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Spin–orbit induced association under ultrafast laser pulse control

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Abstract

The possibility of spin–orbit induced association reactions controlled by optimized femtosecond laser pulses is demonstrated for the example of $\text{Br}^+(\text{}^3\text{P}) + \text{H}(\text{}^2\text{S}) \rightarrow \text{HBr}^+(\text{X}^2\Pi/\text{A}^2\Sigma^+)$ association. The nuclear wavepacket dynamics is simulated on the basis of ab initio data for HBr^+ . To achieve permanent, vibrationally state–selective association, both a Feshbach resonance between collision and vibronic energies and optimal timing between spin–orbit induced and laser pulse assisted transitions are important. The novel method can be effective even when direct photoassociation is forbidden. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The investigation of molecular dynamics on a picosecond or even femtosecond timescale plays an increasingly important role in ultrafast molecular spectroscopy which has emerged into the field of femtochemistry [1]. Applications range from real time observation of wavepacket dynamics [2] to active laser control of unimolecular reaction dynamics [3], e.g., the state-selective population transfer between molecular energy levels and the breaking of bonds in photodissociation of molecules, both in gas phase and in a solution envi-

ronment [4–9]. Recently, these concepts have also been transferred to the study of elementary bimolecular reactions, i.e., the laser control of atomic and molecular collision processes. There has been rapid progress in the field of photoassociation [10–15], in particular the formation of ultracold molecules from cooled and trapped atoms [16,17]. Usually photoassociation spectroscopy involves transitions from free (scattering) states of a collision complex in the ground electronic state to vibrational levels of the well of a suitable electronically excited state via absorption of photons. An alternative approach is the formation of a stable molecule in its ground electronic state by ultrafast laser pulse induced resonant photon emission. In our previous work [18–20] it has been shown that this process can be made very efficient by simultaneous optimization of laser pulse and wavepacket parameters. The high efficiency of the process results from the use

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of ultrashort laser pulses which are much shorter than the typical timescale of Rabi oscillations. At the same time, this process can be made very efficient and extremely state selective (close to 100% with respect to the vibrational/rotational states of the molecular product) [18–20]. In other work it has been demonstrated that even in cases where both processes are amenable for similar wavelengths, the electronic branching can be controlled by ultrashort laser pulses [21]. It is noted that the two types of photoassociation processes bear many similarities with state-selective electronic excitation [8] and ground or excited state photodissociation [4,5,22]. In any of the abovementioned cases, however, it is necessary to obey the selection rules for the corresponding laser-induced dipole transitions, e.g., conservation of electronic multiplicity.

In this Letter, we present a novel scheme for association that is also applicable to cases where a direct photoassociation is forbidden, see Fig. 1. It consists of a spin-orbit induced association process with stabilization of the product by laser pulse control. The first step of this process is the spin-orbit association of a collision pair into an excited bound state which is directly opposed to the predissociative decay of a bound state interacting with repulsive states by means of spin-orbit coupling [23]. As a specific example the $\text{Br}^+(^3\text{P}) + \text{H}(^2\text{S})$ collision pair is chosen because of the relatively

strong spin-orbit coupling leading to a lifetime of predissociative states in the order of 10–100 fs and the availability of extensive theoretical and experimental data [24–27]. During the collision process, the spin-orbit interaction induces transitions from each of the repulsive states to the excited bound state $\text{A}^2\Sigma^+$ most of which are forbidden for direct dipole transitions, e.g., between states of different multiplicity (in our case these are transitions between repulsive $^4\Pi$ or $^4\Sigma^-$ and bound $\text{A}^2\Sigma^+$ states) or with different symmetry ($^2\Sigma^- \rightarrow \text{A}^2\Sigma^+$). As a second step, laser-induced state-selective transitions to long-living vibrational states in the ground ($\text{A}^2\Sigma^+$, $v' = 4 \rightarrow \text{X}^2\Pi$, $v'' = 1$) or excited state ($\text{A}^2\Sigma^+$, $v' = 4 \rightarrow \text{A}^2\Sigma^+$, $v'' = 1$) are employed to prevent subsequent predissociation [24–27]. In order to successfully compete with the predissociation process, these transitions are to be induced by ultrafast laser pulses with durations of hundreds of femtoseconds. Furthermore, we shall demonstrate that the combined process can be highly selective with respect to the vibrational state of the molecular product.

