LETTER TO THE EDITOR

H_2^+ vibrational distribution after single-electron capture in $C^{2+}(2s2p;^3P)+H_2$ collisions

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Abstract. The vibrational distribution of $H_2^+(X^2\Sigma_g^+;\nu)$ after charge transfer in $C^{2+}(2s2p;^3P)+H_2$ collisions is obtained *ab initio* using the semiclassical eikonal method and the sudden approximation. Results are in good agreement with experiment (Leputsch *et al* 1997).

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$C^{2+}+H_2$ collisions have received experimental attention during the last ten years. Unterreiter *et al* (1991) measured absolute total cross sections and state-selective translational energy spectra (TES) for collisions of C^{2+} ions, in both ground $(1s^22s^2;^1S)$ and metastable $(1s^22s2p;^3P)$ states, with H_2. Leputsch *et al* (1997) increased the resolution of the experiment with the metastable projectile $C^{2+}(^3P)$ and obtained peaks in the TES that were assigned to individual vibrational states of H_2^+ formed in the reaction leading to $C^+(1s^22s2p^2;^2D)+H_2^+(X^2\Sigma_g^+)$. In the experimental energy range (600 eV–1 keV), the vibrational distribution displays a noticeable shift compared to the Franck-Condon (FC) one. Other (small) peaks in the TES were assigned to transitions to $C^+(1s^22s2p^2;^2S)+H_2^+(X^2\Sigma_g^+)$ and $C^+(1s^22s^22p;^2P)+H_2^+(B^2\Sigma_g^+)$. Experiments on collisions with C^{2+} have also been carried out in Belfast (Greenwood *et al* 1996, Burns *et al* 1997, Voulot *et al* 2000) using double translational energy spectroscopy. The TES for electron capture in $C^{2+}(^3P)+H_2$ collisions was recorded at E=4 and 6 keV. Although these experiments do not show vibrational resolution, the shape of the peaks is not significantly shifted from the FC prediction.

On the theoretical side, vibrational state-to-state charge transfer cross sections in ion-molecule collisions are often calculated, at very low energies (few eV), using methods

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based on the Infinite Order Sudden Approximation (IOSA) formalism (e.g. Baer 1992 and references therein). At higher energies, our group has developed a method that uses the sudden approximation for vibration and rotation. This method has been applied to evaluate state-to-state vibrational cross sections in Be^{4+}(Errea *et al* 1997), C^{4+} (Errea *et al* 1999*a*) and H^+ (Elizaga *et al* 2000) collisions with H_2 in the impact energy range 50 eV/amu–2 keV/amu. Significant deviations from the simple FC approximation were found, hence, explicit comparison with vibrationally resolved measured data is useful.

With the goal of checking the accuracy of our method with the data of Leputsch *et al* (1997), we treat the process:

$$\mathrm{C}^{2+}(2\mathrm{s}2\mathrm{p};{}^3\mathrm{P}) + \mathrm{H}_2(\mathrm{X}^1\Sigma_\mathrm{g}^+, \nu = 0) \to \mathrm{C}^+(2\mathrm{s}2\mathrm{p}^2;{}^2\mathrm{D}) + \mathrm{H}_2^+(\mathrm{X}^2\Sigma_\mathrm{g}^+, \nu). \quad (1)$$

In a former work on C^{2+}+H_2 collisions (Errea *et al* 1999*b*) (I, hereafter), we evaluated total charge transfer cross sections using the FC approximation. In this work, we enlarge the molecular basis and use the more general sudden approximation.

The method we use is described in detail in I and (Errea *et al* 1999*a*). Here we only summarize the procedure:

(i) Molecular data (energies and dynamical couplings) for the triatomic CH_2^+ are obtained *ab initio* using MELD (Davidson 1990), modified as explained in (Castillo *et al* 1995).

