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Quenching of Na$(4p)$ by He and H_2: A molecular-state treatment

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The collisional quenching of excited Na$(4p)$ by He and H_2 has been studied using the semiclassical, impact-parameter, close-coupling method based on a molecular expansion augmented by the plane-wave translation factor. Interactions between the colliding partners are approximated using suitable pseudopotentials. At low velocities $0.0005 \leqslant v \leqslant 0.001$ a.u., interference oscillations which depend on the spatial alignment of the electron charge distribution before the collision are present in the cross sections for H_2 quenching perturber. The cross sections due to H_2 are larger than those of He atoms throughout the energy region. At $T=470$ K the present quenching rate coefficients show good agreement with the experimental data of Kleiber *et al.* [J. Chem. Phys. **98**, 1101 (1993)]. [S1050-2947(97)10110-X]

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Rydberg atoms along with their peculiar properties in the presence of external fields and in collisions with atoms, ions, molecules, and surfaces have attracted considerable attention, not only for their intrinsic interest but also for their importance to numerous applications [1]. Atomic collision phenomena in which the internal electronic state of one of the colliding partners changes are in general sufficiently complex that only a few examples lend themselves to qualitative interpretation. Recent advances in experimental techniques have made it possible to prepare atoms in an aligned excited state [2] before the collision. The dependence of the collision dynamics on the shape and spatial alignment of an excited Rydberg atom is currently a subject of intensive study [3]. Among atomic Rydberg targets, alkali-metal atoms have enjoyed much favor owing to their simple structure. The recent review of Beigman and Lebedev [4] summarizes the current status of theoretical work on various collisional processes involving high-lying Rydberg atoms. For such collisions, various versions of perturbation theory, the quasi-free-electron model of Fermi, the impulse approximation, and classical methods have been used with success. However, for low-lying Rydberg states the influence of the core makes calculations more challenging and practically all these simple theories are inapplicable. Saha and Lane [5] have investigated state-changing cross sections for collisions of low-Rydberg Na atoms with He atoms and have shown that both differential and integral cross sections are very sensitive to the shape and the alignment of the initial state of the Rydberg target.

Only a few investigations have been reported of collisions of Rydberg atoms in low-lying states with molecules. Molecules have rotational and vibrational degrees of freedom that create computational difficulties. In the study of charge exchange between He^{2+} and H_2, Saha, Lane, and Kimura [6] treated the H_2 molecule as though it was an *atom* with a ionization potential $I_p = 15.4$ eV. Following Saha, Lane, and Kimura, in the present calculation we use a Hellman-type pseudopotential to represent the H_2^+ core. In order to include the effect of electron correlation empirically, we also perform a few calculations in which we vary the ionization potential I_p; each value of which corresponds to a vertical transition of H_2 to H_2^+ at different internuclear separation. We observe that the averaging procedure does soften the oscillation but the structure remains visible in the cross sections. In a recent experiment, Kleiber, Wong, and Bililign [7] measured the quenching rate coefficient out of Na$(4p)$ by He and H_2 perturbers. At thermal velocity, they observed that quenching cross sections for H_2 are substantially larger than those for He. At such low velocities, vibrational channels are unlikely to play a role in charge exchange because they are energetically inaccessible. On the basis of our *ab initio* molecular potential we report in this paper a full analysis of the experimental findings of Kleiber, Wong, and Bililign [7].

We have made a systematic investigation of the following collision processes:

$$\mathrm{Na}(4p,\beta)+\mathrm{He}\rightarrow\mathrm{Na}(3,l',m',\beta')+\mathrm{He} \tag{1}$$

and

$$\mathrm{Na}(4p,\beta)+\mathrm{H}_2(v=0;j=0)\rightarrow\mathrm{Na}(3,l',m',\beta') + \mathrm{H}_2(v'=0,j'=0), \tag{2}$$

where the orbital quantum numbers $l' = 2, 1, 0$, and the magnetic quantum numbers m' can have any values between $-l'$ to l'. Since the collision is fast compared to the vibrational and rotational motion of the bound H_2 molecule, we *freeze* the nuclei at a fixed position throughout the scattering event, neglecting their rotational and vibrational motion. The alignment angle β describes the direction of the principal axis of the Rydberg electron's charge distribution, measured with respect to the initial relative collision velocity $\mathbf{v}_{\mathrm{rel}}$. We choose the z axis to coincide with the initial velocity vector of the relative motion. We use the semiclassical impact-parameter close-coupled method [8], expanding the total wave function in a set of molecular orbitals (MO) that represent the electronic states. Following Saha and Lane we use plane wave electron translation factor (ETF). Its omission from the MO expansion introduces spurious long-range coupling [8]. Using the standard LCAO-MO variational procedure [9], we evaluate the molecular orbitals and the corresponding energy curves. The projectiles (He and H_2) and the

