Energy Transfer through Exciplex Funnel States

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Funnels in excited-state potential energy surfaces play a central role in photochemistry because they are the primary topological feature of potential energy surfaces associated with strong coupling of photoexcited electronic states to the ground state.[1] The prototype funnel is associated with the upper cone of a conical intersection[2-4] of two electronic states. The importance of nonadiabatic passage through conical intersections has been repeatedly invoked in accounting for the reactivity of excited states.[5] Experimental characterization of funnels has typically been indirect, but recently accurate quantum mechanical dynamics calculations have become feasible for molecular collisions involving valence-excited states and conical intersections,[6] and such calculations may now be used to learn about dynamical properties of funnels. In this communication we report converged quantum dynamics studies that reveal resonances,[7] i.e., metastable states, with appreciable lifetimes in funnels associated with a conical intersection. The resonances lead to state-to-state transition probabilities for vibrational and rotational energy transfers that exceed direct (i.e., nonresonant) contributions in collisions with the same energy and angular momentum by 1 order of magnitude or more.

The dynamics calculations were carried out by the outgoing-wave variational principle[8] with an efficient new type of basis function[6] consisting of two-dimensional Gaussians in the Na–H$_2$ and H–H coordinates and direct products of spherical harmonics in the angular coordinates. These were augmented by distorted-wave Green's functions[9] for rotationally coupled distortion potentials defined by projection operations on vibrational sub-manifolds.[10] The calculations include all degrees of freedom, which is important because of the strong anisotropy of the interactions.

The calculations were carried out for collisions of Na with H$_2$ with zero total angular momentum. The first excited state of
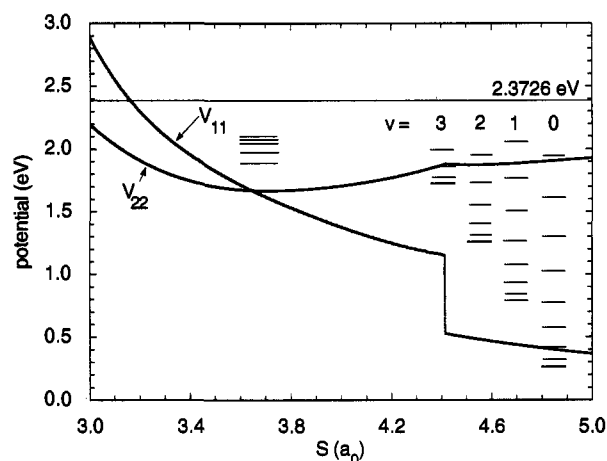

Figure 1. Energies of the two lowest adiabatic potential energy surfaces for the C_{2v} approach of Na to H$_2$ as a function of the distance S from the Na to the center of mass of H$_2$. (For C_{2v} geometries in this system, there is no difference between adiabatic and diabatic potentials, as defined in refs 13 and 22, so these are the diabatic potentials as well.) For each value of S, the value of the H–H distance s is optimized to minimize the excited-state potential V_{22} and then used to calculate both V_{11} and V_{22}. The discontinuous derivative in V_{22} and the jump in V_{11} at $S = 4.33\ a_0$ occur because at this point, as S is decreased, a local minimum in V_{22} with $s = 1.91\ a_0$ becomes deeper than a local minimum with $s = 1.42\ a_0$. (1 $a_0 = 0.529$ Å.) At the minimum of V_{22}, at $S = 3.72\ a_0$, the optimum value of s is 1.98 a_0. The thin line at 2.3726 eV shows the minimum energy required for dissociation to Na(3p) + H$_2$ with zero-point energy. The energy levels in the lower right are the vibrational energies of H$_2$ with Na in the ground 3s state.

this system exhibits a C_{2v} exciplex[11] with a binding energy of 0.44 eV,[12-17] as compared to the excited-state adiabatic dissociation products, Na(3p) + H$_2$. This exciplex is illustrated in Figure 1, which also shows the lowest-energy conical intersection, which occurs very close to the exciplex potential minimum for the surfaces used in the present dynamics calculations.[12] Collisions initiating on the ground electronic state, i.e., collisions of Na(3s), with energies close to the metastable energy states of the funnel, can become trapped in the funnel as Feshbach[18] compound-state resonances. Decay probabilities for the metastable funnel states can lead to significant population in states that are produced with much smaller excitation or deexcitation probabilities in collisions that do not access these states. This is illustrated in Figure 2. Figure 2a shows the transition probabilities for molecules in collisions with initial vibrational quantum number $v = 0$ and rotational quantum number $j = 6$ to become excited to final vibrational quantum number $v' = 2$ and final rotational quantum number $j' = 0$ in the vicinity of the first resonance. The peak is due to the resonance. Figure 2b shows a similar plot for $v = 2$, $j = 2 \rightarrow v' = 1$, $j' = 0$ in the vicinity of the second resonance. Figure 2c shows the total probability of vibrational excitation v

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(12) The potential energy surfaces used in this work are two-state diabatic respresentations[13] of an eight-state valence bond calculation.[14] More accurate calculations are also available[15,16] and lead to somewhat different quantitative features, i.e., a binding energy of 0.41–0.43 eV for the exciplex and a somewhat higher-energy and less extended geometry at the conical intersection. However, the present calculations assume the static properties of ref 13, which neglects electronic angular momentum and spin–orbit coupling, and the dynamics calculations correspond to fully converged nuclear dynamics for this representation.
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Communications to the Editor

