Orientation effects in He^{2+}-H_2^+ collisions at intermediate collision energies

J. Caillat,* N. Sisourat, and A. Dubois
Laboratoire de Chimie Physique-Matière et Rayonnement, Université Pierre et Marie Curie, F-75231 Paris Cedex 05, France

I. Sundvor and J. P. Hansen
Department of Physics and Technology, University of Bergen, N-5007 Bergen, Norway
(Received 16 September 2005; published 20 January 2006)

Orientation effects for electron transfer in keV He^{2+}-H_2^+ collisions are calculated based on a semiclassical close coupling model which accurately describes the electronic dynamics. When direct processes dominate it is shown that a configuration where the molecule is perpendicular to the ion momentum is always most favorable. At lower collision energies, rotational couplings and important contributions from low impact parameters can lead to dominant capture cross sections from molecular target aligned parallel with the collision beam.

DOI: 10.1103/PhysRevA.73.014701 PACS number(s): 34.10.+x, 34.50.Gb, 34.70.+e

Orientation effects in time-dependent interactions are at present investigated experimentally with strong femtosecond laser pulses [1] and with energetic ion beams [2,3]. In the case of photon impact the experiments and calculations [4,5] so far indicate that, for initial molecular σ_g states, ionization is enhanced when the linear polarization of the laser pulse is parallel with the internuclear axis. For ion impact the situation is more complex as charge transfer is usually a stronger process than ionization at low and intermediate energies. Perturbation calculations at high energies performed some time ago [6,7] however, clearly show that the ionization cross section is dominated by perpendicular geometry, i.e., θ=90° (Fig. 1). This tendency has been very recently confirmed by nonperturbative DVR results [8].

For the collision system He^{2+}-H_2^+ Bräuning *et al.* [9] recently measured total capture cross section at intermediate energies (keV range) and compared their results with model calculations. Reiser *et al.* [2] measured orientation effects in the same system and found enhanced capture cross section for the perpendicular case. Caillat *et al.* [10] developed a LCAO like "2+1"-center approach and demonstrated a strong dependence of the reaction dynamics on the internuclear distance. For He^{2+}-H_2^+ electron capture cross sections were found to increase with internuclear distance. These results have recently been confirmed by numerical grid calculations [11,12] which also showed orientation dependence in disagreement with the measurements [2].

In this report we display the orientation dependence of the capture process in He^{2+}-H_2^+ from our "2+1"-center close coupling model which describes final capture states more accurately than grid approaches. The present results confirm the ones reported in Refs. [11,12]. In addition we expose the underlying mechanisms leading to the predicted orientation effects. Atomic units are used unless otherwise stated.

In short we consider processes which take place so fast that (i) the *sudden* approximation is valid, i.e., frozen molecular internuclear vector $\vec{R}_{AB}$ and (ii) a classical description of the projectile-target relative motion applies. For a one-electron system the Hamiltonian then becomes

$$H = -\frac{1}{2}\Delta_{\vec{r}} + V^T(\vec{r},\vec{R}_{AB}) + V^P[|\vec{r} - \vec{R}(t)|], \tag{1}$$

where V^T (V^P) is the two (one)-center attractive potential energy of the electron-target (projectile) subsystem. In the "2+1"-center model [10] the time-dependent Schrödinger equation is solved by expanding the electronic wave function onto a linear combination of two-center orbitals centered on the molecular target and traveling one-center orbitals centered at the projectile. They are augmented with proper electron translational factors and thus describe electron capture very accurately. The cross sections for a given initial molecular alignment, characterized by the angle θ with respect to the beam direction $\vec{v}$ is then

$$\sigma_{if}(R_{AB},\theta) = \int\int d\vec{b}\, P_{if}(\vec{b},R_{AB},\theta,\varphi), \tag{2}$$

where P_{if} is the probability for transition $i \to f$. These cross sections should be averaged over R_{AB} for a given initial vibrational wave function $\psi_\nu(R_{AB})$

$$\sigma_{if}^{(\nu)}(\theta) = \int_0^\infty dR_{AB}|\psi_\nu(R_{AB})|^2\sigma_{if}(R_{AB},\theta). \tag{3}$$

