Model potential treatment of C^{4+} + H_2 collisions at low impact energies.

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Abstract. We present cross sections for electron capture in C^{4+} + H_2 collisions in the energy range 50eV/amu$\leq E \leq$ 6keV/amu, calculated using a model potential aproximation to treat the interaction of the active electron with C^{4+} and H_2^+ cores and an equivalent-electron bielectronic interpretation of the probabilities. The limitations of this method are analyzed by comparison with the two-electron *ab initio* treatment. Double electron capture cross sections are also calculated using *ab initio* and model potential treatments. We propose a modified independent particle model to evaluate single electron capture cross sections.

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1. Introduction

Low energy (E <1keV/amu) collisions between multicharged ions and H_2 molecules have been studied recently using *ab initio* molecular wavefunctions [1]-[5]; however, these methods become cumbersome at higher energies, where a large number of channels has to be included in the close-coupling expansion. An alternative method, widely applied in ion-atom collisions (see [6] and references therein), is the use of effective potentials. In the application of this technique to collisions between fully stripped ions and H_2, one assumes that a target (active) electron moves in the field created by the nuclei and the other (core) electron. The method can be generalized to collisions involving a projectile with a closed-shell electronic structure (e.g. C^{4+} ions), by including a second effective potential to describe the ion core. Such model potential molecular treatments have been applied e.g. by Gargaud and McCarroll [7] to treat C^{4+} , N^{3+} and N^{5+} + H_2 collisions (similar calculations with larger bases are reported in [8]) . Elizaga *et al* [9] considered H^+ and Be^{4+} collisions with H_2 and compared model potential and *ab initio* results. Pseudopotentials have been used by Kumar and Saha [10] for C^{4+} and N^{5+} projectiles. Fritsch [11] has performed atomic model potential calculations for collisions of H^+, He^{2+} and C^{4+} with H_2 . Effective potentials have been also employed in classical treatments of ion-H_2 collisions: Illescas and Riera [12] (H^+), Meng *et al* [13], [14] (He^{2+}, Li^{3+}), Schultz *et al* [15](Be^{4+}), Illescas and Riera [16] (bare A^{q+} ions with q=1,...,8).

The effective potential treatment involves the solution of a one-electron (OE) dynamical problem for the active electron, leading to OE transition probabilities. As shown by Elizaga *et al* [9], a two-electron (TE) interpretation is required to evaluate transition probabilities and cross sections for the physical problem. The most commonly used is the so-called equivalent electrons interpretation [17], where the TE wavefunction is expressed as an antisymetrized product of two identical orbitals, yielding TE transition probabilities as products of the OE ones. This model will be called in this paper the independent particle model (IPM). An alternative, non-equivalent electron interpretation, has been proposed (see [6] and references therein), in which core and active electrons are described by different orbitals. Small differences between cross sections calculated using both interpretations have been found in refs. [18] (for ionization) and [9] (for electron capture).

In this work we employ a model potential approach to treat C^{4+} + H_2 collisions, for which there exist experimental measurements and *ab initio* theoretical calculations at low energy (see [3] and references therein), so that we can test the accuracy of the model potential technique and extend the calculation of charge transfer cross sections to impact energies E> 2 keV/amu. We employ a semiclassical impact parameter treatment, and we use two approximations based on the conclusions of the *ab initio* study of ref. [3]. Firstly, we shall employ a central (model) potential to describe the H_2 molecule, which is justified by the small anisotropy of the molecular data in the region of C^{4+} -H_2 distances where transitions leading to single electron capture take place. Secondly, calculations are carried out in the framework of the Franck-Condon approximation, whose accuracy for total and partial single electron capture (SEC) cross sections was discussed in ref. [3].

Although our work focuses on SEC, double electron capture (DEC) results will be shown. It is well known ([6] and references therein,[16], [19], [20]) that the IPM leads to inaccurate transition probabilities for two-electron processes (e.g. double electron capture or transfer ionization). But, at high energies, since experiments cannot distinguish between electrons produced in target ionization or transfer ionization, measured cross sections cannot be used to test the IPM results. Besides, there is a limited experience on the usefulness of the IPM at low energies. We shall illustrate the behaviour of DEC cross sections obtained with the IPM by comparison with *ab initio* calculations and the influence of this behaviour on calculated SEC cross sections. This analysis will lead us to propose a modification of the IPM to evaluate SEC cross sections.

The paper is organized as follows: In section 2 we outline the use of the IPM for C^{4+} -H_2 collisions, we study its limitations and we introduce a modified IPM (IPM-SEC). In section 3 we compare our SEC and DEC cross sections with existing theoretical and experimental values. Our conclusions are drawn in section 4. Atomic units are used unless otherwise indicated.