(ii) The sudden approximation for rotation and vibration is employed to obtain the vibrational state-to-state cross sections. The electronic transitions are calculated using the semiclassical eikonal method (see e.g. Bransden and McDowell 1992): for fixed H_2 target position, the ion follows rectilinear trajectories with impact parameter $\boldsymbol{b}$ and velocity $\boldsymbol{v}$, $\boldsymbol{R} = \boldsymbol{b} + \boldsymbol{v}t$. The wavefunction Ψ describing the collision is solution of

$$\left(H_{\mathrm{int}} - \mathrm{i}\, \frac{\partial}{\partial t}\bigg|_{r,\rho} \right) \Psi(\boldsymbol{r}, \boldsymbol{\rho}, t) = 0 \quad (2)$$

where H_{int} is the total Hamiltonian without the kinetic energy term associated to the coordinate R . The wavefunction Ψ is expanded as:

$$\Psi(\boldsymbol{r}, \boldsymbol{\rho}, t) = \chi_0(\rho) Y_{JM}(\hat{\boldsymbol{\rho}}) \sum_k a_k(\boldsymbol{\rho}, t)\phi_k(\boldsymbol{r}; \boldsymbol{R}, \boldsymbol{\rho}) \exp\left(-\mathrm{i} \int_0^t \epsilon_k \mathrm{d}t' \right) \quad (3)$$

where $\chi_0(\rho) Y_{JM}(\hat{\boldsymbol{\rho}})$ is the initial rovibrational wavefunction of H_2, and $\phi_k(\boldsymbol{r}; \boldsymbol{R}, \boldsymbol{\rho})$ are electronic wavefunctions of the triatomic quasimolecule CH_2^{2+} with energies ϵ_k.

The wavefunctions ϕ_k depend on three parameters: R, the distance from the projectile to the H_2 centre of mass; ρ, the H-H internuclear distance; and θ, the angle between $\boldsymbol{R}$ and $\boldsymbol{\rho}$. This last angle can be taken constant when anisotropy effects in the projectile-target interactions are small, as is the case in C^{2+}-H_2 because relevant curve crossing leading to charge transfer transitions occur at relatively large R (see I). In this case we have taken θ=0. With this, the coefficients a_k are independent of the orientation angle $\hat{\boldsymbol{\rho}}$. Substituting (3) in (2) leads to a set of differential equations for the coefficients a_k. The probability $P_{\nu f}$ for transition from the vibronic state $\{0i\}$ to $\{\nu f\}$ is given by

$$P_{\nu f}(b,v) = \left| \int \mathrm{d}\rho \chi_0 \chi_\nu \exp\left[-\mathrm{i} \int_0^\infty \mathrm{d}t (\epsilon_f - E_f) \right] a_f(\infty, \rho) \right|^2 \quad (4)$$

where E_f is the asymptotic energy of the vibronic state $\{\nu f\}$. The total cross section for the transition $\{0i\} \rightarrow \{\nu f\}$ is, in the isotropic approximation we are employing (Elizaga *et al* 2000),

$$\sigma_{\nu f}(v) = 2\pi \int_0^\infty b P_{\nu f} \mathrm{d}b\,. \quad (5)$$

It is useful to define the quantities $P_n^e(\rho, b, v)$ and $\sigma_n^e(\rho, v)$ for a fixed ρ and v as

$$P_f^e(\rho, b, v) = |a_f(\infty, \rho)|^2 \quad (6)$$

$$\sigma_f^e(\rho, v) = 2\pi \int_0^\infty b P_f^e(\rho, b, v)\, \mathrm{d}b. \quad (7)$$

When $\rho = \rho_0$, the target equilibrium distance, equations (6) and (7) yield the familiar FC transition probability and cross section respectively.

From equation (5), and using the closure relations for the vibrational functions χ_ν, the total cross section for transition to the electronic state f is given by

$$\sigma_f(v) = \sum_\nu \sigma_{\nu f} = \int_0^\infty \chi_0^2\, \sigma_f^e\, \mathrm{d}\rho\,. \quad (8)$$

Electronic energies and dynamical couplings were calculated (step i) on a grid of 13 equally spaced values of ρ in the range 1.0 to 2.2 a_0 and 70 values of R. The presence of divergent rotational couplings at the conical intersections between states of different angular symmetry was solved by removing the divergent components from the rotational couplings (Elizaga *et al* 1999). The basis of Gaussian orbitals employed in this calculation is the same as in I, and the configuration space was selected in the same way. The asymptotic energy differences between the electronic states included in the equation (3) and the corresponding experimental ones (Moore 1972) are smaller than 10^{-2} Hartree. Our molecular basis set includes 16 wavefunctions ϕ_k whose asymptotic limits are detailed in table 1.

