Quantal Study of Laser-Induced Transitions between Electronic Potential Energy Surfaces in Reactive F + H₂ Collisions

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Results of a rigorous quantal treatment of laser-induced transitions between electronic potential energy surfaces in collinear reactive F (^P_{1/2}) + H₂(υ=0) collisions are presented. Such transitions are dominated by two processes: transmission to HF(υ′=2) + H and inelastic reflection to F(^P_{3/2}) + H₂(υ=0). The onset of these processes as a function of collision energy is delayed due to a dynamic barrier caused by the radiative interaction.

In an earlier paper (ref 1, hereinafter referred to as I) results were presented for a study of electronically nonadiabatic transitions in reactive F + H₂ collisions. A collinear model of the collision system including two electronic potential energy surfaces was described there in some detail. Here we report a rigorous quantal treatment of laser-induced surface switching in the F + H₂ reaction.²

For this first effort we employ a two-surface collinear model of the collision in which surface switching can come about only as a result of coupling to the laser field. The two diabatic potential energy surfaces are those used in I, but with the reactive surface elevated in energy by the field quantum ℏω relative to the field-free case so as to take proper account of resonant photon exchange. Shifting the reactive surface leads to a crossing along a seam on the reactant side of the strong interaction region which, for our choice of photon energy, is a more or less straight line that slices across the reactant valley at an angle.

Our field quantum is that of the HF laser, ℏω = 0.469 eV. It is of course resonant with the υ = 1 to υ = 2 vibrational transition of the product HF, but this resonance is not a factor in the collision region and so may be ignored for present purposes. We confine our attention to the electronic transition, in particular, to transitions from the nonreactive, electronically excited potential energy surface which correlates asymptotically to the reactant state F( ^P_{1/2}) + H₂(^1Σ^+).

Such reaction is predicted in I even when no field is present: collisional coupling of the two surfaces is the driving mechanism in that case. That mechanism is not present in the current model, however; only field-induced electronic transition is represented. Including the purely collisional mechanism and the field-induced coupling at the same time necessitates doubling the number of potential energy surfaces, thus greatly increasing the complexity of the calculation, but is unlikely to yield significantly different results. The electronic transition probabilities are rather small in both cases. Since the two mechanisms act independently of one another, we feel reasonably confident that no great error will be made if we consider the resulting transition probabilities separately.

The computational techniques have been detailed elsewhere.¹⁻⁵⁻⁶ Gordon’s propagation scheme⁴ is used in conjunction with the “most adiabatic” diabatic representation¹⁻⁵ to generate probability amplitudes. Single-photon exchange (in this case, stimulated emission) is assumed as in our earlier systems.³ Coupling to the field comes about via the proximity-induced electronic transition dipole moment which is given purely as a function of the separation between F and the nearer H atom. The same dipole moment has been used in parallel semiclassical work.⁷⁻⁸ It is expressed as an exponential fit to the ab initio calculations of Bender and Davidson⁹

\[ \mu(r) = \mu_0 e^{-\gamma r} \]

where \( \mu_0 = 0.8996 \text{e} \cdot \text{a}_0 = 2.287 \text{D} \) (e is the unit of charge and \( \text{a}_0 \) is the bohr radius) and \( \gamma = 0.5603 \text{a}_0^{-1} = 1.059 \text{Å}^{-1} \). The field strength is \( E_0 = 0.00169 \text{e} \cdot \text{a}_0^2 = 8.66 \times 10^6 \text{V/cm} \), which corresponds to an intensity \( I = 9.95 \times 10^{10} \text{W/cm}^2 \) ≈ 0.1 TW/cm². This is a very strong field, necessitated by the relatively short range of the coupling dipole and by the rather sharp angle with which the two surfaces cross.⁷⁻⁸

The coupling persists in the product HF so long as the field is present. This means that the diagonalizing electronic-field states of the product system mix the two diabatic surfaces so that the ground state is no longer of purely singlet character. The resulting distortion in the HF potential is not great, however; vibrational level shifts are typically on the order of 1% or less relative to the bottom of the potential well as compared to the field-free case. Because the shift is so small, and because the calculation takes no cognizance of coupling among vibrational states on either surface (since no permanent dipole moment functions are included), we may identify the final

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product vibronic states with their field-free counterparts. In Figure 1 we show representative diabatic vibronic-field potential energy curves for the system, and we note their asymptotic energy values to aid the reader in interpreting the results summarized in Figure 2. In this latter figure we sketch three curves, representing the probabilities as functions of energy for (a) elastic $0 \rightarrow 0$ reflection [the notation $v_j$ denotes the $v$-th vibrational state on the $j$-th (diabatic) electronic-field surface, with $j = 0$ for the reactive surface and $j = 1$ for the nonreactive, and if the vibrational index is primed then we are referring to a product state], (b) inelastic $0 \rightarrow 0$ reflection (note that this is endoergic by $0.418$ eV due to stimulated emission), and (c) $0 \rightarrow 2'$ reactive transmission. In the first of these we see a sharp depletion near $E = 0.45$ eV, where $E$ is the initial translational energy of $F(2P_{3/2})$ relative to $H_2(v=0)$. Some of this loss shows up in curve b as a small hump in the probability for nonreactive surface switching, but most is due to reaction, as curve c clearly shows. At this energy essentially all the reactive probability ends up in the second excited vibrational state of the product. At higher energies, however, the broad (though shallow) depletion structure in curve a is due principally to transition to the inelastic reflection channel, with a small additional loss (~1%) to the $v' = 3$ product vibrational state.

The nominal threshold for the $0 \rightarrow 2_0'$ transition of curve b is at $0.004$ eV, but no appreciable activity is seen until $E \gtrsim 0.43$ eV. This long delay is clearly due to the introduction of a barrier where, in the absence of the field, there was none. Shifting the reactive surface upward has given rise to a significant threshold effect. An indication of the barrier height is provided by the energy at which the two lowest-lying potential energy curves cross, $E_0 = 0.375$ eV. (See Figure 1. In the absence of the field there is no crossing at all between the purely electronic potential energy surfaces used in I.) The barrier may also be responsible for the sharply reduced reaction probability seen at energies above the peak height. Transmission over the barrier can be expected to add a further interference factor to the final reaction probabilities, which may act to suppress the strong resonance effects observed in the single-surface $F + H_2$ field-free calculations.

The only transitions from the given $0$, initial state seen with this model within the indicated energy range are those shown in Figure 2 plus the $0 \rightarrow 3_0'$ transition mentioned above. Compared to the case of collision-induced transfer treated in I, we see that the present transition pattern is similar in that the product $v' = 0$ and $v' = 1$ vibrational states end up very little occupied. However, the $0 \rightarrow 2_0'$ threshold resonance peak is very different from either the field-free $0 \rightarrow 2_0'$ or $0 \rightarrow 3_0'$ resonance of I. A stronger field might of course lead to entirely different results, and that is one possibility we shall want to investigate, but the field used here is already very strong, and we are therefore interested first in seeing what else might be done to increase field-induced reactivity from the $0_0$ state. One possibility (that has already been looked at semiclassically\(^9\)) is to try different lasers in an effort to determine the optimal field quantum for a given field strength. Another potentially important modification will be to introduce "permanent", or on-surface, dipole moment functions so as to determine how the field might act to populate vibrational levels that currently are not occupied. This is especially important to carry out in the present instance since the field quantum is resonant with the $v = 1$ to $v = 2$ transition in the product $HF$. Finally, we hope eventually to be able to treat collision-induced and field-induced transitions at the same time in a suitably enlarged representation, so as to test our conjecture that the two effects can be treated independently.

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