

Appendix B

Model Hamiltonian for Spin-Orbit Quenching by Charge Transfer

Electron and exciton transfer in condensed media are commonly described by means of semiempirical one-electron Hamiltonians [1–3], which help to identify the key molecular parameters that determine the reaction rate. We present here a model of this type that is suitable for describing the interplay between charge transfer and spin-orbit coupling in solvated dihalide ions. This model provides a Hamiltonian to go along with the qualitative potential curves sketched in Fig. 4, and provides further insight into the mechanism of solvent-induced spin-orbit quenching.

We begin by reviewing the traditional spin-boson Hamiltonian for a two-level electronic system coupled linearly to a single coordinate representing the nuclear degrees of freedom [2–4]. In solution-phase electron transfer this coordinate is usually the solvent orientational polarization [1, 5], while in solid-state electron or exciton transfer it may include both lattice and intramolecular vibrations [2, 3]; in our clusters, it describes the overall motion of the solvent cage from one side of the solute to the other. We will primarily use the language of solution-phase electron transfer in our discussion. We adopt a diabatic representation in which the basis states describe an electron localized on either of two atoms, labelled A and B , having local site energies ϵ_A and ϵ_B . The model Hamiltonian then takes the form:

$$\mathbf{H} = \begin{bmatrix} \epsilon_A & \beta \\ \beta & \epsilon_B \end{bmatrix} + \left(\frac{p^2}{2m} + u(q) \right) \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} -\gamma q & 0 \\ 0 & \gamma q \end{bmatrix}, \quad (\text{B.1})$$

where β is the electronic resonance integral that parametrizes the chemical bonding interaction between the two sites, q and p are the solvent coordinate and its corresponding momentum, $u(q)$ is the potential energy associated with deforming the solvent configuration, and γ measures the strength of the coupling between the electronic and solvent degrees of freedom. (The product $2\gamma q$, which measures the energy gained by localizing the charge on one site and deforming the solvent around that site, corresponds to the “solvent coordinate” $\Delta\Phi$ used in the main text of this paper.) Eq. B.1 can be rewritten as the sum of an adiabatic electronic hamiltonian \mathbf{H}^{el} and a solvent kinetic energy term T :

$$\mathbf{H} = \begin{bmatrix} \epsilon_A + u(q) - \gamma q & \beta \\ \beta & \epsilon_B + u(q) + \gamma q \end{bmatrix} + \left(\frac{p^2}{2m} \right) \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \equiv \mathbf{H}^{el} + T, \quad (\text{B.2})$$

The diagonal elements of \mathbf{H}^{el} , considered as functions of q , trace out the diabatic potential curves, while the eigenvalues of \mathbf{H}^{el} yield the corresponding adiabatic curves. If the solvent coordinate is treated as a harmonic oscillator, $u(q)$ is quadratic and the diabatic curves are a pair of displaced parabolas. The resonance coupling β depends strongly (typically exponentially) upon the interatomic separation R . The diabatic representation is most useful at large R , where β is small; in this regime an electronic transition between the diabatic states can be viewed as a charge transfer event. These transitions occur primarily where the diabatic curves cross, $\epsilon_A - \epsilon_B = 2\gamma q$, with a probability proportional $|\beta|^2$. For a homonuclear diatomic solute, $\epsilon_A = \epsilon_B$ and the diabatic curves cross at $q=0$.

$$H^a = \begin{bmatrix} \epsilon_A + u(q) - \gamma q & \beta_\Sigma & -\frac{\zeta}{\sqrt{2}} & 0 \\ \beta_\Sigma & \epsilon_B + u(q) + \gamma q & 0 & -\frac{\zeta}{\sqrt{2}} \\ -\frac{\zeta}{\sqrt{2}} & 0 & \epsilon_A + u(q) - \gamma q + \frac{\zeta}{2} & -\beta_\Pi \\ 0 & -\frac{\zeta}{\sqrt{2}} & -\beta_\Pi & \epsilon_B + u(q) + \gamma q + \frac{\zeta}{2} \end{bmatrix}. \quad (\text{B.4})$$