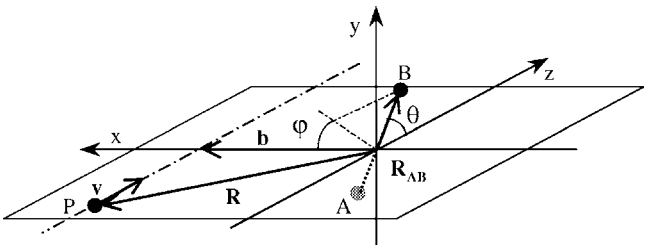

FIG. 1. Collision geometry. The impact parameter **b** and the projectile velocity **v** define the collision plane. The angles θ and ϕ define the orientation of the molecular internuclear axis $\mathbf{R}_{AB}$ with respect to the $\hat{z}$ axis and the collision plane.

*Also at Photonics Institute, Vienna University of Technology, A-1040 Vienna, Austria.

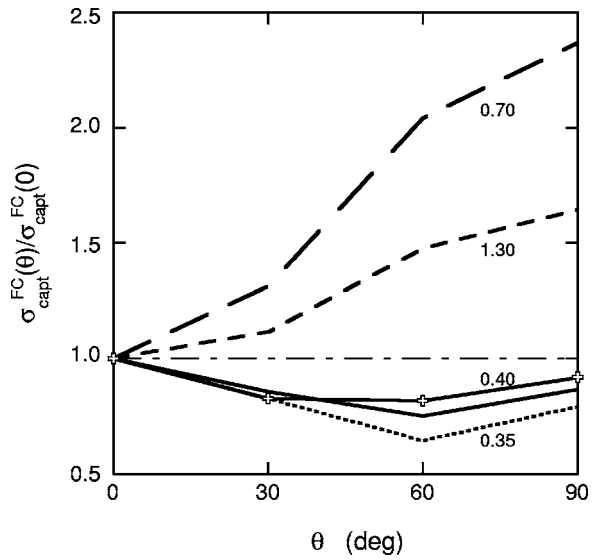

FIG. 2. Normalized total capture cross sections $\sigma^{FC}_{capt}(\theta)/\sigma^{FC}_{capt}(\theta=0^\circ)$ versus H_2^+ initial alignment angle θ (with respect to $\vec{v}$) for four typical relative velocities, marked (in a.u.) on the figure. The solid line with open crosses corresponds to velocity $v=0.4$ a.u. and capture cross sections averaged over an initial Franck-Condon vibrational distribution of the H_2^+ electronic ground state, see text and Ref. [10].

However, in the following, we will consider the H_2^+ molecular target in the vibrational ground state where the Franck-Condon typed cross sections, $\sigma^{FC}_{if}(\theta)=\sigma_{if}(R_{AB,eq},\theta)$ evaluated at the equilibrium internuclear distance ($R_{AB,eq}\approx 2$ a.u.), were shown to be accurate [8,10]. The results presented in the following stem from "2+1"-center calculations using the compact (SB) basis set described in Ref. [10].

In Fig. 2 we show capture cross sections as a function of the angle θ between the internuclear axis and the projectile velocity $\vec{v}$, cf. Fig. 1. For clarity, we have normalized the cross sections to the ones obtained with the parallel configuration ($\theta=0^\circ$). The figure displays two features: (i) a strong orientation effect with the perpendicular geometry ($\theta=90^\circ$) contributing dominantly to the capture processes for most velocities, and (ii) a strong velocity dependence of this effect, with an inversion around $v=0.35$ a.u. We note that when comparing with the experimental results involving vibrational excited molecular targets [2,9] one should average the cross sections $\sigma^{(\nu)}_{if}(\theta)$ over the appropriate initial vibrational distribution. However, this does not alter the orientation effects, as illustrated in Fig. 2 for a Franck-Condon distribution at $v=0.4$ (solid line marked with crosses). Thus three independent calculations, the present ones and those of Refs. [11,12], are in agreement and indicate another orientation dependence of the capture cross sections than the single published experiment. This again calls for further experimental investigations.

