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State-to-state vibrational cross sections in H^+, C^{2+}-H_2 charge transfer reactions.

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The vibrational distribution of $H_2^+(X^2\Sigma_g^+;\nu)$ after charge transfer in H^++H_2 and $C^{2+}(2s2p;^3P)$+H_2 collisions is obtained using the SEIKON approach and *ab initio* molecular data. We also present H_2 vibrational excitation cross sections in H^++H_2 collisions.

I. INTRODUCTION

Vibrational state-to-state charge transfer cross sections in ion-molecule collisions are often calculated, at very low energies (few eV), using methods based on the Infinite Order Sudden Approximation (IOSA) formalism (e.g. Baer 1992 and references therein). At higher energies, our group has implemented the SEIKON approach, which has been applied to evaluate state-to-state vibrational cross sections in ion collisions with H_2 in the impact energy range 50 eV/amu–2 keV/amu [2–4], where significant deviations from the simple Franck-Condon (FC) approximation were found. In this work we present the application of this method to evaluate partial vibrational cross sections in the reactions:

$$H^+ + H_2(X^1\Sigma_g^+, \nu = 0) \to H(1s) + H_2^+(X^2\Sigma_g^+, \nu) \tag{1}$$

$$H^+ + H_2(X^1\Sigma_g^+, \nu = 0) \to H^+ + H_2(X^1\Sigma_g^+, \nu) \tag{2}$$

$$C^{2+}(2s2p;^3P) + H_2(X^1\Sigma_g^+, \nu = 0) \to C^+(2s2p^2;^2D) + H_2^+(X^2\Sigma_g^+, \nu) \tag{3}$$

Reactions (1) and (2) are fundamental processes in ion-molecule collisions. We have also considered reactions with the isotopic species D_2, DT and T_2, because of their interest in fusion research. As an illustration, we present results for reactions (1) and (2) with H_2 and DT targets. In previous work [4], we have calculated total and partial vibrational cross sections for reaction (1). Total cross section for reaction (1) of ref. [4], show good agreement with experiment [8] for $E \geq$150 eV, but discrepancies were found at lower energies. Reaction (3), where the incident C^{2+} is on a metastable state, has been chosen because the results can be compared with the experimental data of ref. [5], allowing to check the accuracy of both our results and the experimental data. A detailed study of C^{2+}+H_2 collision, considering the importance of metastable ions in the incident beam has been presented in [6], in the framework of the FC approximation.

II. THEORY

The method we use is described in detail in [3] and [6]. Here we only summarize the procedure:

1. Molecular data (energies and dynamical couplings) for the triatomic molecules H_3^+ and CH_2^+ are calculated *ab initio*

2. The sudden approximation for rotation and vibration is employed to obtain the vibrational state-to-state cross sections. The electronic transitions are treated using the semiclassical eikonal method (see e.g. [7]): for fixed H_2 target position, the ion follows rectilinear trajectories $\boldsymbol{R} = \boldsymbol{b}+\boldsymbol{v}t$ with respect to the diatom with impact parameter $\boldsymbol{b}$ and velocity $\boldsymbol{v}$. The wavefunction Ψ describing the collision is a solution of

$$\left(H_{\rm int} - {\rm i} \left.\frac{\partial}{\partial {\rm t}}\right|_{{\rm r},\rho} \right) \Psi(\boldsymbol{r}, \boldsymbol{\rho}, t) = 0 \tag{4}$$

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

$$\Psi(\boldsymbol{r},\boldsymbol{\rho},t) = \chi_0(\rho) Y_{JM}(\hat{\boldsymbol{\rho}}) \sum_k a_k(\boldsymbol{\rho},t)\phi_k(\boldsymbol{r};\boldsymbol{R},\boldsymbol{\rho}) \exp\left(-\mathrm{i}\int_0^{\mathrm{t}} \epsilon_{\mathrm{k}} \mathrm{d}t'\right) \tag{5}$$

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 with energies ϵ_k.

Since we have found that the anisotropy effects in H_3^+ and CH_2^+ are small for the R distances involved, we have carried out the dynamical calculation for the collinear geometry. Substituting (5) in (4) leads to a set of differential equations for the coefficients a_k. From them, we calculate the total cross section $\sigma_{\nu f}$ for transition from the vibronic state $\{0i\}$ to $\{\nu f\}$:

$$\sigma_{\nu f}(v) = 2\pi \int_0^\infty \mathrm{d}b\, b \left| \int \mathrm{d}\rho \chi_0 \chi_\nu \exp\left[-\mathrm{i}\int_0^\infty \mathrm{d}t(\epsilon_{\mathrm{f}} - \mathrm{E}_{\mathrm{f}})\right] a_f(\infty,\rho)\right|^2 \tag{6}$$

where E_f is the asymptotic energy of the vibronic state $\{\nu f\}$. It is useful to define electronic cross sections $\sigma_n^e(\rho,v)$ for a fixed ρ and v as

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

When $\rho=\rho_0$, the target equilibrium distance, equation (7) yields the familiar FC cross section.

