Influence of the metastable ion content in the initial beam in C^{2+}+H, H_2 and O^{2+}+H collisions

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We present *ab initio* calculations of cross sections for electron capture by C^{2+} ions in their ground (^{1}S) and metastable (^{3}P) states, from H and H_2. We explain the difference between C^{2+}+H_2 collisions, where the content of metastable ions is critical, and C^{2+}- H collisions, where it is less important. We also present preliminary results for electron capture by O^{2+} in ground (^{3}P) and metastable (^{1}D, ^{1}S) states from H.

I. INTRODUCTION

The experimental determination of capture cross section in ion-atom (molecule) collisions is difficult when unknown quantities of metastable ions are present in the initial beam. In such a case the theoretical determination of these cross sections can be very useful This problem is known to be especially severe for collisions of C^{2+} with He and H_2 [1–4] for which capture by the metastable impurity C^{2+}($1s^2 2s2p\ ^3$P) prevails over that by ground state ($1s^2 2s^2\ ^1$S) ions. C^{2+} collisions with H have also been considered in experimental [5–7] and theoretical works [8], where total cross sections for electron capture by ground state ions were reported. We have recently carried out calculations [9] for this system considering both ground and metastable state projectiles, which have been compared with DTES experiments [10]. Here we compare our results for C^{2+}+H,H_2 collisions.

Capture cross sections in O^{2+}+H collisions were measured in ref. [11]. For this system, calculations of ref. [12] suggested a high proportion (60%) of metastable O^{2+}(^{1}D) in the initial beam of [11]. In the present work we report preliminary results for O^{2+}+H collisions. In contrast with the findings of ref. [12], we obtain a much smaller fraction of metastable ions in the experiment of [11].

II. COMPUTATIONAL METHOD

Our treatment of the dynamics follows the usual procedure for ion-atom collisions at low to intermediate relative nuclear velocities. We employ the impact parameter method, in which the position vector $\boldsymbol{R}$ of the incident ion with respect to the target atom follows straight-line trajectories $\boldsymbol{R} = \boldsymbol{b} + \boldsymbol{v}t$. The electronic motion is described by the wavefunction $\Psi(\boldsymbol{r}, b, t)$, which is a solution of the equation:

$$\left(H_{\rm elec} - {\rm i}\frac{\partial}{\partial {\rm t}}\bigg]_{\boldsymbol{r}} \right) \Psi(\boldsymbol{r}, b, t) = 0 \tag{1}$$

where the operator $H_{elec}(\boldsymbol{r}; R)$ is the Born-Oppenheimer electronic Hamiltonian, for fixed R values. $\Psi(\boldsymbol{r}, b, t)$ is expanded in terms of the eigenfunctions of the electronic Hamiltonian, fulfilling $H_{elec}\phi_j = \epsilon_j \phi_j$:

$$\Psi(\boldsymbol{r}, b, t) = D(\boldsymbol{r}, t) \sum_j a_j(b, t)\, \phi_j(\boldsymbol{r}, R)\, \exp\left[-i \int_0^t \varepsilon_j {\rm d}t' \right] \tag{2}$$

where D is a common translation factor (CTF) [13, 14], Substituting (2) into (1) leads to a system of differential equations for the coefficients a_j, which is solved with the initial condition $a_j(b, -\infty) = \delta_{ij}$ to obtain the transition probabilities $P_f(b)$

$$P_f(b) = \lim_{t\to\infty} |a_f(b, t)|^2 . \tag{3}$$

The total cross section for transitions to state f is given by:

$$\sigma_f = 2\pi \int_0^\infty P_f(b) b\ {\rm d}b \tag{4}$$

The molecular energies and dynamical couplings, which include the corrections due to the CTF of ref. [14], were obtained by using our modified Self-Consistent-Field Multireference Configuration Interaction (SCF-MRCI) program MELD [15–17]. The details about the Gaussian basis set and the configuration selection used in C^{2+}-H, H_2 collisions can be found in [4]. The Oxygen Gaussian basis set is that of ref. [18], and a similar configuration selection was employed to obtain molecular energies and dynamical couplings for the OH^{2+} quasimolecule. The cross sections for C^{2+} reactions with H_2 were obtained in the framework of the Franck-Condon approximation and using *ab initio* wavefunctions of the triatomic quasimolecule CH_2^{2+}.