2. Theory

2.1. The equivalent-electron interpretation.

The first step in the application of the IPM to ion-H_2 collisions is the solution of a OE collision problem in which one considers explicitily the motion of the active electron. In the impact parameter approximation, the OE wavefunction $\psi^m(\boldsymbol{r},t)$ is a solution of

$$\left(h^m - \mathrm{i}\frac{\partial}{\partial t}\right)\psi^m(\boldsymbol{r},t) = 0 \tag{1}$$

The ion follows a rectilinear trajectory $\boldsymbol{R} = \boldsymbol{b} + \boldsymbol{v}t$ with impact parameter $\boldsymbol{b}$ and velocity $\boldsymbol{v}$, and $\boldsymbol{R}$ is the position vector of the incident ion with respect the midpoint of the H-H internuclear axis. The OE Hamiltonian h^m includes two model potentials, V_C and V_H, which describe the interaction of the active electron with C^{4+} and H_2^+ respectively:

$$h^m(\boldsymbol{r}; R) = -\frac{1}{2}\nabla^2 + V_C(r_C) + V_H(r_H) \tag{2}$$

In the calculations of this paper both model potentials, V_C and V_H are given by

$$V_k = -\frac{Z - N_c}{r_k} - \frac{N_c}{r_k}(1 + \alpha r_k)\exp(-\alpha' r_k) \tag{3}$$

For V_C, $r_k = r_C$ is the distance from the the electron to the C nucleus, $N_c = 2$, $Z = 6$, and α=4.1805, α'= 7.7260 (the accuracy of this model potential was checked in ref. [21]). For V_H, $r_k = r_H$ is the electron distance to the midpoint of the H-H internuclear axis, N_c=1, $Z = 2$, and α=3.93, $\alpha' = 2\alpha$ were obtained by fitting the H_2 ionization potential for a fixed internuclear distance of 1.4 a_0.

Equation (1) is solved with the initial condition:

$$\psi^m(\boldsymbol{r}, t) \sim_{t\to-\infty} \varphi_1^H(\boldsymbol{r}) D_H \exp(-\mathrm{i}\varepsilon_1 t) \tag{4}$$

where φ_1^H is an orbital of energy ε_1, and D_H is a plane wave translation factor which describes the translational motion of the active electron attached to the H_2 molecule. The OE probability p_j for the transition to the orbital φ_j is:

$$p_j = \lim_{t\to\infty} |< \varphi_j D_j \exp(-\mathrm{i}\varepsilon_j t)|\psi^m >|^2 \tag{5}$$

The solution $\psi^m(\boldsymbol{r}, t)$ is expanded in a set of molecular orbitals (MO) χ_j, which are (approximate) eigenfunctions of the Hamiltonian of eq. (2).

$$h^m \chi_j(\boldsymbol{r}; R) = \epsilon_j(R)\chi_j(\boldsymbol{r}; R) \tag{6}$$

The close-coupling expansion has the form:

$$\psi^m(\boldsymbol{r}, t) = D(\boldsymbol{r}, t) \sum_j a_j(t)\chi_j \exp(-\mathrm{i}\int_0^t \epsilon_j \mathrm{d}t') \tag{7}$$

where D($\boldsymbol{r}$,t) is a common translation factor (CTF) [22]. In the calculations of this paper, we have employed the CTF of ref. [23].

In order to relate the OE transition probabilities to those of the actual many-electron problem, we start by assuming that the C^{4+} closed shell core does not change during the collision, which reduces our discussion to a two-electron problem. The corresponding TE Born-Oppenheimer electronic Hamiltonian is:

$$H(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{R}) = h(\boldsymbol{r}_1) + h(\boldsymbol{r}_2) + \frac{1}{r_{12}} \tag{8}$$

with

$$h(\boldsymbol{r}_i) = -\frac{1}{2}\nabla_i^2 + V_C(r_i) - \frac{1}{r_{iH_1}} - \frac{1}{r_{iH_2}} \tag{9}$$

Where r_{H_1}, r_{H_2} are the electron distances to the H nuclei. The electronic wavefunction $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t)$ is solution of the impact parameter equation

$$\left[H - \mathrm{i}\frac{\partial}{\partial t}\right]\Psi = 0 \tag{10}$$

In the equivalent-electron IPM, H is replaced by the approximate Hamiltonian H^{IPM}

$$H^{IPM} = h^m(1) + h^m(2) \tag{11}$$

and the solution of (10) is approximated as an antisymetrized product of two identical orbitals. For a collision where H_2 is initially in its ground state, the initial TE wavefunction is a singlet, and since the Hamiltonian does not contain spin-orbit coupling, the TE wavefunction $\Psi^{IPM}(\boldsymbol{r}_1, \boldsymbol{r}_2, t)$ is:

$$\Psi^{IPM}(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = ||\psi^m \overline{\psi^m}|| \tag{12}$$

where the orbital ψ^m is a solution of equation (1) and $||\ ||$ denotes a Slater determinant.