2. Model

We illustrate this idea by numerical wavepacket propagation within a one-dimensional model, i.e., we neglect molecular rotation for the ultrashort timescales considered in the present work (for extensions to models of rotating molecules, see e.g., [9,20]). The dynamics of the collision pair is treated in a quantum-mechanical Schrödinger picture. The initial state is described by a localized Gaussian wavepacket in the internuclear distance r :

$$\psi(r) = \left(\frac{2}{\pi a^2}\right)^{1/4} \exp\left[ikr - \left(\frac{r-r_0}{a}\right)^2\right], \quad (1)$$

where the two atoms are assumed to be initially at an average distance of r_0 well outside the interaction region. The initial momentum $\hbar k < 0$ of the incident wavepacket corresponds to a relative collision energy of $T = \hbar(k^2 + 1/a^2)/(2m)$, where m stands for the reduced mass.

Our model consists of five electronic states, see Fig. 1. Apart from the attractive electronic ground

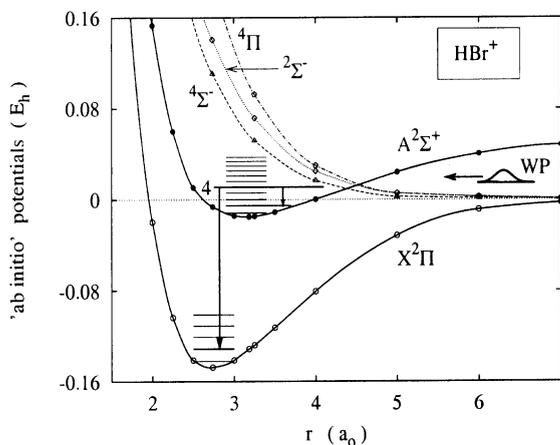


Fig. 1. Ab initio potential energy curves and association scheme for the relevant vibronic states of HBr^+ .

state ($X^2\Pi$), we consider three repulsive states, $^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$, which are coupled through spin-orbit interaction to another bound state ($A^2\Sigma^+$) which asymptotically connects to the $\text{Br}^+(^1\text{D}) + \text{H}(^2\text{S})$ limit [24,25]. Furthermore, radiative transitions are allowed between states of equal multiplicity, i.e., between the ground state and the two doublet states, with the corresponding transition dipole moments being perpendicular to the molecular axis. Finally, permanent dipole moments for the two bound states (X and A) which are parallel to the molecular axis are taken into account.

In the framework of the semiclassical dipole approximation [28], the time evolution is given by coupled time-dependent Schrödinger equations for the wavefunctions describing the relative nuclear motion in the five electronic states introduced above:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi_X(t) &= \left[\hat{T} + V_X - \mu_X E_{\parallel}(t) \right] \psi_X(t) \\ &\quad - \mu_{XA} E_{\perp}(t) \psi_A(t) - \mu_{X2} E_{\perp}(t) \psi_2(t), \\ i\hbar \frac{\partial}{\partial t} \psi_A(t) &= \left[\hat{T} + V_A - \mu_A E_{\parallel}(t) \right] \psi_A(t) \\ &\quad - \mu_{XA} E_{\perp}(t) \psi_X(t) + \sum_{j=1}^3 H_{Aj}^{SO} \psi_j(t), \\ i\hbar \frac{\partial}{\partial t} \psi_j(t) &= \left[\hat{T} + V_j \right] \psi_j(t) - \delta_{j,2} \mu_{X2} E_{\perp}(t) \psi_X(t) \\ &\quad + H_{Aj}^{SO} \psi_A(t), \end{aligned} \quad (2)$$

where $j = 1, 2, 3$ stands for $^4\Sigma^-$, $^2\Sigma^-$, $^4\Pi$ states and \hat{T} is the kinetic energy operator. Note that all potential energy functions $V(r)$, permanent and transition dipole moments $\mu(r)$, and spin-orbit couplings $H_{Aj}^{SO}(r)$ are adapted from ab initio data in the literature [24–26] which makes the HBr^+ cation a favorable choice for the theoretical investigation of radiative and non-radiative processes. The components of the electric field parallel, $E_{\parallel}(t)$, and perpendicular, $E_{\perp}(t)$, to the molecular axis are assumed to have a \sin^2 -shaped envelope of the electric field

$$E(t) = E_0 \sin^2 \left(\frac{\pi t}{\tau} \right) \cos(\omega t), \quad 0 \leq t \leq \tau \quad (3)$$

with amplitude E_0 , carrier frequency ω , and pulse duration τ .