We now transform this Hamiltonian from the Hund's Case (a) representation, in which the spin-orbit terms couple basis states that are purely Σ or Π in character, to the Hund's Case (c) representation in which the spin-orbit terms appear on the diagonal. Case (c) is appropriate when the spin-orbit splitting exceeds the resonance coupling, as is always the case at sufficiently large interatomic distances; for isolated I_2^- the electronic wave functions are well described in Hund's Case (c) for R greater than about 6 \AA [6]. Since the transformation mixes Σ and Π states, one ends up with localized basis states that interact through linear combinations of β_Σ and β_Π :

$$H^c = \begin{bmatrix} \epsilon_A + u(q) - \gamma q + \zeta & \frac{1}{3}(\beta_\Sigma - 2\beta_\Pi) & 0 & \frac{\sqrt{2}}{3}(\beta_\Sigma + \beta_\Pi) \\ \frac{1}{3}(\beta_\Sigma - 2\beta_\Pi) & \epsilon_B + u(q) + \gamma q + \zeta & \frac{\sqrt{2}}{3}(\beta_\Sigma + \beta_\Pi) & 0 \\ 0 & \frac{\sqrt{2}}{3}(\beta_\Sigma + \beta_\Pi) & \epsilon_A + u(q) - \gamma q - \frac{1}{2}\zeta & \frac{1}{3}(2\beta_\Sigma - \beta_\Pi) \\ \frac{\sqrt{2}}{3}(\beta_\Sigma + \beta_\Pi) & 0 & \frac{1}{3}(2\beta_\Sigma - \beta_\Pi) & \epsilon_B + u(q) + \gamma q - \frac{1}{2}\zeta \end{bmatrix}. \quad (\text{B.5})$$

The upper 2×2 block of H^c describes the resonance interaction between an I^- ion and an I^* atom, and the lower to the interaction between I^- and I in its spin-orbit ground state. Indeed, one can think of the linear combinations of β_Σ and β_Π as arising from p-orbitals that are tilted away from the internuclear axis by 30 and 60 degrees. The diagonal elements of H^c , considered as functions of q , correspond to the diabatic potential curves in Fig. 4 (although Fig. 4 also includes the $\Pi_{3/2}$ states that have been omitted here). Within each spin-orbit block, charge transfer occurs primarily near $q=0$ where the diabatic curves cross. However, Eq. B.5 also includes

matrix elements $\frac{\sqrt{2}}{3}(\beta_{\Sigma} + \beta_{\Pi})$ that couple the spin-orbit blocks. Since these matrix elements are also made up from interatomic resonance integrals, they also describe charge-transfer events, and they will become important when the diabatic curves arising from **different** spin-orbit blocks cross, as in Fig. 4. In the homonuclear case ($\epsilon_A = \epsilon_B$) the condition for such a crossing is that

$$\frac{3}{2}\zeta = \pm 2\gamma q \equiv \Delta\Phi, \quad (\text{B.6})$$

i.e., the differential solvation energy is equal to the spin-orbit splitting in the iodine atom. Thus, these are the matrix elements responsible for spin orbit relaxation via solvent-induced charge transfer.

At a given R, we expect that β_{Σ} will be much larger than β_{Π} since a p orbital hole that is aligned with the internuclear axis will have a larger overlap with the charge cloud on the I^- ion than one which is aligned perpendicular to that axis. This expectation is confirmed by the relative depths of the Σ and Π state wells in I_2^- : the ground state (${}^2\Sigma_{u,1/2}$) is bound by 1.01 eV [7] while the binding energy in the first excited state (${}^2\Pi_{g,1/2}$) is estimated to be about 0.1 eV [6]. To a first approximation, we may regard all the charge-transfer events as driven by β_{Σ} , whose amplitude is distributed in varying amounts over the spin-orbit coupled Hund's Case (c) states. All of the charge-transfer matrix elements in H^c are then of the same order of magnitude; if anything, the terms associated with charge-transfer between the two spin-orbit manifolds are somewhat larger than those associated with charge transfer in the spin-orbit excited state. Thus there are no matrix-element restrictions on spin-orbit relaxation by charge transfer: the electron hops to whichever orbital is closest in energy. When the two atoms are equally solvated ($q \approx 0$), the charge is transferred within a spin-orbit manifold, but in a highly asymmetric solvent environment ($2\gamma q \approx \pm \frac{3}{2}\zeta$), charge transfer involves a transition between the spin-orbit manifolds.

The model outlined above has one significant unphysical property: the Hamil-

tonian is cylindrically symmetric. This is a result of compressing the solvent effects into a single coordinate that describes only the overall difference between the solvation energies at the two atoms, not the finer details of the complicated electrostatic environment around the solute. When these details are included, as they are in our simulations, Ω is no longer a good quantum number and the electronic Hamiltonian cannot be reduced to four states. As a result the spin-orbit excited states are quenched into all four lower states, rather than into one pair as in the model above. This is seen in the simulations. Aside from this, the Hamiltonian model describes well the overall features of the solvent-mediated spin-orbit quenching mechanism: the process does not occur at all until a threshold value of the solvent coordinate is reached, but once this criterion is met the process is highly efficient.

References for Appendix B

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