The TE transition probabilities are obtained by projecting Ψ^{IPM} onto the corresponding asymptotic forms of the TE states in the limit $t \to \infty$:

$$\begin{aligned}
&\text{Entrance channel :}\\
&\Phi_1 = \exp(-\mathrm{i}E_1 t)||\varphi_1^H D_H\, \overline{\varphi_1^H} D_H||\\
&\text{SEC channels :}\\
&\Phi_j^{SC} = \exp(-\mathrm{i}E_j t)\frac{1}{\sqrt{2}}\left[||\xi^H D_H\, \overline{\varphi_j^C} D_C|| + ||\varphi_j^C D_C\, \overline{\xi^H} D_H||\right]\\
&\text{DEC channels :}\\
&\Phi_m^{DC} = \exp(-\mathrm{i}E_m t)\sum_{jk} c_{jk}^m \frac{N_{jk}}{\sqrt{2}}\left[||\varphi_j^C D_C\, \overline{\varphi_k^C} D_C|| + ||\varphi_k^C D_C\, \overline{\varphi_j^C} D_C||\right]\\
&\text{Single excitation channels :}\\
&\Phi_n^{EX} = \exp(-\mathrm{i}E_n t)\sum_{l\neq 1} c_l^n \frac{1}{\sqrt{2}}\left[||\varphi_1^H D_H\, \overline{\varphi_l^H} D_H|| + ||\varphi_l^H D_H \overline{\varphi_1^H} D_H||\right]
\end{aligned} \tag{13}$$

with $N_{jk} = 1$ for $j \neq k$ and $N_{jk} = 2^{-1/2}$ for $j = k$. The coefficients c_{jk}^m, c_l^n are obtained by diagonalizing the matrix corresponding to the asymptotic form of the 'exact' Hamiltonian H in the basis of TE functions $\frac{N_{jk}}{\sqrt{2}}\left[||\varphi_j^C\, \overline{\varphi_k^C}|| + ||\varphi_k^C\, \overline{\varphi_j^C}||\right]$ and $\frac{1}{\sqrt{2}}\left[||\varphi_1^H\, \overline{\varphi_l^H}|| + ||\varphi_l^H \overline{\varphi_1^H}||\right]$ respectively, and E_p are the energies of these states. In (13)

ξ^H is the ground MO of H_2^+ and we have assumed that the entrance channel wavefunction is represented by a single configuration. SEC transition probabilities are given by:

$$P_j^{SC} = \lim_{t\to\infty} |< \Phi_j^{SC} \mid \Psi^{IPM} >|^2 = 2p_j p_1 \tag{14}$$

where $p_1 =| a_1(\infty) |^2$ and p_j, the OE transition probability to φ_j^C(see ec.(5)), is obtained by solving (1) with the initial condition (4). We have taken, as usual (see e.g. [6] and references therein),$< \xi^H \mid \varphi_1^H >= 1.0$. In deriving (14) we have assumed that φ_j^C is the asymptotic form of the MO χ_j. Similarly DEC and single excitation probabilities are:

$$P_m^{DC} = \lim_{t\to\infty} |< \Phi_m^{DC} \mid \Psi^{IPM} >|^2 = \sum_{jk} |c_{jk}^m|^2 p_j p_k \tag{15}$$

and

$$P_n^{EX} = \lim_{t\to\infty} |< \Phi_n^{EX} \mid \Psi^{IPM} >|^2 = \sum_{l\neq 1} |c_l^n|^2 p_l p_1 \tag{16}$$

The total probabilities for SEC and DEC are obtained by summing P_j^{SC} and P_m^{DC}, respectively, over all exit channels:

$$\begin{aligned} P^{SC} &= \sum_j P_j^{SC} = 2p_1 p_c \\ P^{DC} &= \sum_m P_m^{DC} = p_c^2 \\ P^{EX} &= \sum_n P_n^{EX} = 2p_1 p_{ex} \end{aligned} \tag{17}$$

where p_c is the total OE capture probability and p_{ex} the total OE excitation probability. The total cross section σ_j is obtained by using:

$$\sigma_j = 2\pi \int_0^\infty b P_j(b) \mathrm{d}b \tag{18}$$

where $P_j(b)$ is the corresponding transition probability.

The TE transition probabilities obtained from eqs. (17) show two characteristics: 1) The SEC probability P^{SC} is always less than $\frac{1}{2}$. 2) The ratio between P^{SC} and P^{DC} is equal to $2p_1/p_c$, which implies that P^{DC} always increases when P^{SC} increases. These two properties are in general not found in many-electron calculations, pointing to a limitation of the IPM.

2.2. The IPM-SEC approximation

To improve the IPM in the treatment of SEC, we draw from the conclusions of Elizaga *et al* [9] who showed that, when a diabatic molecular basis is employed, there exists a simple relationship between matrix elements of H (eq. (8)) and H^{IPM} (eq. (11)).