The coupled equations (2) are solved numerically using fast Fourier transform (FFT) methods for the transformation between coordinate and momentum space. The corresponding wavefunctions are represented on an equidistant grid in coordinate space. The number of points varies from $N = 1024$ to $N = 8192$ with a distance of $\Delta r = 0.05a_0$. Absorbing boundary conditions are used to prevent artificial reflection from the edge of the grid. Propagation in time is achieved by the $\mathcal{O}(\Delta t^3)$ split-operator technique [29]. Typically, a time step of $\Delta t = 24\hbar/E_h$ was chosen. The time-dependent population of the i th electronic state is simply obtained as $\langle \psi_i(t) | \psi_i(t) \rangle$ while populations of bound vibrational states are obtained by projection of the non-stationary wavefunctions $\psi_X(t)$ or $\psi_A(t)$ on the vibrational states $v_X = v''$ or $v_A = v'$ of the respective potentials where the vibrational eigenfunctions are computed by means of the Fourier grid Hamiltonian method [30].

3. Spin-orbit induced association

As a first step, we study a scattering event in the absence of external (laser) fields. In this case the process can be viewed as a sequence of a spin-orbit induced association and predissociation. The asymptotic state of the atomic pair $\text{Br}^+(^3\text{P}) + \text{H}(^2\text{S})$ splits at smaller internuclear distances into four molecular states ($X^2\Pi$, $^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$), see Fig. 1. The ground state association process ($X^2\Pi$) has been discussed in detail in [18–21] and shall not be considered here. Instead, let us consider the case of the system occupying the lowest repulsive state, $^4\Sigma^-$. Although the collision process without laser field will be very similar for the other repulsive states, it is emphasized that for the quartet state a direct photoassociation into doublet states is multiplicity-forbidden for dipole transitions.

For a typical choice of the momentum, $\hbar k = 6.17\hbar a_0^{-1}$, or corresponding scattering energy, $T = 0.0105E_h$ (0.285 eV), and width parameter, $a = 3.5a_0^{-1}$, the relatively strong spin-orbit coupling ($H_{A1}^{SO} \approx 0.003E_h$) gives rise to a substantial intermediate population of more than 70% in the

excited bound $A^2\Sigma^+$ state (especially $v' = 4$), see Fig. 2. Subsequently, this population is decaying again through spin–orbit coupling with all three repulsive states being populated. The dependence of the $A^2\Sigma^+$ state population and lifetime on the wavepacket parameters of Eq. (1) is of crucial importance for the laser pulse induced stabilization of the collision complex investigated below. It is clear that the laser pulse duration τ must be on the same timescale as the lifetime of the $A^2\Sigma^+$ state population. The latter one depends on the relative velocity of collision partners, the spatial extent of the wavepacket (parameter a), and the predissociation lifetime of the metastable states $v' > 2$ which are populated by the association process. On the one hand, the pulse duration τ should not be too long ($\tau \approx 1$ ps) in order to exclude rotational effects. On the other hand, extremely short pulses ($\tau \approx 10$ fs) would deteriorate the vibrational state selectivity [8]. In order to achieve a suitable lifetime of about 100 fs, a value of $3a_0 < a < 12a_0$ has to be chosen.

The role of the initial momentum $\hbar k$ (or scattering energy T) is illustrated in Fig. 3. The maximum population of the $A^2\Sigma^+$ state during a scattering process (solid line labeled ‘Sc’) has a sharp threshold near $T = 0.004E_h$ and pronounced Feshbach resonances near the zero order eigen-

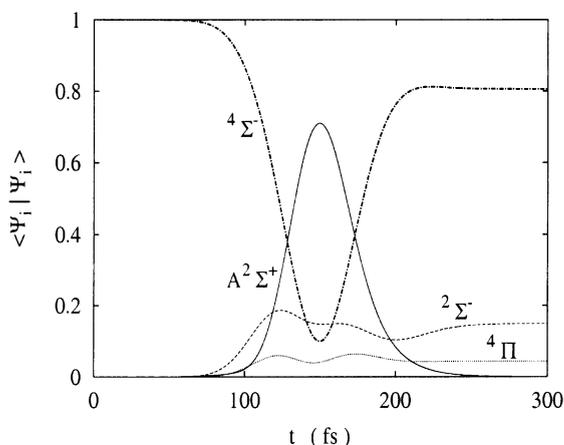


Fig. 2. Spin–orbit induced association and subsequent predissociation: population dynamics of HBr^+ electronic states during a collision process.