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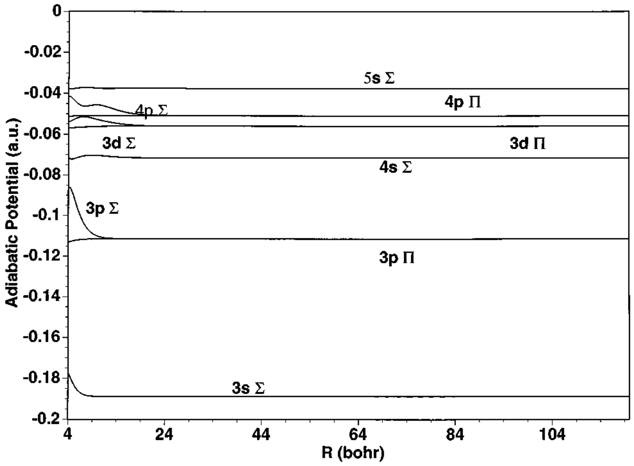

FIG. 1. Adiabatic potential energies for $3s_\Sigma$, $3p_{\Sigma,\Pi}$, $3d_{\Sigma,\Pi}$, $4s_\Sigma$, $4p_{\Sigma,\Pi}$, and $5s_\Sigma$ states of NaHe. In the separated atom limit $3s$, $3p$, $3d$, $4s$, $4p$, and $5s$ refer to the Rydberg atomic states.

target core Na$^+$ ion are represented by pseudopotentials [10] that reproduce the Rydberg energy levels for Na(n,l) very well. The electronic energy curves for He atom are shown in Fig. 1 for the states $4p_{\Sigma,\Pi}$, $3d_{\Sigma,\Pi}$, $3p_{\Sigma,\Pi}$, and $5s_\Sigma$, where $4p$, $3d$, $5s$ etc. refer to the Rydberg atomic state that correlates, in the separated-atom limit, with the molecular state. Because the quantum defects for these Rydberg states are large (for s and p states of Na they are 1.35 and 0.86, respectively), the adiabatic molecular states are well separated.

In the expansion of the system wave function, the coefficients satisfy a set of linear first-order, coupled differential equations, with initial conditions that specify a particular initial state; the asymptotic value of these coefficients represents transition amplitudes for various final states. These equations are solved numerically for a sufficiently large number of impact parameters b to ensure convergence, and cross sections are calculated by integrating the resulting square of the amplitudes over b. Values of $b<2.0a_0$ are not included in order to avoid internuclear separations where the pseudo-potential representation begins to fail [8]. In the present studies, we focus on the integral cross sections, summed over all impact parameters. Since the basis states are molecular orbitals, the calculated probability amplitudes and cross sections describe transitions between molecular states. However, since initially the internuclear axis is parallel to the relative velocity vector, the cross section for an initially aligned Na($4p$) to any final f states can be expressed as [5]

$$\sigma(4p,\beta\rightarrow f)=\sigma(4_{p\Sigma}\rightarrow f)\cos^2\beta+\sigma(4_{p\Pi}\rightarrow f)\sin^2\beta, \tag{3}$$

where the cross sections $\sigma(4p\Sigma\rightarrow f)$ and $\sigma(4p\Pi\rightarrow f)$ are calculated in the body fixed coordinate system from the Σ and Π components of the initial $4p$ wave function of the Na atoms, respectively.

In Fig. 2, we plot the calculated quenching cross sections out of an Na($4p$) excited state colliding with He as function of relative collision velocity. We have tested convergence in calculations that retain molecular four states ($4p_{\Sigma,\Pi}$ and $3d_{\Sigma,\Pi}$) and five states ($4p_{\Sigma,\Pi}$, $3d_{\Sigma,\Pi}$, and $5s_\Sigma$); the agreement between the resulting cross sections is within 1%. We only show the five-state results, which we feel have all important couplings for such low energies. The contribution of the initial $4p_\Pi$ state is larger than that of $4p_\Sigma$ state, because rotational coupling between $4p_\Pi$ and $3d_\Sigma$ is strong. Using their measured rate coefficient, Kleiber, Wong, and Bililign [7] have estimated the cross sections by a model rate equation. Their estimated cross section, shown in the figure, agrees reasonably well with ours.