Diabatic MOs ,$\{\chi_j^d\}$, are constructed [24] by a unitary transformation of the set $\{\chi_j\}$ of eq. (6) so that the radial part (including the CTF corrections) of the one-electron dynamical coupling vanishes. The transformation is defined so that diabatic MOs tend to atomic orbitals at large internuclear distances. We then construct the set of TE wavefunctions $\phi_{kl}(\boldsymbol{r}_1, \boldsymbol{r}_2, t)$:

$$\phi_{kl} = \frac{N_{kl}}{\sqrt{2}} \left[||\chi_k^d \overline{\chi_l^d}|| + ||\chi_l^d \overline{\chi_k^d}|| \right] \tag{19}$$

where N_{kl} was defined after eq. (13). The 'exact' TE wavefunction Ψ is expanded as:

$$\Psi = D(\boldsymbol{r}_1, t) D(\boldsymbol{r}_2, t) \sum_{kl} a_{kl}(t) \phi_{kl}(\boldsymbol{r}_1, \boldsymbol{r}_2) \exp[-\mathrm{i} \int_0^t E_{kl} \mathrm{d}t'] \tag{20}$$

with $E_{kl} =< \phi_{kl}|H|\phi_{kl} >$. Substitution of (20) in (10) yields a system of differential equations for the expansion coefficient a_{jk}:

$$\begin{aligned} \mathrm{i}\frac{\mathrm{d}a_{jk}}{\mathrm{d}t} &= \sum_{lm} a_{lm} < \phi_{jk} D(\boldsymbol{r}_1, t) D(\boldsymbol{r}_2, t) | H - \mathrm{i}\frac{\partial}{\partial t} | \phi_{lm} D(\boldsymbol{r}_1, t) D(\boldsymbol{r}_2, t) > \times \\ &\times \exp[-\mathrm{i} \int_0^t (E_{lm} - E_{jk})] \mathrm{d}t' \end{aligned} \tag{21}$$

The transition probabilities can be expressed in terms of the coefficients a_{kl} of (20). In particular, those considered in the IPM expressions (14), (15), (16) are now:

$$\begin{aligned} \mathcal{P}_j^{SC} &= \lim_{t \to \infty} |a_{1j}|^2 \\ \mathcal{P}_m^{DC} &= \lim_{t \to \infty} \sum_{jk} |c_{jk}^m a_{jk}|^2 \\ \mathcal{P}_n^{EX} &= \lim_{t \to \infty} \sum_{l} |c_{ln}^n a_{l1}|^2 \end{aligned} \tag{22}$$

The explicit comparison between the matrix elements of H and H^{IPM} in the *ab initio* and IPM formalisms, is shown in the appendix. This extends the analysis of ref. [9] by including more than two molecular orbitals, and explicitely considering DEC wavefunctions. From this comparison we conclude that the main difficulty in applying the IPM lies on the matrix elements involving DEC functions, which contain unphysical repulsive terms of the form $< \varphi_1^H \chi_j^d | \frac{1}{r_{12}} | \varphi_1^H \chi_l^d >$. These do not vanish at large internuclear separations and are related to the impossibility of describing, by means of the effective potential treatment (eqs. (2) and (11)), the electron-electron interaction when both electrons are near the projectile nucleus. Differences between exact and approximate expressions are less important for the Hamiltonian matrices in the basis of the entrance channel ϕ_{11} and the SEC functions ϕ_{1j}. In particular, exact and approximate matrices are identical (except for a constant shift of the diagonal matrix elements) if:

1) $\chi_1^d \simeq \varphi_1^H$, which is required to ensure that the interactions between the entrance channel ϕ_{11} and SEC functions ϕ_{1j} from eqs. (A.3) and (A.2) are identical. It is clear from this that the transformation to diabatic MOs is needed to keep the asymptotic character of the function χ_1^d.
2) The extra term $< \varphi_1^H \chi_1^d | \frac{1}{r_{12}} | \varphi_1^H \chi_1^d > \simeq < \varphi_1^H \varphi_1^H | \frac{1}{r_{12}} | \varphi_1^H \varphi_1^H >$, appearing in the diagonal matrix elements of the approximate Hamiltonian (see (A.2)), is roughly constant. Then this unphysical term only introduces a shift of the energies.
3) The exchange terms, which do not appear in the approximate expression (A.2) $< \chi_1^d \chi_j^d | \frac{1}{r_{12}} | \chi_k^d \chi_1^d >$, can be neglected.

In general these conditions are fulfilled at large enough R.

For systems where the interactions between both the entrance channel and SEC functions with DEC functions are not effective, these DEC functions can be removed from the expansion (20). Assuming that conditions 1-3 are fulfilled to a reasonable approximation, the matrix elements of H can be replaced by those of H^{IPM} in eq. (21), yielding SEC and excitation transition probabilities (eq. (22)). This approximation will be called IPM-SEC to distinguish it from the IPM (eqs. (14), (15), (16)). In practice, the computational effort involved in this approximation is similar to that of the usual IPM, since the same number of coupled channels is involved in both, and the TE coupling matrix elements are simple combinations of the OE ones required to evaluate the transition probabilities p_j of (5).