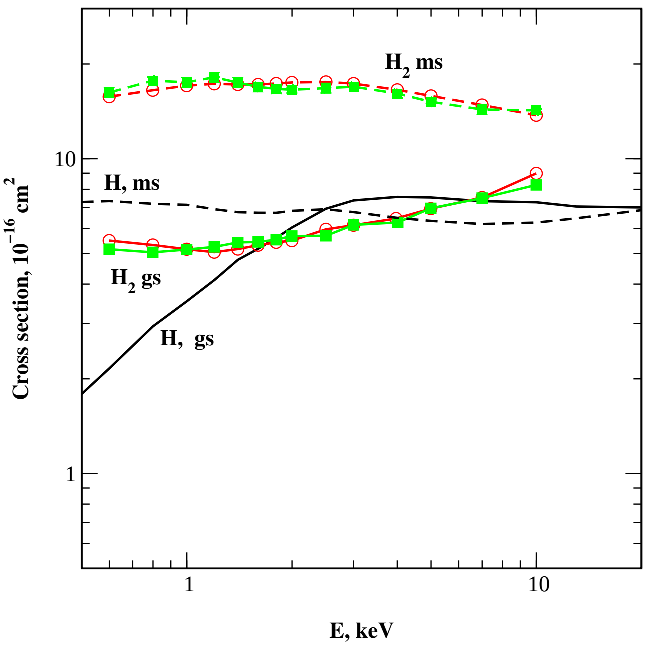

FIG. 1: Cross sections for electron capture in C^{2+}+H,H_2 collisions. gs: Collisions with ground state $C^{2+}(^1S)$ ions; ms: Collisions with metastable $C^{2+}(^3\ P)$ ions. For collisions with H_2 we have plotted results of calculations for two orientations of the H-H axis with respect to the C-H_2 axis: $\circ, 0°$; $\blacksquare, 90°$

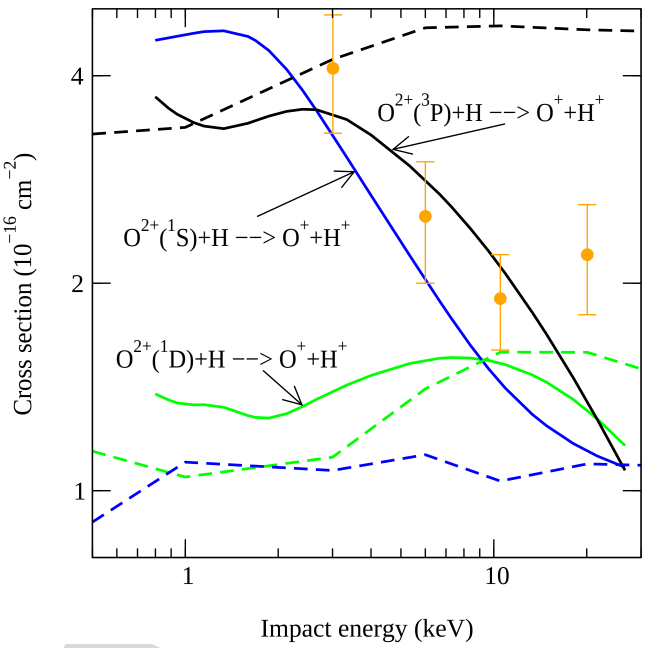

FIG. 2: Cross sections for electron capture in O^{2+}+H collisions: full lines, present calculation; dashed lines, molecular calculation of ref. [12]; $\bullet$, experimental results of ref. [11].

III. RESULTS AND DISCUSSION

We show in Fig. 1 our results for electron capture by C^{2+} from H and H_2. The dynamical calculation for C^{2+}+H_2 was carried out by assuming that the orientation of the C-H_2 axis is with respect the H-H axis is fixed during the collision. This is justified by results for two orientations (parallel and perpendicular), included in Fig. 1, illustrating the small anisotropy of the cross sections for these collisions. From the large difference between the cross sections for collisions of ground and metastable C^{2+} ions with H_2, any contamination by metastable ions should be noticeable in the experiments for the energy range of Fig. 1. On the other hand, for C^{2+}+H collisions the cross sections for incident ions in the ground and the metastable states are very similar for energies above 2keV, and accordingly it is expected that contamination by metastable ions pass unnoticed for these energies. This explains the good agreement (see [9]) between theoretical total cross sections for collisions with ground state ions and experiments with unknown content of metastable ions in the incident beam.

The large difference between cross sections for electron capture by $C^{2+}(^3P)$ from H and H_2 is a consequence of the different spin multiplicities involved in both cases: In $C^{2+}(^3P)$ collisions with $H_2(^1\Sigma_g^+)$ only triplet molecular states are involved, while with $H(^2S)$ targets the electronic wavefunction is a statistical mixture of doublet and quadruplet molecular states, with weights 1/3 and 2/3 respectively. The mechanism of the charge transfer reaction in the doublet subsystem is similar to that of the reaction with H_2, but capture cross section in the quadruplet subsystem is negligible. The 1/3 statistical factor is then responsible for the decrease of the cross section in the reaction with H with respect to that in the reaction with H_2.

The basic mechanism of O^{2+} electron capture from H has been explained in [12]. For the reaction with the ground state O^{2+} (^{3}P), doublet and quadruplet molecular states are involved, and the charge transfer reaction takes place mainly through transitions in the avoided crossing between the entrance channel and the molecular quadruplet state dissociating into $O^+(^4P)$+H^+. We have carried out a dynamical calculation in a basis of 17 molecular states (those dissociating into $O^{2+}(^3P,\ ^1D,\ ^1S)$+H (^{2}S) and $O^+(^4P,^2D)$ + H^+), similar to that of [12], and , unlike that reference, our results for electron capture by ground state O^{2+} (see Fig. 2) show good agreement with the experimental data, so that a high proportion of metastable ions in the initial beam is not required to get agreement with the data of ref. [11].

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