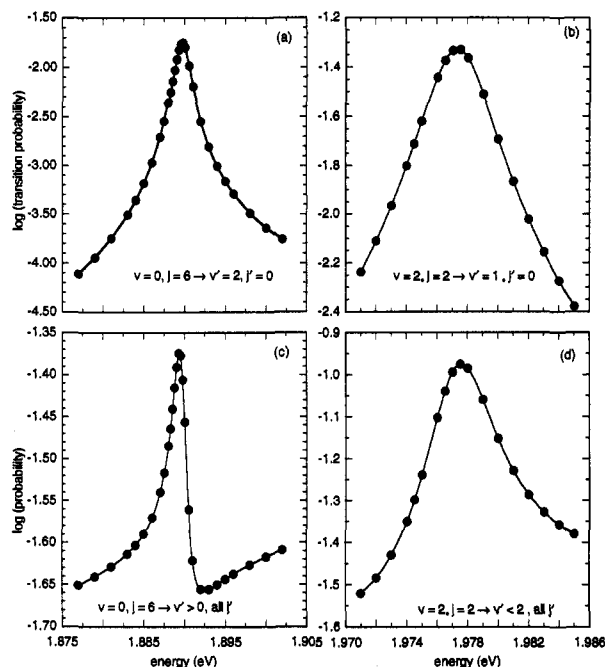*J. Am. Chem. Soc., Vol. 115, No. 14, 1993* 6437

Figure 2. Logarithms to the base 10 of state-to-state transition probabilities, where v and j are initial vibrational quantum numbers of H_2 and v' and j' denote final values, and of probabilities of vibrational excitation or deexcitation.

$= 0$, $j = 6 \to v' > 0$ at the first resonance, and Figure 2d shows the total vibrational deexcitation probability $v = 2$, $j = 2 \to v'$ < 2 at the second resonance. Each curve in Figure 2 shows a strong enhancement of the indicated inelastic process in the vicinity of the resonance, with enhancements over the background inelasticity (due to direct processes) of factors of 1.8–10^3. Such enhancements may be observable in differential cross sections, especially for nearly backwards scattering, or in integral cross sections, and they may play important roles in photochemistry or in the interaction of metal atoms with H–H or C–H bonds. Figure 2 also shows that the full widths at half maximum, Γ, of these resonances are about 2 and 5 meV, respectively.

The resonances were further characterized by the energy dependence of their eigenphase sums,[19] leading to resonance energies E_{res} and total widths Γ. The latter were converted to resonance lifetimes by the formula[20] $\tau = 2\hbar/\Gamma$. Resonance energies and lifetimes are tabulated for the five lowest-energy even-symmetry resonances in Table I. Bound-state calculations[21] on the upper diabatic[13,22] surface yielded resonance energies within 4 meV of the values obtained from the two-surface scattering calculations, indicating that motion in the resonance states is well described as electronically diabatic, and they were used to assign vibrational quantum numbers to the metastable states. Vibrational modes v_1 and v_2 have a_1 symmetry and correspond respectively to the H–H stretch and the Na–H$_2$ stretch; these modes may also be called the bend and the H–Na–H symmetric stretch. Mode v_3 has b_1 symmetry and corresponds to the H–Na–H asymmetric stretch.

Table I. Energies, Widths, Quantum Numbers, and Lifetimes of the Metastable States

energy (eV)	width (meV)	ν_1	ν_2	ν_3	τ (ps)
1.890	2.0	0	0	0	0.70
1.977	4.7	0	1	0	0.28
2.053	5.7	0	2	0	0.23
2.08	a	0	0	2	b
2.105	2.5	1	0	0	0.53

a Wide. b Small.

The resonance lifetimes are much longer than the associated vibrational periods. Nevertheless, one does not expect to observe fluorescence from exciplex states because they dissociate more rapidly than the radiative lifetime.[23] Vivie-Riedle *et al.*[16] observed spectroscopic lines that they attributed to transitions into vibrational modes of the Na·H$_2$ exciplex that lie above the Na(3p) + H$_2$ dissociation limit. Resonance states in the funnel, such as predicted here, should be observable as predissociated[4] lines to the red of the metal atomic line, such as observed,[24] e.g., in Cd·H$_2$. The present newly demonstrated ability to obtain converged solutions of the coupled nuclear-motion Schrödinger equations for such states without reduced-dimensionality approximations should be very useful for interpreting the predissociation lifetimes more realistically. For Cd·H$_2$, Breckenridge and co-workers[24] measured widths decreasing from 0.4 to 0.1 meV as the excitation energy in the Cd–H$_2$ stretching coordinate (v_2) increased from 160 to 212 meV and presented a pseudodiatomic calculation that predicted a width of 2 meV for the exciplex ground state; as a consequence, their calculated and measured resonance lifetimes for the progression in v_2 increase from 0.8 ps for the ground state to 11 ps for the highest state observed. They emphasized the need for accurate three-dimensional calculations such as presented here. In our calculations, the lifetimes are a nonmonotonic function of the excitation energy; however, they decrease with increasing quanta in v_1, v_2, or v_3, and the v_2 trend is especially interesting in that such excitation presumably moves the metastable-state vibrational amplitude farther from the conical intersection. Correlation of lifetimes with distances of vibrational turning points from conical intersections, when it holds, can give information about conical intersection locations when such states are seen in experimental systems.[24]

In summary, we have found metastable states associated with the funnel of a molecular exciplex, and we have performed quantum dynamics calculations of their widths and lifetimes. Collisions that access these resonances lead to large increases in energy transfer probabilities. It is clear that the resonances have interesting differences in the way that they couple to deexcitation mechanisms. The study of resonance states in exciplexes will permit a deeper understanding of funnel regions of potential energy surfaces and the way that they convert electronic excitation energy into internuclear motion in the ground electronic state.

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