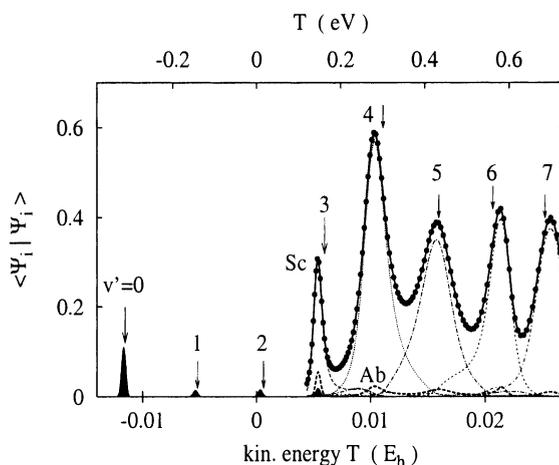


Fig. 3. Eigenenergies and Feshbach resonances for the $A^2\Sigma^+$ states of HBr^+ ion. Maximum population during a $Br^+(\text{^3P}) + H(^2S)$ scattering event (solid curve ‘Sc’) versus zero order eigenenergies (vertical arrows). Excitation (filled peaks) and absorption spectrum (‘Ab’) for $v'' = 1 \rightarrow v'$ transitions are shown for comparison.

energies, i.e., vibrational levels v' of the $A^2\Sigma^+$ state, calculated in the absence of spin–orbit coupling. For comparison, the figure also includes excitation (black peaks for $v' = 0, 1, 2, 3$) and absorption (dashed line labeled ‘Ab’ for $v' = 3, \dots, 7$) spectra for an initial $v'' = 1$ level of the $X^2\Pi$ ground state where the excitation spectrum has been obtained for a laser pulse with $\tau = 500$ fs and $E_0 = 5$ MV/cm. The absorption spectrum coincides with the excitation spectrum for $v' = 0, \dots, 2$ but it shows also the higher levels ($v' > 3$) which do not appear in the latter because they are predissociating on a faster timescale. The shortest lifetime is found for the $v' = 5$ resonance state which predissociates within about 10 fs [24,25]. The coincidence of the resonances of excitation and absorption spectra with the ones in the association probability points to the common origin, i.e., the spin–orbit coupling of vibrational levels of the $A^2\Sigma^+$ state with scattering states of the repulsive electronic states. Note that similar Feshbach resonances have been observed earlier in photoassociation spectroscopy [31–33]. The width of the association resonances of approx. $0.002E_h$ reflects both the energetic spread of the wavepacket and the lifetime of the predissociating complex. The maxima of the various

spectra are slightly shifted with respect to the vibrational energy levels of the zero order $A^2\Sigma^+$ vibrational states as indicated by the vertical arrows in Fig. 3 in accordance with the semiclassical Landau–Zener picture [34], see also [24,25]. Note that the minima correspond to association probabilities around 20% which demonstrates that, although being useful, the use of Feshbach resonances is not a necessary condition for the process of spin–orbit induced association.

4. Laser pulse induced stabilization

Based on this study of the spin–orbit induced association, we investigate optimal laser pulse induced transitions to stabilize the metastable collision complexes formed in the $A^2\Sigma^+$ state. The first strategy involves a mid-infrared laser pulse polarized parallel to the molecular axis. It is used to stimulate transitions from the predissociative levels of the $A^2\Sigma^+$ state ($v' > 2$) down to bound states ($v' \leq 2$). As an example, a frequency close to the transition from $v' = 4$ to $v' = 1$ was chosen where the exact value of the frequency, $\omega = 1174 \text{ cm}^{-1}$, as well as the amplitude, $E_0 = 36 \text{ MV/cm}$, are optimized numerically to achieve maximum population below the threshold for predissociation of the $A^2\Sigma^+$ state. For a fixed laser pulse duration of $\tau = 310 \text{ fs}$ in (3) which corresponds to 126 fs FWHM, the population dynamics for the laser-controlled process is shown in Fig. 4. The population of about 40% in the $A^2\Sigma^+$ state built up by the spin–orbit induced association process during the collision (from initial $4\Sigma^-$ state with $k = -6.3a_0^{-1}$, $a = 12a_0$) can be almost completely transferred to stable vibrational levels. Moreover, the photoinduced stabilization achieves a high vibrational state selectivity, i.e., more than 80% of the final (permanent) $A^2\Sigma^+$ state population is found in a single vibrational state ($v' = 1$).

