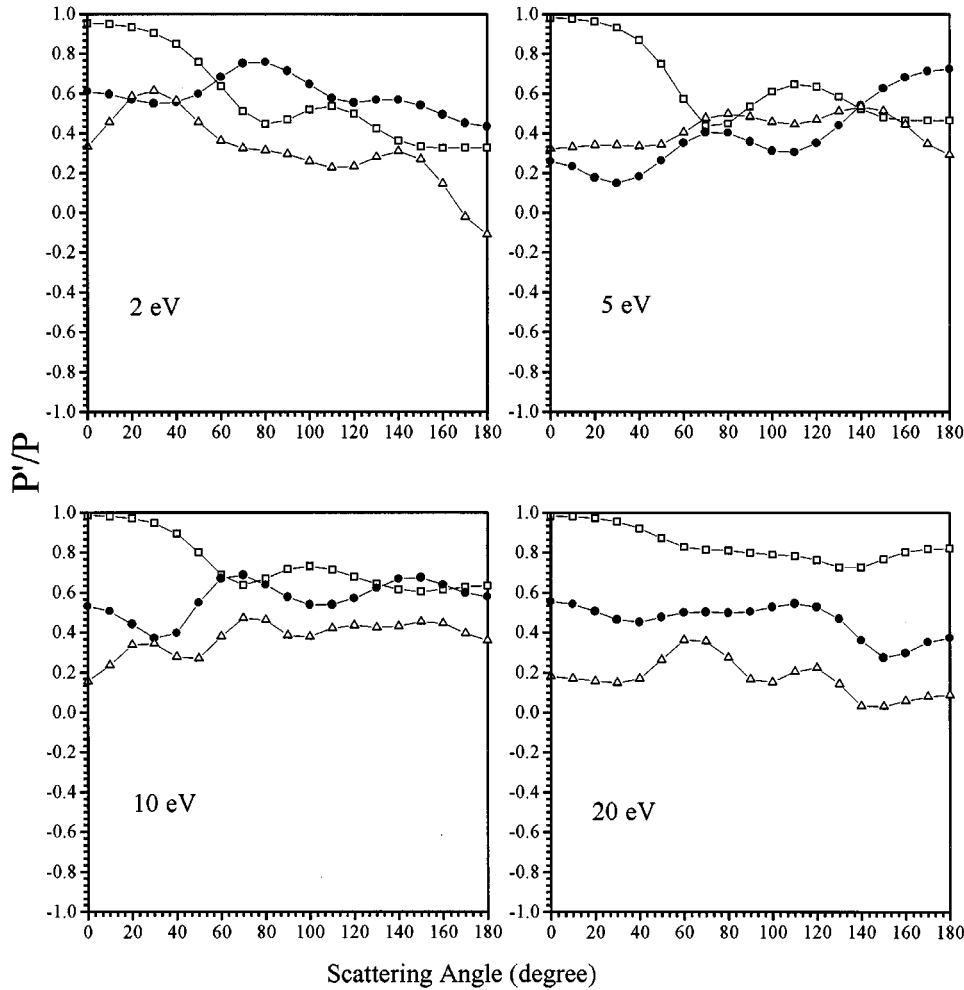
FIG. 3. Polarization fractions for transitions from the c $^3\Pi_u$ state of H_2. Open squares: c $^3\Pi_u$ → c $^3\Pi_u$; closed circles: c $^3\Pi_u$→ a $^3\Sigma_g^{(+)}$, open triangles: c $^3\Pi_u$ → b $^3\Sigma_u^{(+)}$. Results obtained with target description (see text) of type 2 for $R_{H-H} = 1.96a_0$.