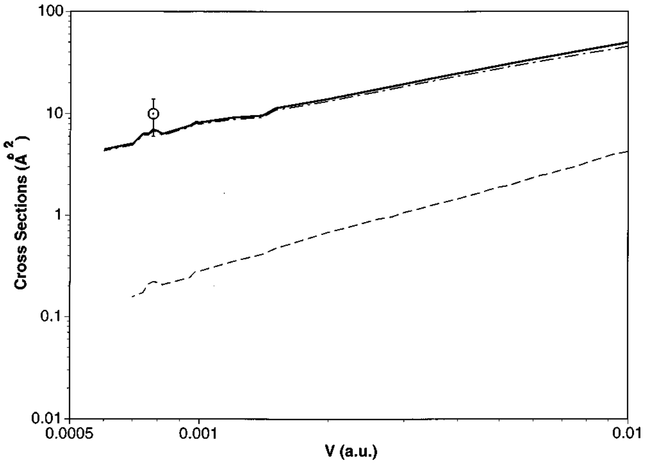

FIG. 2. Total integrated cross sections (A^{0^2}) from present calculation and compared to experimental data of Kleiber, Wong, and Bililign [7]. The solid curve represents the total cross sections; the dashed curve represents the contribution due to the formation of different Σ states; the chain curve denotes the contribution due to the formation of different Π states.

In Fig. 3 we show adiabatic potential energy curves for collisions with H_2. Comparison of Figs. 1 and 3 reveals that in the latter case there is a very closely avoided crossing around $R\approx4.0a_0$ between the $4p_\Sigma$ and the immediate neighboring $3d_\Sigma$ state. The energy defect ΔE between the initial $4p_\Sigma$ and final $3d_\Sigma$ state is much larger than their He coun-

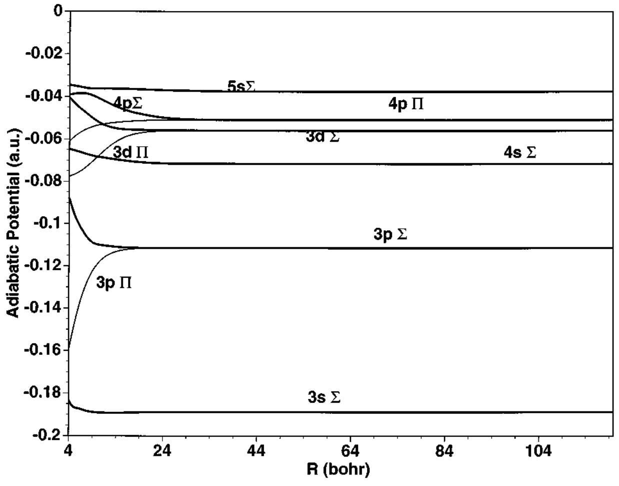

FIG. 3. Adiabatic potential energies for $3s_\Sigma$, $3p_{\Sigma,\Pi}$, $3d_{\Sigma,\Pi}$, $4s_\Sigma$, $4p_{\Sigma,\Pi}$, and $5s_\Sigma$ states of NaH_2. In the separated atom limit $3s$, $3p$, $3d$, $4s$, $4p$, and $5s$ refer to the Rydberg atomic states.

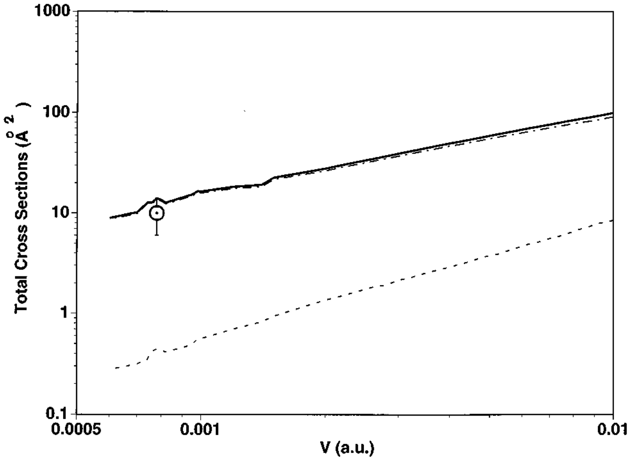

FIG. 4. Total integrated cross sections (A^{0^2}) from present calculation and compared to experimental data of Kleiber, Wong, and Bililign [7]. The solid curve represents the total cross sections; the dashed curve represents the contribution due to the formation of different Σ states; the chain curve denotes the contribution due to the formation of different Π states.