3. Calculations.

3.1. Molecular calculation.

As was explained in ref. [3], the electronic energies of the entrance channel (which dissociates into $C^{4+}(1s^2)$ + H_2 ($X^1\Sigma_g^+$)) and the main SEC states (dissociating into $C^{3+}(1s^2 3l)$+ $H_2^+(X^2\Sigma_g^+)$) , lie above those of the Rydberg series formed by states dissociating into $C^{2+}(1s^2 2lnl)$ + H^+ + H^+. Since these states are only populated at very low energies, they were removed from the *ab initio* basis using a block diagonalization (BD) technique, which lead to a basis containing only the entrance channel and SEC molecular functions. The dependence of the *ab initio* molecular data with α, the angle between the vectors $\boldsymbol{R}$ and $\boldsymbol{\rho}$, is small (see ref. [3]), especially in the regions where the most important transitions leading to SEC take place. To compare with model potential results and to explain the mechanism of SEC, we have plotted in fig. 1 (curves

1B-7B) the energies calculated in ref [3] for $\alpha = 45°$(the value employed in the dynamical calculation of [3]) and fixed H-H internuclear distance ρ=1.4 a_0 . In this figure narrow avoided crossings between 4B, and 5B, 6B and 7B curves have been crossed diabatically.

In the present work we have evaluated the MOs using the model potential approach of eqs. (2), (3) and (6). These MOs are expressed in terms of a basis $\{\mathcal{F}_k\}$, which includes a set of 20 two-center functions, that are solutions of the two-Coulomb-center Schrödinger equation:

$$\left(-\frac{1}{2}\nabla^2 - \frac{4}{r_c} - \frac{1}{r_H}\right)\mathcal{F}_k = \lambda_k \mathcal{F}_k \tag{23}$$

These functions are therefore one-electron-diatomic-molecule (OEDM) orbitals for the quasimolecule BeH^{4+}. As in ref. [21], we have added a set of 48 Gaussian type orbitals (30 centred on C and 18 on H_2) to increase the flexibility of the basis in order to describe the effect of the cores on the MOs. Diagonalization of the OE Hamiltonian matrix in the basis yields a set of 68 MOs. From them we have selected 20 MOs to include in the dynamical treatment; these are the MOs correlating at $R \to \infty$ to C^{3+}(nl) orbitals with n = 2, 3 and 4, and the MO (χ_1 in the notation of section 2) which correlates to the ground orbital of H_2 . In the IPM, the wavefunction ψ^m is expressed as a linear combination of these MOs (eq. (7)). To apply the IPM-SEC formalism, we have transformed the MOs χ_j into diabatic functions χ_j^d and we have constructed a set of TE functions $\{\phi_{1j}\}$ with j=1,2,...,20 (see eq. (19)). The coupling matrix elements of eq. (21) are easily evaluated as combinations of the OE matrix elements $< \chi_j^d D | h^m - \mathrm{i}\partial/\partial t | \chi_k^d D >$. It can be noted that, since in both cases DEC channels are removed, the IPM-SEC method can be regarded as the model potential counterpart of the BD *ab initio* treatment.

In order to compare IPM-SEC molecular data with the *ab initio* ones of ref. [3], we have diagonalized the IPM-SEC Hamiltonian matrix $\underline{\boldsymbol{H}}^{IPM}$, whose elements are $H_{jk}^{IPM} =< \phi_{1j} | H^{IPM} | \phi_{1k} >$, yielding energies E_n, which are compared in fig. 2 with those from the BD calculation. As explained in ref. [3], there is a one-to-one correspondence between the wavefunctions obtained in the BD procedure and diagonalizing the whole $\underline{\boldsymbol{H}}$ matrix (the adiabatic states) for $R > 4.0 a_0$, with energy differences between both calculations smaller than 10^{-3}Hartree. Likewise, the good agreement between IPM-SEC and BD energy differences for $R > 4.0$ a_0 indicates that they also agree with the adiabatic ones. For $R < 4.0$ a_0, the interaction between SEC and DEC functions starts to be sizeable, and we find some discrepancies between BD and IPM-SEC energies in fig.2.

To complete the comparison between *ab initio* BD and IPM-SEC methods, we have calculated the radial couplings between the IPM-SEC functions Ψ_m by using the relationship (see [25] and refs. therein):

$$M_{mn} = \underline{\boldsymbol{b}}_m^\dagger \underline{\boldsymbol{b}}_n^R = (E_n - E_m)^{-1}\, \underline{\boldsymbol{b}}_m^\dagger (\frac{\mathrm{d}}{\mathrm{d}R}\underline{\boldsymbol{H}}^{IPM})\underline{\boldsymbol{b}}_n \tag{24}$$

where M_{mn} is the component of the dynamical coupling $< \Psi_m D(\boldsymbol{r}_1, t) D(\boldsymbol{r}_2, t) | H^{IPM} - \mathrm{i}\partial/\partial t | \Psi_n D(\boldsymbol{r}_1, t) D(\boldsymbol{r}_2, t) >$ proportional to the radial velocity . The superscript R indicates derivation with respect to R, and $\underline{\boldsymbol{b}}_m$ is the column vector whose components b_{jm} are the coefficients of the expansion of Ψ_m in terms of the basis functions ϕ_{1j}. It must be noted that, since the diabatic MOs were obtained by integrating the radial component of the OE dynamical couplings, which included the translation factor corrections, the TE couplings calculated in (24) also include these corrections. As an illustration, we compare in fig. 3 the most important couplings with the corresponding ones of ref. [3]. Although general good agreement is found, small differences in the height of the peaks are noticeable.