tions. It includes the supereslastic c $^3\Pi_u$→ b $^3\Sigma_u^{(+)}$, c $^3\Pi_u$→ X $^1\Sigma_g^{(+)}$, the *almost elastic* c $^3\Pi_u$→ a $^3\Sigma_g^{(+)}$, and also the elastic c $^3\Pi_u$→ c $^3\Pi_u$ transitions. For comparison, our results for the X $^1\Sigma_g^{(+)}$→ c $^3\Pi_u$, and experimental results for the X $^1\Sigma_g^{(+)}$→ X $^1\Sigma_g^{(+)}$ channel [19,20] are also included. Our results show that the elastic cross section of the c $^3\Pi_u$→ c $^3\Pi_u$ transition are in general larger than the corresponding cross sections of the elastic ground-state channel by a factor of 3 but, at small energies, the ratio can be more than one order of magnitude. The cross sections for the c $^3\Pi_u$→ a $^3\Sigma_g^{(+)}$, and c $^3\Pi_u$→ b $^3\Sigma_u^{(+)}$ transitions can be very large at small energies when compared with the elastic scattering cross sections from the ground state. Our calculation shows that the cross section for the c $^3\Pi_u$→ a $^3\Sigma_g^{(+)}$ transition is always larger than the cross section for the c $^3\Pi_u$→ b $^3\Sigma_u^{(+)}$ transition. This reflects a well-known fact for excitation from the ground state: optically allowed transitions have larger cross sections.

The lack of experimental and other theoretical results limits the discussion. Nevertheless, the magnitude of the calculated cross sections indicates that some of these processes may be more important than expected for plasma modeling. For instance, in a recent publication Capitelli *et al.* [8] studied the role of superelastic collisions from electronic excited states in affecting the electron energy distribution function in a nonequilibrium H_2 discharge. In their model the superelastic scattering always occurs between the excited state and the ground state. The present study suggests that for the c $^3\Pi_u$ state, it is more likely that the superelastic scattering occurs to another excited state. The cross sections for the c $^3\Pi_u$→ a $^3\Sigma_g^{(+)}$ are larger than those for the c $^3\Pi_u$→ X $^1\Sigma_g^{(+)}$ transition by a factor of 20 and the cross section for the c $^3\Pi_u$→ b $^3\Sigma_u^{(+)}$ transitions are larger than the cross section for the c $^3\Pi_u$→ X $^1\Sigma_g^{(+)}$ transition by a factor of 4. As a result, the collision of an electron with the c $^3\Pi_u$ excited state of H_2 will most probably produce another excited state (a $^3\Sigma_g^{(+)}$ or b $^3\Sigma_u^{(+)}$) rather than the ground state. In addition, the b $^3\Sigma_u^{(+)}$ state is dissociative and the a $^3\Sigma_g^{(+)}$ state decays by light emission to the b $^3\Sigma_u^{(+)}$, so in both cases the net result is the production of fast H atoms. This may affect the dynamics of the discharge environment.

We also calculated spin-flip cross sections and spin-polarization fractions. The deviation from unity of the polarization fraction P'/P at a given scattering angle is a measure of the strength of the exchange process at that angle. The results for P'/P are shown in Fig. 3 for transitions starting from the c $^3\Pi_u$ to the final states c $^3\Pi_u$, a $^3\Sigma_g^{(+)}$ and b $^3\Sigma_u^{(+)}$ at incident energies of 2, 5, 10, and 20 eV. Surprisingly, our results show a much richer angular behavior than those obtained experimentally or theoretically for the elastic ground-state *gas-phase* molecules like O_2 and NO [13,14,21,22]. As the impact energy increases, the exchange interaction becomes less relevant for the elastic transition (c

$^3\Pi_u \to c\ ^3\Pi_u$). In electronically inelastic processes the ratio P'/P shows a stronger deviation from unity even for 20 eV. Excited states are made of more extended orbitals. These Rydberg orbitals have a bigger overlap with one-particle continuum functions, which may result in stronger exchange interactions. This effect, combined with the fact that the one-body potential influences more strongly the elastic channel, may explain why the exchange interaction is more important for inelastic transitions between excited states. Finally, it is noted that, at 20 eV, the role of the exchange interaction follows the expected pattern: it is more important in the elec-tric quadrupole allowed transition (c $^3\Pi_u \to$ b $^3\Sigma_u^{(+)}$), less important in the dipole allowed transition (c $^3\Pi_u \to$ a $^3\Sigma_g^{(+)}$) and even less important in the elastic transition (c $^3\Pi_u \to$ c $^3\Pi_u$).

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