In the following we discuss the systematics of the orientation dependence in more details. In Fig. 3 we plot the normalized cross sections as a function of projectile velocity for three different angles and for two important internuclear separations, $R_{AB}=2$ and 3 a.u. We see clearly that for most velocities the perpendicular orientation is favored. However, for velocities around 0.35 a.u. (i.e., 3 keV/amu) there is a near R_{AB}-independent valley where parallel orientation ($\theta=0^\circ$) dominates. It is also a fact that this valley is present for all important internuclear distances (cf. Fig. 3 for $R_{AB}=3$ a.u.), thus making an experimental observation feasible.

To get a deeper insight into the dynamics we plot in Fig. 4 the impact parameter dependence of the capture probability for two typical collision velocities, inside the valley ($v=0.35$ a.u.) and outside ($v=0.7$ a.u.). We note first that much smaller impact parameters contribute at the lowest velocity. Thus, a large fraction of the corresponding cross sections stems from trajectories which actually penetrate the molecule. At higher velocities where larger impact parameters dominate, the orientation dependence is determined by pure steric effects, thus the capture cross sections increase with θ. The question is then how the $\theta=0^\circ$ configuration becomes more dominant around $v=0.35$ a.u. This originates from complex dynamics involving the three-center nature of the system, as displayed for $v=0.35$ a.u., $b=1$ a.u., and $\theta=0^\circ$ in Fig. 5. In the first stage of the collision (first three panels) the electron probability density transfers to a large degree onto the projectile. Then, after the turning point, the transferred charge cloud might return to the target as a typical feature of unfavorable crossing parameters. This is consistent with the weak capture observed generally for parallel geometry where the interaction time is the longest and in favor of back transfer. However, for velocities within the *valley* (Fig. 3), rotational couplings populate capture states which do not couple back to the target. The signature of the rotational couplings in the capture mechanism is clearly visible in the last panels of Fig. 5.

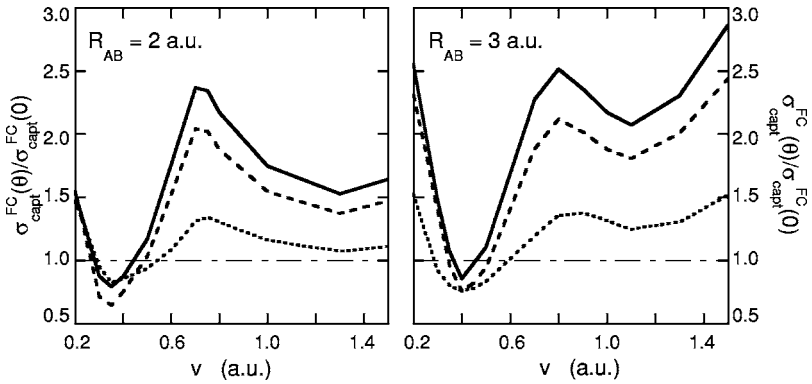

FIG. 3. Normalized total capture cross sections $\sigma^{FC}_{capt}(\theta)/\sigma^{FC}_{capt}(\theta=0^\circ)$ versus impact velocity, for three orientations $\theta=90^\circ$ (solid line), $\theta=60^\circ$ (dashed line), and $\theta=30^\circ$ (dotted line). Left panel is for the H_2^+ equilibrium internuclear distance $R_{AB}=2$ a.u. and right panel is for $R_{AB}=3$ a.u.