Although the peak observed in the experimental TES of Leputsch *et al* (1997) at $\Delta E \simeq 3.8$ eV was ascribed to the reaction channel $C^+(2s^22p;^2P)+H_2^+(B^2\Sigma_g^+)$, we do not include any state with this asymptotic limit since the equilibrium distance for $H_2^+(B^2\Sigma^+)$ is about 8 a_0 and, in the range of values of ρ where the initial vibronic wavefunction is not negligible, the energy of this state is far too high to have any relevance in the collision.

As explained in I, the entrance channel of reaction (1) is a statistical mixture of ϕ_{11}, ϕ_{12} and ϕ_{13}; the main charge transfer mechanism involves radial transitions ϕ_{11}–ϕ_1, ϕ_{12}–ϕ_2 and ϕ_{13}–ϕ_3 in avoided crossing regions, which results in $C^+(^2D)+H_2^+$ as the main output of the charge transfer process. We show in figure 1 the potential energy curves obtained for three values of ρ. For $\rho = 1.0$ a_0, the energy of the entrance channels

Table 1. Asymptotic ($R \to \infty$) limits of molecular states.

ϕ_1=C$^+$(1s^{2}2s2p^2;^{2}D$_\sigma$) +H$_2^+$($^2\Sigma_g^+$)	
ϕ_2=C$^+$(1s^{2}2s2p^2;^{2}D$_{\pi_x}$) + H$_2^+$($^2\Sigma_g^+$)	ϕ_3=C$^+$(1s^{2}2s2p^2;^{2}D$_{\pi_y}$) + H$_2^+$($^2\Sigma_g^+$)
ϕ_4=C$^+$(1s^{2}2s2p^2;^{2}D$_{\delta_{x^2-y^2}}$) + H$_2^+$($^2\Sigma_g^+$)	ϕ_5=C$^+$(1s^{2}2s2p^2;^{2}D$_{\delta_{xy}}$) + H$_2^+$($^2\Sigma_g^+$)
ϕ_7=C$^+$(1s^{2}2s2p^2;^{2}S) + H$_2^+$($^2\Sigma_g^+$)	
ϕ_8=C$^+$(1s^{2}2s2p^2;^{2}P$_\sigma$) + H$_2^+$($^2\Sigma_g^+$)	
ϕ_9=C$^+$(1s^{2}2s2p^2;^{2}P$_{\pi_x}$) + H$_2^+$($^2\Sigma_g^+$)	ϕ_{10}=C$^+$(1s^{2}2s2p^2;^{2}P$_{\pi_y}$) + H$_2^+$($^2\Sigma_g^+$)
ϕ_{11}=C^{2+}(1s^{2}2s2p;^{3}P$_\sigma$) + H$_2$($^1\Sigma_g^+$)	
ϕ_{12}=C^{2+}(1s^{2}2s2p;^{3}P$_{\pi_x}$) + H$_2$($^1\Sigma_g^+$)	ϕ_{13}=C^{2+}(1s^{2}2s2p;^{3}P$_{\pi_y}$) + H$_2$($^1\Sigma_g^+$)
ϕ_{14}=C$^+$(1s^{2}2s^{2}2p;^{2}P$_\sigma$) + H$_2^+$($^2\Sigma_u^+$)	
ϕ_{15}=C$^+$(1s^{2}2s^{2}2p;^{2}P$_{\pi_x}$) + H$_2^+$($^2\Sigma_u^+$)	ϕ_{16}=C$^+$(1s^{2}2s^{2}2p;^{2}P$_{\pi_y}$) + H$_2^+$($^2\Sigma_u^+$)