The alternative approach employs perpendicularly polarized near-UV light to stimulate transitions down to vibrational levels of the ground electronic state $X^2\Pi$. Fig. 5 shows that a laser pulse with $\tau = 210 \text{ fs}$ (75.6 fs FWHM), $\omega = 31084 \text{ cm}^{-1}$, and $E_0 = 180 \text{ MV/cm}$ can be used to transfer the collision complex from the

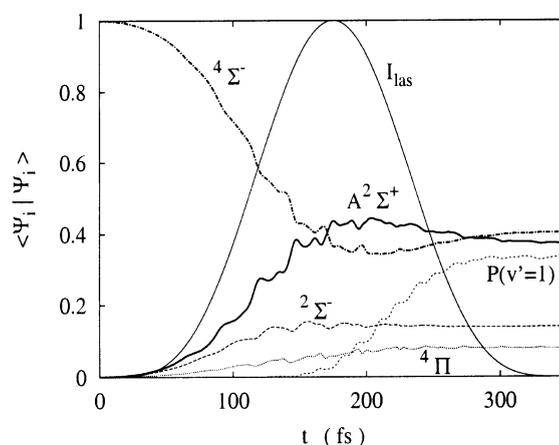


Fig. 4. Stabilization of spin–orbit associated HBr^+ collision complex: population transfer to the $v' = 1$ vibrational level of the $A^2\Sigma^+$ excited state induced by a laser pulse with parallel polarization.

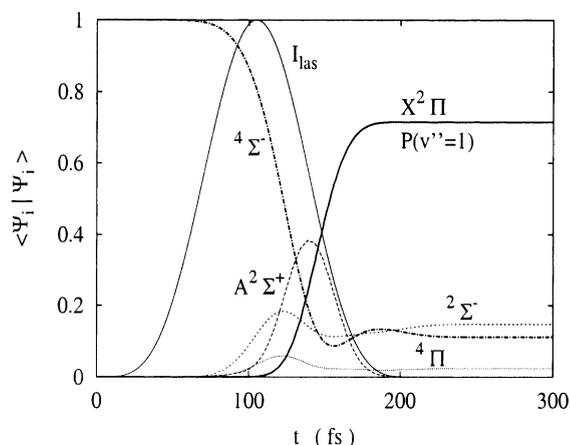


Fig. 5. Stabilization of spin–orbit associated HBr^+ collision complex: population transfer to the $v'' = 1$ vibrational level of the $X^2\Pi$ ground state induced by a laser pulse with perpendicular polarization.

initial $4\Sigma^-$ state with $k = -6.17a_0^{-1}$, $a = 3.5a_0$ through the intermediate population of the $A^2\Sigma^+$ state (in this case around 70%) completely to the ground state before predissociation takes place. The vibrational state selectivity is much higher than previously, i.e., close to 100% of the ground state population is found in a single vibrational level ($v'' = 1$).

5. Conclusions

In summary, permanent association of a collision pair for which direct photoassociation is multiplicity-forbidden proceeds via spin-orbit coupling between repulsive and bound electronic states. In this type of collisions metastable complexes are formed where the association probability can be enhanced considerably if a Feshbach resonance is employed. To prevent the complexes from predissociation, the collision is assisted by a laser-induced transition to a bound state leading to permanent stabilization of the associated molecule. For optimized, ultrashort laser pulses with a duration of 100 fs, the proposed strategy is both very effective and vibrationally state-selective. In passing we note that the concept of effective and state-selective population transfer by means of ultrashort laser pulses can also be extended to the case of rotating molecules [9] or rotating collision pairs [20].

As already mentioned above, the choice of HBr^+ as a model system to demonstrate the mechanism of spin-orbit induced association was mainly motivated by the availability of high level ab initio potential energy curves, transition dipole moments and spin-orbit coupling matrix elements as well as experimental data. When applying the proposed scheme to another collision system, it is important to (roughly) match the timescales of predissociation/preassociation, wavepacket scattering, and pulse duration of the light sources to be used. Essentially, this leads to a constraint on the magnitude of the spin-orbit coupling effect. Also the use of ionic systems is by no means general. However, ions offer the possibility of experimentally controlling the collision pairs and the molecular product by means of external electrostatic fields.

An experimental strategy to prepare the initial wavepacket-like states could be to create the reactants by a photoinduced process which would in principle allow to control the geometric and temporal characteristics of the collision pair [4]. However, it is believed that the proposed scheme can also work in a thermal sample. First, the spin-orbit induced process selects only those collision pairs with impact parameter and angular momen-

tum within a certain range. Second, the photo-induced process should be relatively robust with respect to small variations of the collision complex due the large spectral width of the ultrashort pulses. Moreover, it has been shown that impact parameter and orientation can be even controlled to some extent in bimolecular reactions [12].

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