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Hot Injection Dynamics: Design Mechanisms and Ideas

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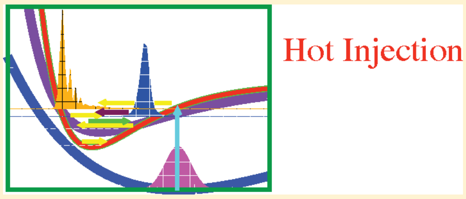
ABSTRACT: A minimal quantum mechanical model for efficient molecular capture of photon energy is presented. The model is constructed from a bright electronic state which is accessed by a photoinduced transition from the ground state and an acceptor excited state which stores the photoenergy. The model permits rational design of the bright and acceptor electronic states to improve the capture of solar energy. The main design factors are analyzed through examples.



■ INTRODUCTION

The Franck−Condon principle, coupled with the fact that excited state and ground state energy minima occur at different geometries, suggests that photoexcited states are born with vibrational potential energy. Here we discuss a mechanism, based on decoherence in the excited-state manifold, that permits this vibrational energy to be captured as useful electronic energy in a second, dark excited state.

With the advent of ultrafast lasers, the topic of quantum dynamics and its control in molecular systems has become one of the most exciting in chemical physics. One of the simplest forms of such control involves photoexcitation of a molecule, which (following a vertical excitation) starts to evolve as a vibrational wave packet on the excited bright state that has been occupied. The evolution of that state is then a bit complicated: the advent of vibrational relaxation works to convert some of the initial energy from higher vibrational levels toward the vibrational ground level, while encounters with other electronic states (through potential energy surface crossings, described most simply in the diabatic limit) change the electronic composition of the evolving initial wave packet.

Manifestations of this excited state dynamics have been at the center of quantum dynamical studies for nearly two decades. Important early work focused on the measurement of time-dependent Stokes shifts and their interpretation in terms of the onset of thermalization in the excited state[1,2] and on so-called femtochemistry,[3,4] in which the focus was on the electronic evolution involved in bond breaking or state changing.

If a second excited state, whose potential energy minimum is actually higher in energy than that of the initially reached bright state, were to receive the wave packet amplitude before significant vibrational relaxation or dephasing could occur, and if it could be arranged that the wave packet, once in this higher excited state (that we will call the acceptor) could be prevented from recrossing into the bright state, it would be possible to convert the excited wave packet energy, which had begun as kinetic energy in the nuclei, into electronic energy in the acceptor state (see Figure 1). Such a process has been called "hot injection" and has been of particular interest in applications to molecular injection into semiconductors, such as in dye-sensitized solar cells.[5,6]

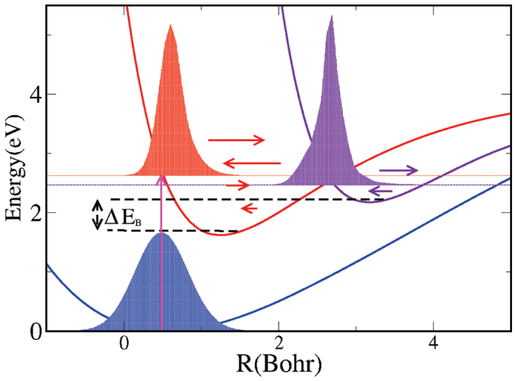


Figure 1. Scheme I: Ground state (blue), the bright state (red), and the dark acceptor state (purple). The different potentials and wave functions are indicated. The amount of energy captured by the hot injection is designated as ΔE_B.

Formally, the processes of femtochemistry and curve crossings in the excited state occurring before vibrational relaxation are examples of the failure of Vavilov's rule,[7−10] an empirical generalization of molecular behavior that originally suggested that no chemical processes evolving from an initially photoexcited state can occur before that state relaxes to its vibrational minimum. Although Vavilov's rule is expected to be obeyed in many cases (for example very large, strongly vibronically coupled molecules in a polar environment or situations where there is no second

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excited state with effective curve crossings within the energetic window of the initial vertical excitation), it clearly fails when the time scale for curve crossing between excited states is shorter than the intramolecular vibrational relaxation time.