sharply pseudocrosses those of the C$^+$(^{2}D)+H$_2^+$ states at $R \sim 9$ a$_0$. When ρ increases, these avoided crossings move to shorter R and get broader; for example, for $\rho = 1.4$ a$_0$ (the H$_2$ equilibrium distance), the crossings appear at $R \simeq 6.0$ a$_0$, and at $R \simeq 5.0$ a$_0$ for $\rho = 1.8$ a$_0$. The same happens to the avoided crossings between the entrance channels and the state ϕ_7; for example, for $\rho = 1.4$ a$_0$ they appear at $R \simeq 12.0$ a$_0$ (and they are traversed diabatically), while for $\rho = 1.8$ a$_0$ appear at $R \sim 7$ a$_0$ and yield sizeable transitions.

In figure 2, we present $\sigma^e_{^2\mathrm{D}}(\rho)$ (equation 7) to C$^+$(^{2}D)+H$_2^+$ for several values of ρ. We find that, at the largest velocities, there is a plateau of $\sigma^e_{^2\mathrm{D}}$ as a function of ρ at values around 1.4 a$_0$ (corresponding to the FC approximation). At lower velocities, the variation with respect to ρ is more marked and the maximum of $\sigma^e_{^2\mathrm{D}}$ is obtained with $\rho \simeq$1.3 a$_0$. This is related to the fact that the avoided crossings shift towards larger R as ρ decreases (see figure 1). We also include in figure 2 the more accurate total cross section $\sigma_{^2\mathrm{D}}$ calculated using (8). Good agreement between this and the FC approximation is found for high energies, but differences are noticeable at the low impact energies.

In figure 3, we show the vibrational distribution of H$_2^+$(X$^2\Sigma_g^+, \nu$) for reaction (1) at four impact energies. As in Leputsch *et al* (1997), in the range of impact energies (0.6–1 keV), our distributions show a maximum at $\nu = 4$, which moves to smaller ν as the impact energy increases, approaching the FC prediction. This behaviour can be qualitatively explained by expanding $a_f(\rho)$ in powers of $(\rho - \rho_c)$ in equation (4) and (5). To first order, one obtains

$$\sigma_{\nu f} \simeq F_{0\nu}^2 \sigma_f^e(\rho_c) - F_{0\nu} \left.\frac{\mathrm{d}\sigma_f^e}{\mathrm{d}\rho}\right|_{\rho=\rho_c} (F_{0\nu}\rho_c - G_{0\nu}) \tag{9}$$

where $F_{0\nu} = \int_0^\infty \chi_0\chi_\nu \mathrm{d}\rho$ and $G_{0\nu} = \int_0^\infty \rho\chi_0\chi_\nu \mathrm{d}\rho$, and ρ_c is the position of the centroid (the maximum of the vibrational product $\chi_0\chi_\nu$). The first term of equation (9) corresponds to the centroid approximation (see Errea *et al* 1996); the second term introduces a velocity-dependent shift to the vibrational distribution. Since only real quantities are involved in (9), interferences between transition amplitudes corresponding to different values of ρ are not taken into account, unlike in the more accurate