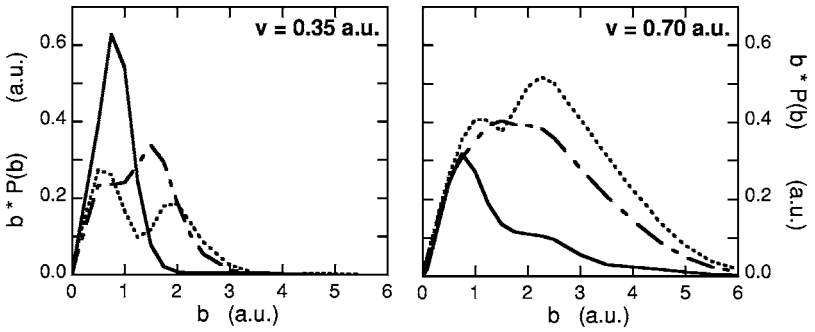

FIG. 4. Impact parameter dependence of the total capture probability (at $R_{AB}=R_{AB,eq}$) for $v=0.35$ a.u. (left) and $v=0.7$ a.u. (right) and for three orientations of the molecule: $\theta=0°$ (full curve), $\theta=60°$ (chain curve), and $\theta=90°$ (dotted curve).

This is confirmed by a detailed inspection of the state-selective capture probabilities (not shown). At large impact parameters ($b>2$ a.u.) capture to $He^+(2s)$ and $He^+(2p_0)$ is the most probable for $\theta=90°$. This is due to couplings working at large internuclear (projectile-target) distances, between the states connected asymptotically to the $H_2^+(\sigma_g)$ ground state, the intermediate first excited $H_2^+(\sigma_u)$ state and the $He^+(n=2)$ manifold. On the other hand in the low impact parameter range capture populates preferentially the $He^+(2p_{\pm1})$ states, especially for the $\theta=0°$ geometry. The orientation effect observed at velocities inside the *valley* is therefore related to the interplay between the decay of the direct mechanism active at large internuclear distances and the strength of the short range rotational couplings.

As mentioned above, the *ungerade* first excited state of H_2^+ plays a decisive role in the dynamics of the system. It is