Vavilov's rule is a historic observation, based on long-time populations, which were the only easily observed phenomena until recently. The advent of laser spectroscopy (as remarked above) changed this entirely, and now considerations of the evolution of the initial vertical excited state are generally posed in terms of system/bath dynamics. Here we discuss the problem of "hot injection" using the simplest possible model: three electronic states (a ground state, a vertically excited state which we will call the bright state, and the acceptor state). We will consider only one active vibration, along which the potential energy curves are plotted and understood. We will also describe the dynamics within a system/bath model, with the bath corresponding to a combination of the other vibrational manifold states within the molecule, and the solvent or environmental bath. The total effect of the bath dynamics on the system will be described in terms of the stochastic surrogate Hamiltonian method, which has been shown to deal well with both short time and long time relaxation in such systems.[11,12]

There are several time scales involved in this problem. The most obvious ones are the inverse vibrational frequency of the active vibration, the inverse Landau/Zener crossing rates for the transition between acceptor and bright states, the inverse fluorescence and electronic nonradiative decay rates to the ground state, and the different times associated with the bath and the system/bath interactions. These latter include times for vibrational relaxation, vibrational dephasing, and electronic dephasing. These decoherence processes, that are crucial to the evolution, are well-described by the stochastic surrogate model. The model includes relaxation dynamics that are not present in the standard spin/boson descriptor[13] and which may dominate under certain conditions such as the "sluggish bath" that has been posited[14] to permit the coherent oscillations recently seen in large molecular biosystems. From a control point of view,[11,12,15−18] the analysis here will focus on a situation in which control is exerted by capitalizing on the nature of the system/bath interactions rather than by specific pumping or multiphoton schemes.

■ MODEL

The model represents a molecular system coupled to a radiation field. The molecular system is subject to dissipative forces due to coupling to a primary bath. In turn the primary bath is subject to interactions with a secondary bath:

$$\hat{\mathrm{H}}_{\mathrm{T}} = \hat{\mathrm{H}}_{\mathrm{S}} + \hat{\mathrm{H}}_{\mathrm{B}} + \hat{\mathrm{H}}_{\mathrm{B}''} + \hat{\mathrm{H}}_{\mathrm{SB}} + \hat{\mathrm{H}}_{\mathrm{BB}''} \tag{1}$$

where $\hat{\mathrm{H}}_{\mathrm{S}}$ represents the system, $\hat{\mathrm{H}}_{\mathrm{B}}$ represents the primary bath, $\hat{\mathrm{H}}_{\mathrm{B}''}$ the secondary bath, $\hat{\mathrm{H}}_{\mathrm{SB}}$ the system−bath interaction, and $\hat{\mathrm{H}}_{\mathrm{BB}''}$ the primary/secondary bath interaction. The system Hamiltonian $\hat{\mathrm{H}}_{\mathrm{S}}$ describes a ground electronic state and two coupled excited electronic states

$$\hat{H}_{\mathrm{S}} = \begin{pmatrix} \hat{H}_{\mathrm{g}} & \hat{\mu}_{\mathrm{gb}}\varepsilon(t) & 0 \\ \hat{\mu}_{\mathrm{bg}}\varepsilon^{*}(t) & \hat{H}_{\mathrm{b}} & \hat{V}_{\mathrm{ba}} \\ 0 & \hat{V}_{\mathrm{ab}} & \hat{H}_{\mathrm{a}} \end{pmatrix} \tag{2}$$

where the operators are functions of the nuclear coordinates:

$\hat{\mathrm{H}}_k = (\hat{\mathrm{P}}^2/2m) + \hat{\mathrm{V}}_k$ is the surface Hamiltonian and $\hat{\mathrm{V}}_k$ is the ground (g), bright (b), or acceptor (a) potential.