3.2. Dynamical calculations.

3.2.1. Single electron capture cross sections. As is by now well known, the absence of ionization channels in the basis can lead to overpopulation of charge transfer channels when ionization starts to be sizeable. Then calculated charge transfer cross sections really correspond to the sum of charge transfer and ionization ones (see [26]). Extrapolation to low v of the experimental results [27] indicates that ionization starts to compete with SEC at E >10keV/amu, and accordingly we observe an increase of the calculated SEC cross section at these energies, so that we have plotted our results in fig. 4 up to 6keV/amu.

Cross sections were obtained from eq. (18) with the transition probabilities evaluated in three different ways: 1) the IPM-SEC (eq. (22)), 2) the IPM formalism (eq. (14)), and 3) monoelectronic transition probabilities p_j defined in (5). This last calculation is presented to illustrate the need of a TE interpretation and to compare with previous calculations. The corresponding total cross sections, $\sigma^{SC} (= \sum_j \sigma_j^{SC})$, are shown in fig. 4a together with the sudden approximation results of ref. [3] and experimental values of Phaneuf *et al* [28] , Dijkkamp *et al* [29] and Itoh *et al* [30]. We have also included in this figure the results for SEC into $C^{3+}(1s^2\ 3l)$ (σ_3) of Hoekstra *et al* [31], because at low v σ^{SC} is practically identical to σ_3. Comparison with total cross sections from previous effective potential calculations (refs. [7],[8], [10], [11]), as well as with the FC results of [3] is shown in fig. 4b.

From the comparison of fig. 4a, it is clear that the IPM calculation underestimates σ^{SC} for $E < 1$keV/amu, while at higher energies differences with the experimental values are smaller than 10%, hence than experimental error bars. The monoelectronic calculation underestimates σ^{SC} in the whole energy range of fig. 4a, and the IPM-SEC calculation leads to σ^{SC} cross sections in reasonably good agreement with both *ab initio* and experimental values. The experimental error bars at $E >$1keV/amu do not allow us to conclude on the quality of the different calculations by comparison with experiments.

Previous calculations of Gargaud and McCarroll [7], [8] and Kumar and Saha [10] do not use any TE interpretation, so that they are similar to our monoelectronic calculation. In both works V_H was determined by fitting the experimental H_2 ionization potential, which is the difference between H_2^+ and H_2 energies at their equilibrium distances, rather than, according to the FC approximation, for a fixed H-H internuclear distance of 1.4 a_0. A compensation of errors introduced by these two approximations is responsible for the larger total SEC cross obtained in the calculations of refs. [8] and [10] when compared with our IPM values. In spite of the similar treatment employed in [8] and [10], large discrepancies betweeen both calculations are noticeable in fig.4. To understand their origin, we have recalculated σ^{SC} using the model potential of refs. [7], [8] and their largest (7-term) basis set. We have found small differences (less than 5 %) with the values of ref. [8], and similar differences for E<1keV/amu when the size of the basis set is increased from 7 to 20 MOs, which indicates that differences between the results of refs. [10] and [8] are not due to the smaller basis set used in the latter calculation. We conclude that the odd shape of the cross section of [10] is probably due to an inaccurate molecular calculation. In particular, we note that the maxima of the radial couplings at $R \simeq 8$ and 9.5 a_0 in fig. 3 appear in ref. [10] at $R \simeq$10.75 and 12.0 a_0 respectively, which explains that we are not able to reproduce the results of [10].

Partial cross sections $\sigma_{S,P,D}$ for SEC into C^{3+}(3s, 3p and 3d) respectively are presented in fig. 5a-c. The general behaviour is similar to that described for σ^{SC} with the exception of the IPM result for σ_S at $E <$500eV/amu, which shows better agreement with experiment than *ab initio* and IPM-SEC results. However, the IPM σ_S does not reproduce the shape of the experimental cross section, and the agreement with the experiment at low v is due to the general underestimate of the SEC cross section by the IPM. To further illustrate this point, we have plotted in fig. 6, for E=250eV/amu, the products $b\,P^{SC}_{S,P}(b)$ for population of C^{3+}(3s, 3p) levels. Transition probabilities P^{SC}_{S}, obtained in the IPM-SEC and *ab initio* calculations are very similar, while a strong discrepancy with the IPM results for P^{SC}_{S} is found. The small σ^{SC}_{S} obtained in the IPM calculation (fig. 5a) is a consequence of the limitations of this method at low velocities, where the Stuckelberg-type oscillations of the transition probabilities cannot be reproduced by eq. (17). At higher energies ($E > 800$eV/amu), phase effects become less important, and the IPM yields SEC cross sections in good agreement with experiments (see figs. 4a and 5a). It can be noted that the largest differences in fig 6a appear at impact parameters where the *ab initio* transition probabilities are larger than 0.5, a value which cannot be attained in the IPM (see section 2). Since the values of P^{SC}_{P} are smaller than 0.5, the differences between IPM and *ab initio* transition probabilities are smaller for this last transition probability. Finally, although the overall shape of IPM-SEC P^{SC}_{P} is very similar to that obtained in the *ab initio* calculation, some differences are noticeable in fig. 6 which are probably due to the different height of the peak of the radial coupling $2B - 4B$ at $R \simeq 9.5$ a_0 (see fig. 3).