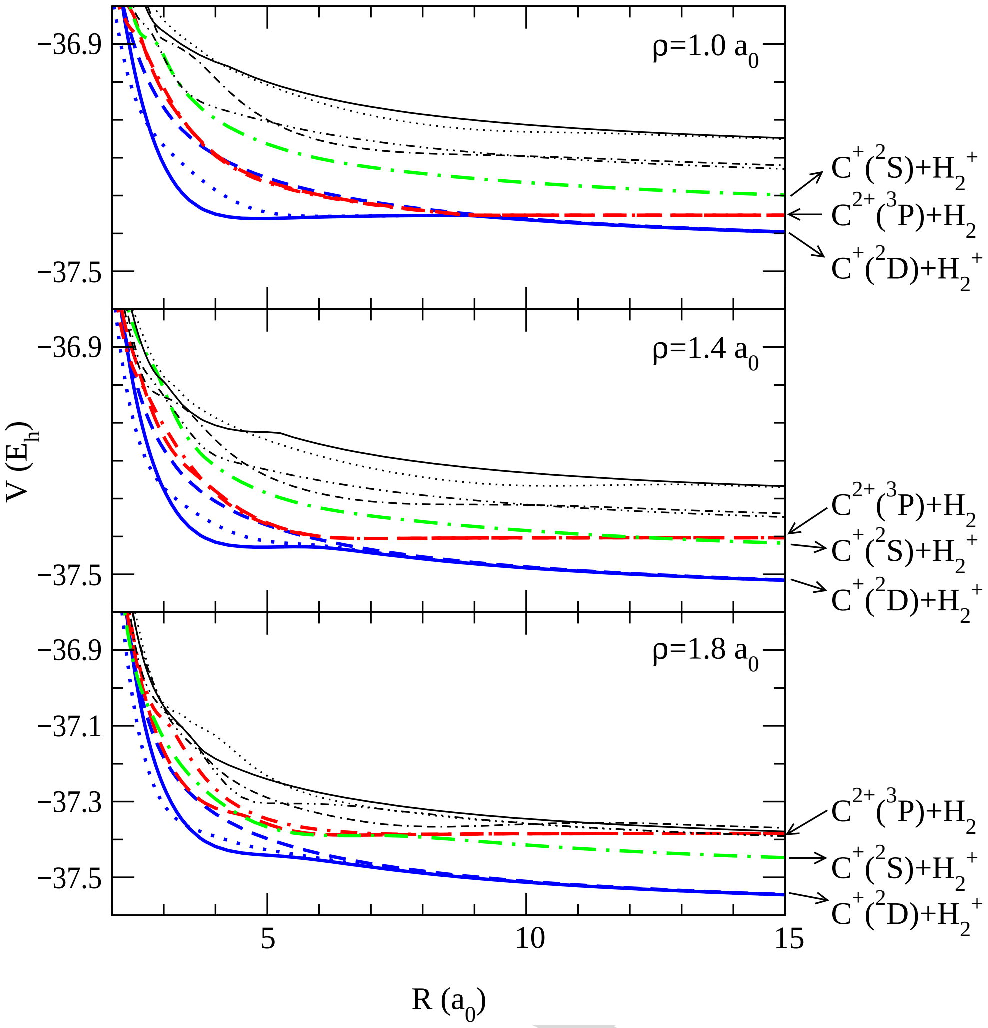

Figure 1. Correlation diagram for the CH_2^{2+} system at three ρ distances for the co-linear geometry.

expression (4). At high velocities, the cross section σ_f^e does not depend on ρ, the second term of (9) vanishes and the expression reduces to the familiar FC approximation. Results using equation (9) are also included in figure 3 and are seen to be close to the more exact results.

The calculated state-to-state charge transfer cross sections are compared to the experimental TES of Leputsch *et al* (1997) at $E = 1$ keV in figure 4. The experimental data have been normalized to ours by comparing the area under both curves in the energy range 4< ΔE <6.5 eV. We find very good agreement for the vibrational distribution of H_2^+ associated with the $C^+(^2D)$ ions. For the small $C^+(^2S)$ band, we obtain a vibrational distribution with a maximum at $\nu = 2$ rather than the experimental $\nu = 0$. We think that this discrepancy is due to limited precision of our calculated small cross sections.

In conclusion, we have obtained vibrationally-resolved charge transfer cross sections in collisions $C^{2+}(2s2p;^3P)+H_2(X^1\Sigma_g^+; \nu = 0)$ at energies between 50 eV and 20 keV. The