Table 1. Potential Parameters[a]

scheme I	values	units	scheme II	values	units
D_{g}	5.0	eV	D_{g}	5.0	eV
α_{g}	0.5	bohr^{-1}	α_{g}	0.5	bohr^{-1}
$\bar{r}_{\mathrm{g}}$	0.649	bohr	$\bar{r}_{\mathrm{g}}$	3.78	bohr
E_{g}	0.	eV	E_{g}	0.	eV
D_{b}	4.275	eV	D_{b}	4.275	eV
α_{b}	0.675	bohr^{-1}	α_{b}	0.675	bohr^{-1}
$\bar{r}_{\mathrm{b}}$	1.35	bohr	$\bar{r}_{\mathrm{b}}$	1.35	bohr
E_{b}	1.6	eV	E_{b}	1.4	eV
D_{a}	2.925	eV	A_{a}	27.22	eV
α_{a}	0.78	bohr^{-1}	α_{a}	1.9	bohr^{-1}
$\bar{r}_{\mathrm{a}}$	3.27	bohr	$\bar{r}_{\mathrm{a}}$	1.4	bohr
			C_{a}	1.9	eV bohr^2
E_{a}	2.1	eV	E_{a}	1.9	eV
V_{c}	0.1	eV	V_{c}	0.17	eV
α_{c}	1.2	bohr^{-2}	γ_{c}	0.5	bohr^{-1}
$\bar{r}_{\mathrm{c}}$	2.65	bohr			

[a] The electronic states are chosen in scheme I as Morse potentials where $\hat{\mathrm{V}}_k(r) = D_k[1 - \exp(-\alpha_i(r - \bar{r}_k))]^2 + E_k$ where k is the surface index. $\hat{\mathrm{V}}_{\mathrm{ba}}(r) = V_{\mathrm{c}} \exp(-\alpha_{\mathrm{c}}(r - \bar{r}_{\mathrm{c}})^2)$. In scheme II the acceptor dark state is represented by $\hat{\mathrm{V}}_{\mathrm{a}}(r) = A_{\mathrm{a}} \exp(-\alpha_{\mathrm{a}}(r - \bar{r}_{\mathrm{a}})) - (1 - \Gamma(r,\alpha_{\mathrm{a}},\bar{r}_{\mathrm{a}}))C_{\mathrm{a}}/r^2 + E_{\mathrm{a}}$ where $\Gamma(r,\alpha_{\mathrm{a}},\bar{r}_{\mathrm{a}})$ is the incomplete Gamma function. $\hat{\mathrm{V}}_{\mathrm{ba}}(r) = V_{\mathrm{c}}e^{-\gamma_{\mathrm{c}}r}$.

$\hat{\mathrm{V}}_{\mathrm{ba}}$ represents the nonadiabatic coupling between the excited surfaces.

$\hat{\mu}$ represents the transition dipole operator which is chosen to couple only the ground and the bright excited state.

$\varepsilon(t)$ represents the time dependent electromagnetic field. A Gaussian excitation pulse is used: $\varepsilon(t) = \Omega_0 \exp[-(t^2/2\tau_0^{\,2}) + i\omega_0 t]$ where Ω_0 is the light intensity and τ_0 is the temporal pulse width.

The potential forms used are summarized in Table 1. Figure 1 presents the system Hamiltonian and the different couplings. The isolated case will be represented by $\hat{\mathrm{H}}_{\mathrm{S}}$ alone.