3.2.2. Double electron capture cross sections. In order to study the limitations of the IPM for this particular system, we have carried out an *ab initio* calculation of DEC cross section using approximations similar to those employed in the model potential approach: the FC approximation and a fixed angle (45°) between vectors $\boldsymbol{R}$ and $\boldsymbol{\rho}$. Since no DEC channels are obtained in the BD calculation, we have selected them from the adiabatic states obtained by diagonalizing the full Hamiltonian matrix (see [3]); these states have been added to the BD basis set, and their energies are plotted (dashed lines) in fig. 1. One can note in this figure that the energy of the ground state of the BD calculation (1B) joins smoothly with that of the fourth adiabatic state for $R \simeq 4.5$ a_0, thus allowing us to use the BD state for large internuclear distances and the adiabatic state for $R < 4.5$ a_0. The DEC reaction takes place through transitions from the molecular state of character C^{4+}+ H_2 to those dissociating into $C^{2+}(1s^2 2s3l)$ + H^+ + H^+; these are populated in the avoided crossings region at $R \simeq 4.0$ a_0. Given the large energy gaps, transitions from SEC to DEC states are unlikely, and couplings between them have been neglected.

The calculated DEC cross sections are compared in fig. 7 with experimental results of refs. [30], [33]. SEC cross sections are practically identical to those of ref. [3] already shown in figs. 4 and 5. Given the small number of DEC states in the calculation and the fact that the anisotropy of the molecular data has not been taken into account, the agreement with experiment is reasonable. In particular, the similar dependence on E of calculated and measured DEC cross sections confirms that $C^{2+}(1s^2 2s3l)$ states are the main products of the DEC reaction, and that the dominant mechanism for DEC involves transitions at the avoided crossings region $R \simeq 4a_0$.

In fig. 7 we have also included the DEC cross sections obtained by using the IPM expression (15), which leads to a large overestimation, similar to those found in IPM classical calculations [16]. Analysis of our IPM results shows that, in contrast to experiments and the *ab initio* data, in the IPM calculation the contributions to the DEC cross section from transitions to C^{2+} bound states are very small at E <1keV/amu, while the main output are the autoionizing states C^{2+}(3l3l'). However, population of C^{2+}(3l3l') in a close coupling calculation is in fact unlikely since the corresponding molecular energy curves show narrow avoided crossings at very large R, which are traversed diabatically. Besides, doubly excited C^{2+} ions would ionize before reaching the detector, producing C^{3+}(n=2), which is not observed. Therefore,the description of DEC in the IPM is unphysical.

4. Conclusions.

We have carried out a calculation of SEC cross sections in C^{4+}+ H_2 collisions using a model potential to describe the interaction of the active electron with the H_2^+ core. Comparison to previous experimental and theoretical works, allows us to discuss the limitations of these approach. For C^{4+} + H_2 collisions, SEC takes place at large internuclear separations where anisotropy is not important, therefore, in the energy range considered in this paper, the approximation of using a central model potential is less critical than the difficulty derived from the two electron interpretation of the transition probabilities. Then, as found in [9], the critical point in the use of one-electron effective potentials is the TE interpretation used to evaluate the transition probabilities from the OE molecular data. Our results show that the usual IPM leads to incorrect SEC cross sections for $E \lesssim 800$eV/amu where SEC transition probabilities are larger than 0.5. In this energy range, the IPM yields unphysical large DEC cross sections and underestimates the SEC cross section.

For C^{4+} + H_2 collisions, an alternative to the IPM is the IPM-SEC treatment proposed in this work. In this treatment, the DEC channels, which are incorrectly described in the IPM, are removed from the basis set. This method allows us to accurately calculate SEC total cross sections for impact energies in the energy range 50eV/amu< E <6keV/amu (with possible extensions to higher energies by including pseudostates in the basis set). Our results indicate that one can employ an effective potential for the H_2 molecule to calculate SEC cross sections provided that two-electron processes are not competitive. At high impact energies where SEC transition probabilities are small, the usual IPM is appropriate to evaluate SEC cross sections. The IPM-SEC allows to enlarge this energy range in a simple way. However, a different modification is required to treat systems where DEC compete with SEC.

Appendix

The model potential of eq. (3) can be considered in an approximate way as a particular case of:

$$V_H(r) = -\frac{1}{r_{H_1}} - \frac{1}{r_{H_2}} + \int \mathrm{d}\boldsymbol{r}' \varphi_1^{H*}(\boldsymbol{r}') \frac{1}{|\boldsymbol{r}' - \boldsymbol{r}|} \varphi_1^H(\boldsymbol{r}') \tag{A.1}$$