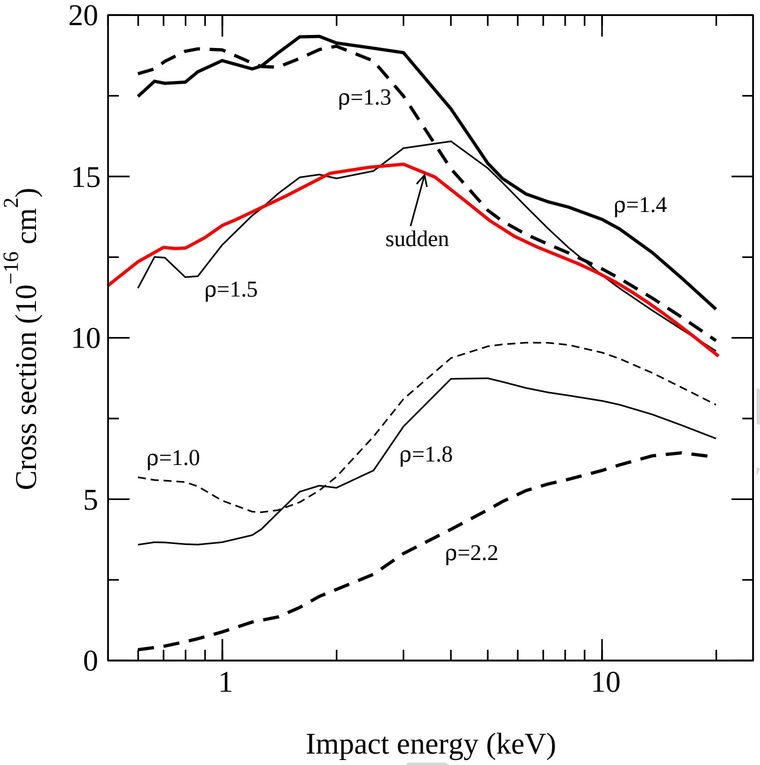

Figure 2. Charge transfer cross section for the $C^+(^2D)$ channel for a selection of H-H distances. Also included is the cross section obtained with the sudden approximation (equation 8).

good agreement with the experiment of Leputsch *et al* (1997) confirms the accuracy of the vibrational sudden approximation method for this energy range (and the accuracy of the experimental data).

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References

Baer M (1992) *in State-Selected and State to State Ion-Molecule Reaction Dynamics. Advances in Chemical Physics Vol LXXXII, Edited by Michael Baer and Cheuk-Yiu Ng* (John Wiley & Sons, Inc.)

Bransden B H and McDowell (1992) *Charge Exchange and the Theory of Ion-Atom Collisions* (Oxford: Clarendon)

Burns D, Greenwood J B, Bajajova K, McCullough R W, Geddes J and Gilbody H B 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 1531

Castillo J F, Errea L F, Macías A, Méndez L and Riera A 1995 *J. Chem. Phys.* **103** 2113–16

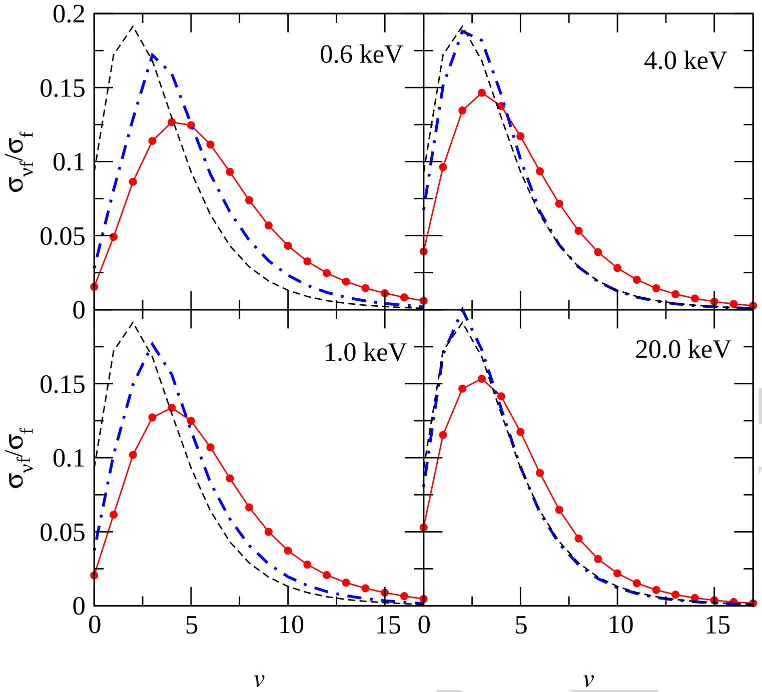

Figure 3. Relative cross section $\sigma_{\nu f}/\sigma_f$ for the charge transfer reaction (1) as a function of $H_2^+(X^2\Sigma_g^+)$ vibrational state (ν). Dotted continuous line are the sudden approximation results (equation 5). The dot-dashed line are the corrected FC results of equation (9) and the dashed line the FC results.