terpart (see Fig. 1). This feature enhances the Na-H_2 cross section, as we will see later. Around $R \approx 4.0 a_0$, the radial coupling matrix element has a sharp peak that plays a major role in transferring probability among adjacent states. The angular coupling matrix elements between $3d_\Sigma$ and $4p_\Pi$ remain important even at large internuclear separation ($R > 30 a_0$). In order to study the sensitivity of these cross sections to our model H_2 potential we have performed calculations using ionization potentials I_p ranging between 15.4 and 16.0 eV. Different values of I_p correspond to different fixed values of the H-H separation. The integrated cross sections averaged over I_p shown in Fig. 4 agree well with the experimental data [7].

To illustrate the differences between probability transfer due to collisions with He and H_2, we show in Fig. 5 the probability times the impact parameter b at relative velocity $v_{\mathrm{rel}} = 1.5 \times 10^{-3}$ a.u. as function of b. The oscillations for H_2 extend to larger b than do those for collisions with He. In the latter case, the peaks of these oscillations are smaller by an order of magnitude. Note that we multiply our results for He by 20 to make them visible. For the He projectile the incident channel ($4p_\Sigma$ or $4p_\Pi$) does not have a close encounter with any adjacent state to share the probability throughout the collision event (see also Fig. 1). When the Na atom is aligned perpendicular to the quantization axis, the interaction of both the projectiles is much longer than in other alignments. As a result the transition probability is large, producing a large laser polarization. At 400 K, the alignment ratios ($\perp/\parallel$) for He and H_2 are 31 and 26, respectively. The integrated cross sections as a function of the alignment angle (not shown) show uniform $\sin^2\beta$ dependence as expected for both the He and H_2 quenching gases. The calculated rate coefficients at $T = 470$ K are compared with experimental data in Table I. We have calculated these quenching rate coefficients by integrating over the Maxwellian velocity distribution corresponding to $T = 470$ K. The agreement with the experimental findings for H_2 is much better than for He atoms. The rate coefficient out of the $4p$ state for He is much small than for H_2; as was observed earlier by Kleiber, Wong, and Bililign [7].

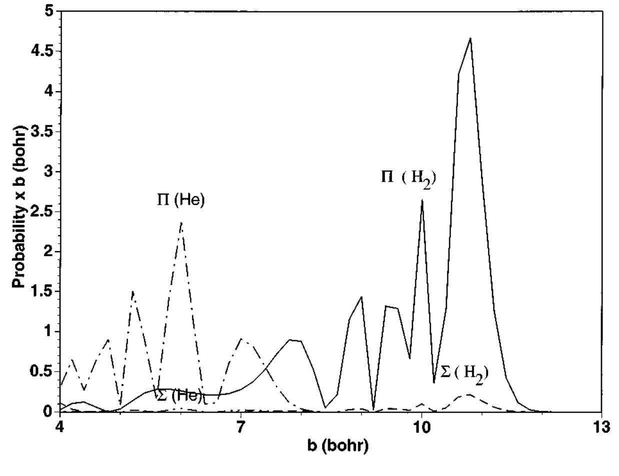

FIG. 5. Variation of the product of the transition probability and the impact parameter b with b at a relative velocity $v = 1.5 \times 10^{-3}$ a.u. The results due to He are multiplied by 20 for proper visibility. The contribution due to the formation of Σ (He) is negligibly small.

TABLE I. Experimental and calculated collisional quenching rates ($\times 10^{-10}$ cm^3/s) out of the Na(4p) state for collisions with He and H_2 at $T = 470$ K.

Projectile	Present	Experiment [7]
He	0.36	0.5 ± 0.2
H_2	1.98	1.9 ± 0.9

In conclusion, using an MO treatment with the inclusion of the plane-wave ETF we have calculated the quenching cross sections of excited Na(4p) by He and H_2. In our calculation we use a local spherically symmetric H_2 interaction potential. Our results are in reasonably good agreement with the measurement of Kleiber, Wong, and Bililign [7]. In conformity with the experiment, we found that at 400 K the rate coefficient for H_2 is much higher than for He. This model potential can be applied easily to collisions with other atoms, where theory is scare or nonexistent.

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