III. RESULTS AND DISCUSSION.

A H^++H_2 collisions

Our results for reactions (1) and (2) and illustrated in Figs. 1 and 2 respectively. For the H_2 target, the H_2^+ vibrational distribution after reaction 1 shows a noticeable shift with respect to the FC distribution at low impact energies. This shift is less marked for the heavier targets because the initial vibrational wavefunction is more concentrated near ρ=1.4 a_0. For the excitation reaction (2), we obtain a fast decrease of the population of H_2 vibrational levels when ν increases (see Fig. 2), in qualitative agreement with the calculations at lower impact energies of ref. [1]. Total cross sections for H_2 vibrational excitation reaction (2) are larger than the charge transfer ones at low impact energies (E <200eV). Divergence between theoretical and experimental total charge transfer cross sections at these [4] energies would seem to indicate that, for this system, these energies are too low to apply the vibrational sudden approximation.

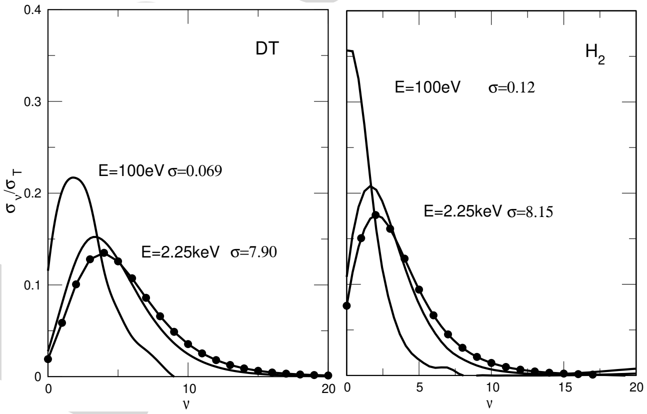

FIG. 1: Vibrational state selected distribution (σ_ν/σ) for reaction (1), as functions of the final vibrational level ν. The values (in 10^{-16}cm^2) of the total cross section σ are indicated in the figure. (•) FC prediction.

B C^{2+}+H_2 collisions

The calculated state-to-state charge transfer cross sections are compared to the experimental TES of [5] at E=1 keV in Fig. 3. The experimental data have been normalized to ours by using 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. Some discrepancies for the small $C^+(^2S)$ band are obtained, which are probably due to, not enough precision in our calculation for small cross sections. As in [5], 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, (see Fig. 4). This behaviour can be qualitatively explained by expanding $a_f(\rho)$ in powers of $(\rho-\rho_c)$. To first order, one obtains

$$\sigma_{\nu f} \simeq F_{0\nu}^2 \sigma_f^e(\rho_c) - F_{0\nu} \left.\frac{\mathrm{d}\sigma_f^e}{\mathrm{d}\rho}\right|_{\rho=\rho_c} (F_{0\nu}\rho_c - G_{0\nu}) \tag{8}$$

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 Eq. (8) corresponds to the centroid approximation (see [9]); the second term introduces a velocity-dependent shift to the vibrational distribution. Since only real quantities are involved in (8), interferences between transition ampli-

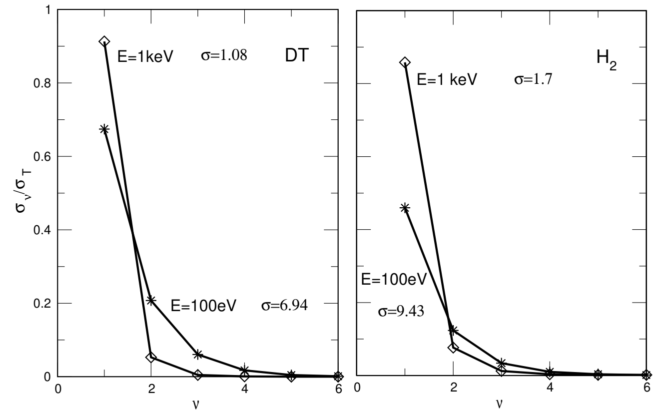

FIG. 2: Same as Fig. 1 for reaction (2)

tudes corresponding to different values of ρ are not taken into account, unlike in the more accurate expression (6). 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.