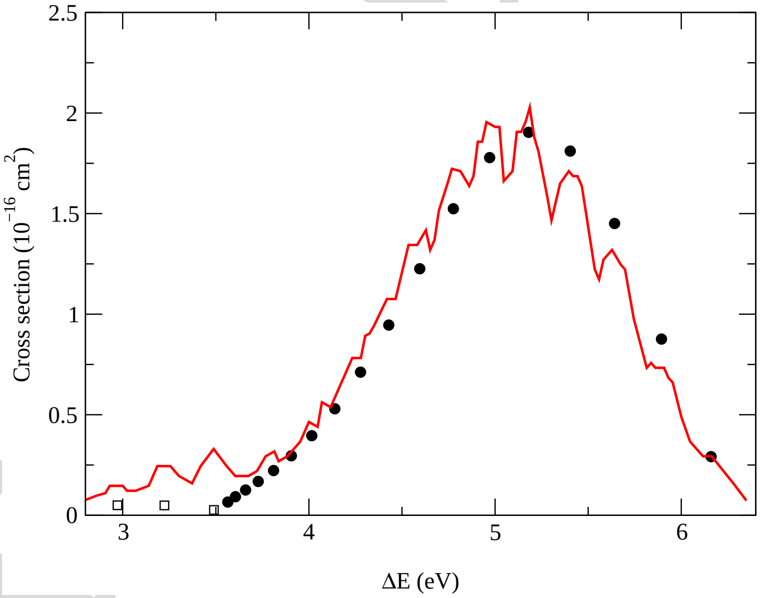

Figure 4. Calculated cross section for the charge transfer reactions $C^{2+}(^3P)+H_2(X^1\Sigma_g^+,\nu'=0)\rightarrow C^+(^2D)+H_2^+(X^2\Sigma_g^+,\nu)$ (●) and $C^{2+}(^3P)+H_2(X^1\Sigma_g^+,\nu'=0)\rightarrow C^+(^2S)+H_2^+(X^2\Sigma_g^+,\nu)$ (□) at E = 1 keV as a function of energy defect. Line corresponds to Leputsch *et al* (1997) experiment.

Davidson (1990) *in* E Clementi, ed., 'MOTECC, Modern Techniques in Computational Chemistry' ESCOM Publishers B. V., Leiden

Elizaga D, Errea L F, Gorfinkiel J D, Macías A, Méndez L, Riera A and Rojas A 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** 2037–56

Elizaga D, Errea L F, Macías A, Méndez L, Riera A and Rojas A 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** L697

Errea L F, Gorfinkiel J D, Harel C, Jouin H, Macías A, Méndez L, Pons B and Riera A 1996 *Physica Scripta* **T62** 33–8

Errea L F, Gorfinkiel J D, Macías A, Méndez L and Riera A 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 3855–72

——1999*a* *J. Phys. B: At. Mol. Opt. Phys.* **32** 1705–21

Errea L F, Macías A, Méndez L and Riera A 1999*b* *J. Phys. B: At. Mol. Opt. Phys.* **32** 4065–77

Greenwood J B, Burns D, McCullough R W, Geddes J and Gilbody H B 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 5867

Leputsch P, Dumitriu D, Aumayr F and Winter H P 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 5009–24

Moore C E (1972) *Atomic Energy Levels, Nat. Stand. Ref. Data Series vol 1* (US National Bureau of Standards)

Unterreiter E, Schweinzer J and Winter H P 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** 1003

Voulot D, Gillen D R, Thompson W R, Gilbody H B, McCullough R W, Errea L, Macías A, Méndez L and Riera A 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** L189–L192