Where r_{H_1}, r_{H_2} are the electron distances to the H nuclei and φ_1^H the orbital describing the core electron state. Substituting (A.1) into (2) and (11), we obtain the following expressions for the matrix elements of H^{IPM}:

$$\begin{aligned} < \phi_{jk}|H^{IPM}|\phi_{lm} > &= (h_{jl}\delta_{km} + h_{km}\delta_{jl} + h_{jm}\delta_{kl} + h_{kl}\delta_{jm} + \\ &+ < \varphi_1^H \chi_j^d|\frac{1}{r_{12}}|\varphi_1^H \chi_l^d > \delta_{km} + < \varphi_1^H \chi_k^d|\frac{1}{r_{12}}|\varphi_1^H \chi_m^d > \delta_{jl} + \\ &+ < \varphi_1^H \chi_j^d|\frac{1}{r_{12}}|\varphi_1^H \chi_m^d > \delta_{kl} + \\ &+ < \varphi_1^H \chi_k^d|\frac{1}{r_{12}}|\varphi_1^H \chi_l^d > \delta_{jm}) N_{jk} N_{lm} \end{aligned} \tag{A.2}$$

where $h_{jk} =< \chi_j^d|h|\chi_k^d >$ with h the OE Hamiltonian of (9). $N_{jk} = 1$ for$j \neq k$ and $N_{jk} = 1/\sqrt{2}$ for$j = k$. ϕ_{11} represents the entrance channel, ϕ_{1j} are SEC functions and ϕ_{jk} DEC ones.

The matrix elements of the Hamiltonian (8) are:

$$\begin{aligned} < \phi_{jk}|H|\phi_{lm} > &= (h_{jl}\delta_{km} + h_{km}\delta_{jl} + h_{jm}\delta_{kl} + h_{kl}\delta_{jm} + \\ &+ < \chi_j^d \chi_k^d|\frac{1}{r_{12}}|\chi_l^d \chi_m^d > + \\ &+ < \chi_j^d \chi_k^d|\frac{1}{r_{12}}|\chi_m^d \chi_l^d >) N_{jk} N_{lm} \end{aligned} \tag{A.3}$$

The main conclusions drawn from the comparison of eqs. (A.3) and (A.2) are:

(i) The interaction between the entrance channel ϕ_{11} and the SEC functions ϕ_{1j} are identical in the exact and approximate expressions (see also [9]) if one assumes that the diabatic MO χ_1^d is identical to φ_1^H, the ground MO of H_2 .

(ii) The diagonal matrix elements of H^{IPM} for the entrance channel and SEC functions contain the extra term $< \varphi_1^H \chi_1^d | \frac{1}{r_{12}} | \varphi_1^H \chi_1^d > \simeq < \chi_1^d \chi_1^d | \frac{1}{r_{12}} | \chi_1^d \chi_1^d >$, i.e. they include electron-electron repulsion terms twice.

(iii) The interaction between DEC functions ϕ_{jk} and ϕ_{lm} includes, in the approximate expressions, unphysical electron-electron repulsion terms of the form $< \varphi_1^H \chi_j^d | \frac{1}{r_{12}} | \varphi_1^H \chi_l^d >$. Similar unphysical terms are found in the interactions between SEC and DEC functions. However, repulsive terms of the form $< \chi_j^d \chi_k^d | \frac{1}{r_{12}} | \chi_l^d \chi_m^d >$ do not appear in the approximate expression (A.2).

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Figure captions

Figure 1. Energies of the electronic states of the CH_2^{4+} quasimolecule for ρ =1.4 $a_0$and α=45 °. Full lines, energies of the first seven roots of the block diagonalization calculation of ref. [3]. Dashed lines, energies of the adiabatic states included in the calculation of the DEC cross section.

Figure 2. Energy differences for the states mentioned in the figure. —, *ab initio* calculation of ref. [3]; - - - , IPM-SEC calculation.

Figure 3. CTF modified radial couplings. —, *ab initio* calculation of ref. [3]; - - - , IPM-SEC calculation.

Figure 4. Total SEC cross sections. (a)Comparison with *ab initio* and experimetal data.Present results: ...◇..., IPM-SEC; - - ×- - , monoelectronic; - - ○- - , IPM. –◆– *ab initio*, sudden approximation results of ref. [3]. Experimental results for total SEC: ▼ charge analysis results of ref. [29]; ■, spectroscopic results of ref. [29]; ◁, [30]; * [28]. •, experimental results of ref. [31] for SEC into C^{3+}(n=3). (b) Comparison with other calculations: Present result, as in fig. 4a; - - + - -, FC *ab initio* results of ref. [3]; - - ■ - -, [8]; -·-·, [10]; - -□- -, [11].

Figure 5. Partial SEC cross sections (a)σ_S, (b)σ_P, (c)σ_D for population of C^{3+}(3s, 3p, 3d) levels. ▲,ref. [32]. The other symbols as in fig.4.

Figure 6. $bP(b)$ for electron capture into C^{3+}(3s, 3p) at E=250eV/amu: full line, *ab initio* calculation; dotted-dashed line, IPM result; dashed line, IPM-SEC result; dotted line, monolectronic result.

Figure 7. DEC cross sections. +—+ , *ab initio* calculation; - - × - - , IPM total DEC cross section; - - *- - , IPM result for DEC into C^{2+}(2s3l) states. Experimental results: ■, ref. [33]; ref.[30].