In conclusion, our results for reactions (1) and (2) indicate that the vibrational sudden approach is appropriate for calculating partial vibrational cross sections for collisions energies above 200 eV for reaction (1) and at least for E >600eV for reaction (2. At lower energies it is possible that the assumption that the initial vibrational wavefunction is unchanged during the collision needs improvement. This is a subject that we plan to investigate.

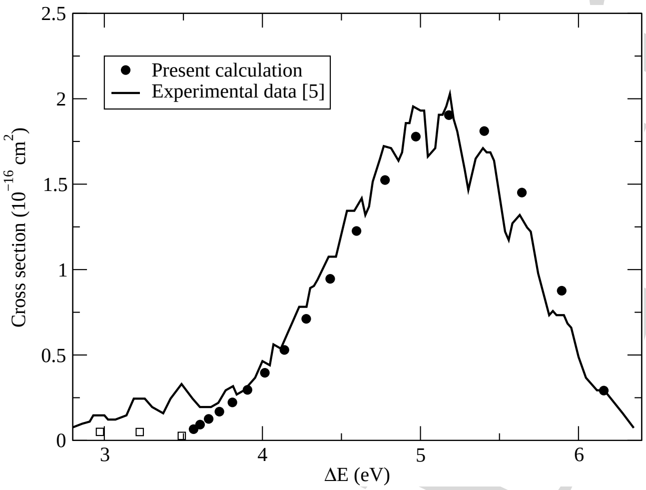

FIG. 3: Calculated cross section for the charge transfer reactions $C^{2+}(^3P)+H_2(X^1\Sigma_g^+,\nu'=0)\rightarrow C^+(^2D)+H_2^+(X^2\Sigma_g^+,\nu)$ (•) and $C^{2+}(^3P)+H_2(X^1\Sigma_g^+,\nu'=0)\rightarrow C^+(^2S)+H_2^+(X^2\Sigma_g^+,\nu)$ (□) at E =1 keV as a function of energy defect. Line corresponds to the experiment of ref. [5].

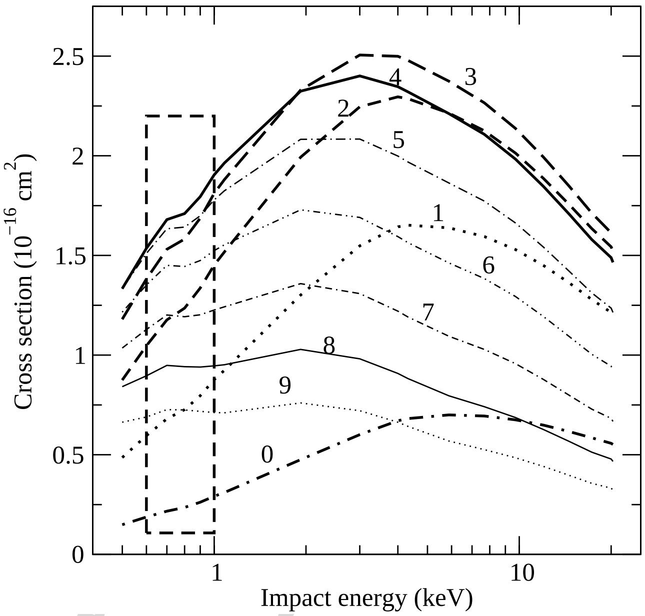

FIG. 4: Calculated cross section for the charge transfer reactions $C^{2+}(^3P)+H_2(X^1\Sigma_g^+,\nu'=0)\rightarrow C^+(^2D)+H_2^+(X^2\Sigma_g^+,\nu)$ as functions of the impact energy. The curves labels are the corresponding values of ν and the box indicates the energy range of the experiment of ref. [5].

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REFERENCES

[1] Baer M *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.) (1992)
[2] Errea L F *et al.J. Phys. B* **30** 3855 (1997)
[3] Errea L F *et al.J. Phys. B* **32** 1705 (1999)
[4] Elizaga D *et al.J. Phys. B* **33** 2037 (2000)
[5] Leputsch P, Dumitriu D, Aumayr F and Winter H P 1997 *J. Phys. B* **30** 5009 (1997)
[6] Errea L F, Macías A, Méndez L and Riera A 1999 *J. Phys. B* **32** 4065 (1999)
[7] Bransden B H and McDowell *Charge Exchange and the Theory of Ion-Atom Collisions* (Oxford: Clarendon) (1992)
[8] Gealy M W and Van B I *Phys. Rev. A* **36** 3091 (1987)
[9] Errea L F *et al.Physica Scripta* **T62** 33 (1996)