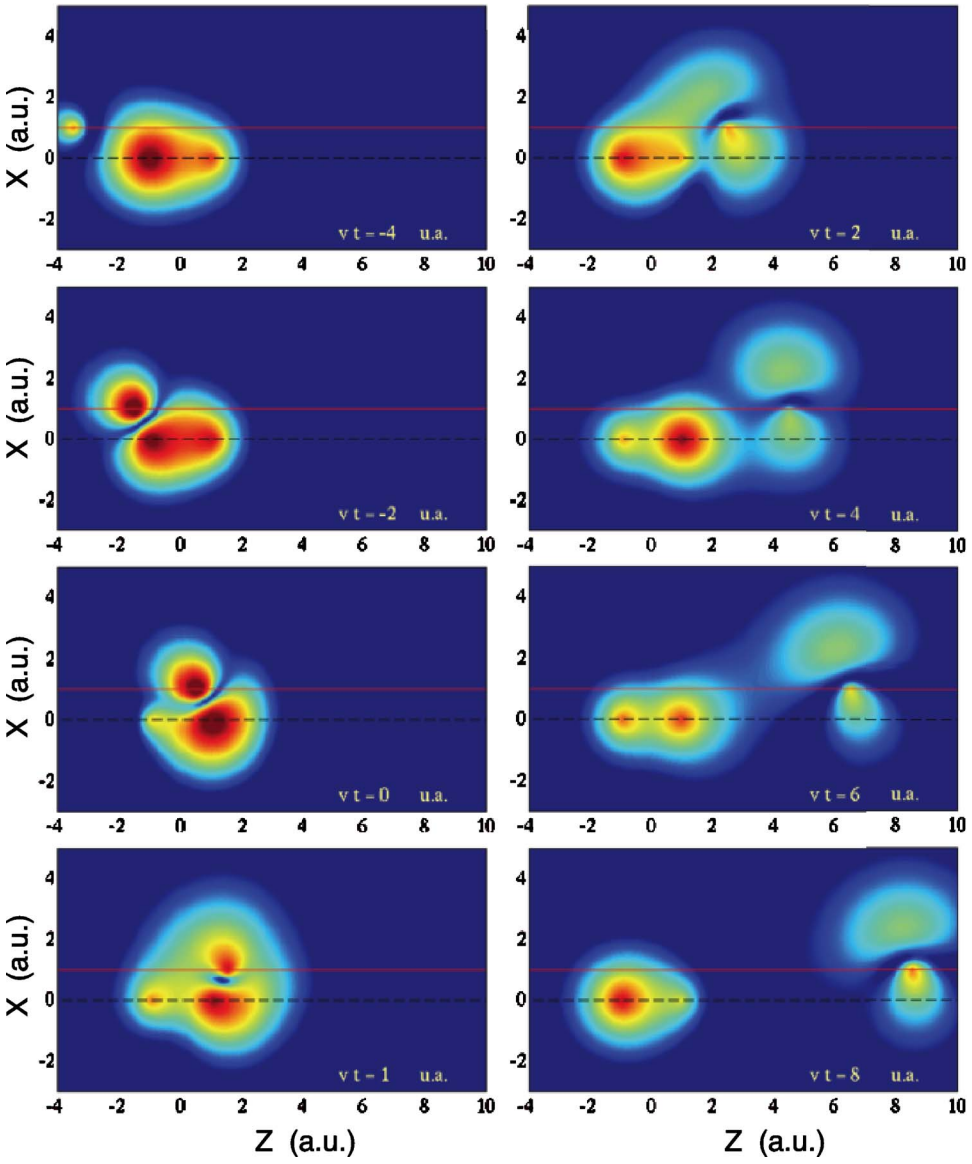

FIG. 5. (Color online) Snapshots of the electron probability density (in the xz plane) during the collision for $v=0.35$ a.u., $b=1$ a.u., and $\theta=0°$ ($R_{ab}=2$ a.u.). Time increases from top to bottom in the left column and then in the right one.

obvious in Fig. 5 where oscillations of the electronic cloud are observed between the two nuclei of the target, as the result of the coherent mixing of the $H_2^+(\sigma_g)$ and $H_2^+(\sigma_u)$ states. Note that coupled channel calculations excluding the ungerade state from the basis do not predict preferential capture in the parallel geometry at $v=0.35$ a.u.

In conclusion, we have calculated orientation dependent cross sections and probabilities for electron capture in He^{2+}-H_2^+ collisions. From geometric considerations it is demonstrated that perpendicular orientation with respect to the ion beam dominates at intermediate velocities where large impact parameters are important. At low velocities or, in general, when smaller impact parameters dominate the transfer process, the orientation dependence is much more complex. In the present system it is found that, consistently, parallel orientation dominates for capture around $v=0.35$ a.u. We remark that in this region the results show the same tendencies that the ones observed for ionization of diatomic molecules by strong femtosecond laser pulses.

This research is supported by the Norwegian Research Council and the Direction de la Recherche of Université Pierre et Marie Curie. The Laboratoire de Chimie Physique-Matière et Rayonnement is Unité Mixte de Recherche du CNRS (UMR 7614).

[1] I. V. Litvinyuk *et al.*, Phys. Rev. Lett. **90**, 233003 (2003).
[2] I. Reiser, C. L. Cocke, and H. Bräuning, Phys. Rev. A **67**, 062718 (2003).
[3] N. Stolterfoht *et al.*, Phys. Rev. Lett. **87**, 023201 (2001).
[4] Z. X. Zhao, X. M. Tong, and C. D. Lin, Phys. Rev. A **67**, 043404 (2003).
[5] T. K. Kjeldsen and L. B. Madsen, J. Phys. B **37**, 2033 (2004).
[6] R. Shingal and C. D. Lin, Phys. Rev. A **40**, 1302 (1989).
[7] Y. D. Wang and J. H. McGuire, Phys. Rev. A **44**, 367 (1991).
[8] K. Sakimoto, Phys. Rev. A **71**, 062704 (2005).
[9] H. Bräuning *et al.*, J. Phys. B **34**, L321 (2001).
[10] J. Caillat, A. Dubois, I. Sundvor, and J.-P. Hansen, Phys. Rev. A **70**, 032715 (2004).
[11] S. C. Cheng and B. D. Esry, Phys. Rev. A **72**, 022704 (2005).
[12] D. J. Phalen, M. S. Pindzola, and F. Robicheaux, Phys. Rev. A **72**, 022720 (2005).