The bath is described by a fully quantum formulation. The method employed is the stochastic surrogate Hamiltonian.[11,12] Briefly the bath is divided into a primary part interacting with the system directly and a secondary bath which eliminates recurrence. The primary bath Hamiltonian is composed of a collection of two-level-systems.

$$\hat{\mathrm{H}}_{\mathrm{B}} = \sum_j \omega_j \,\hat{\sigma}_j + \hat{\sigma}_j \tag{3}$$

The energies ω_j represent the spectrum of the bath. The system-bath interaction $\hat{\mathrm{H}}_{\mathrm{SB}}$ can be chosen to represent different physical processes.[11,12,19,20] Specifically (following[11]) we choose an interaction leading to vibrational relaxation

$$\hat{\mathrm{H}}_{\mathrm{SB}} = f(\hat{\mathrm{R}}_{\mathrm{s}}) \otimes \sum_j^N \lambda_j(\hat{\sigma}_j^{\dagger} + \hat{\sigma}_j) \tag{4}$$

where $f(\hat{\mathrm{R}}_{\mathrm{s}})$, is a dimensionless function of the system coordinate $\hat{\mathrm{R}}_{\mathrm{s}}$. λ_j is the system-bath coupling frequency of bath mode j. When the system-bath coupling is characterized by a spectral density $J(\omega)$ (units of frequency) then $\lambda_j = [J(\omega_j)/\rho_j]^{1/2}$ and $\rho_j = (\omega_{j+1} - \omega_j)^{-1}$ is the density of bath modes.

The secondary bath is also composed of noninteracting two-level-systems (TLS) at temperature T with the same frequency spectrum as the primary bath. At random times the states of primary and secondary bath modes of the same frequency are

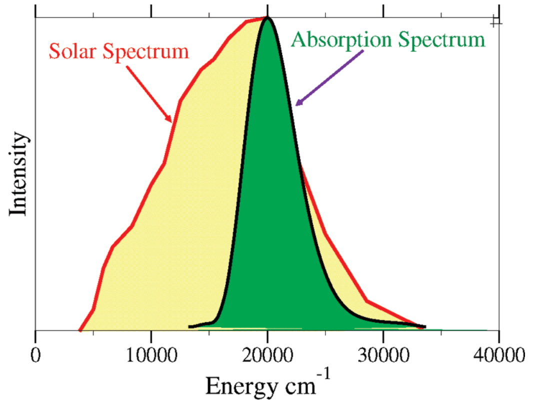

Figure 2. Absorption spectrum of the model superimposed on the solar spectrum.

swapped at a rate Γ_j.[11,12,19,21] The bath employed leads to a vibrational relaxation time of approximately T_1 = 1 ps in the different potentials. The swapping procedure permits description of both dephasing and energy relaxation. The final results are obtained by averaging the stochastic realizations. The swap makes the bath effectively infinite. Each swap operation eliminates the quantum correlation between the system and remaining bath with the mode swapped. This loss of system-bath correlation leads to dephasing.

The stochastic surrogate Hamiltonian approach is a fully quantum treatment of system—bath dynamics. The method is not Markov constrained and is based on a wave function construction. The system and bath are initially correlated, since the initial state is obtained from the combined thermal state. It is generated by propagating in imaginary time $t = \beta/2$ using the coupled system—bath Hamiltonian. Additional entanglement is generated by the dynamics. Convergence of the model is obtained by increasing the number of bath modes and the number of stochastic realizations.

IMPROVING SYSTEM DESIGN

The following design principles can be used to optimize the process.

1. Absorption spectra: in the energy band of possible solar capture, the absorption spectrum should match the high energy part of the solar spectrum. (Cf. Figure 2).

2. Nonadiabatic transfer: positioning of the bright/acceptor crossing point just above the energy for vertical excitation from the ground state.

3. Efficient tunneling from the bright state to the acceptor state, requiring a small tunneling distance and an adequate coupling matrix element.

4. Stabilization by fast nuclear relaxation and/or dephasing in the acceptor state.

5. Slow nuclear relaxation, dephasing in the bright state.

6. High vibrational frequency in the bright state allowing multiple passing to the dark acceptor state.

The efficiency of the storage process with respect to energy is defined as

$$\eta_{\mathrm{E}} = \frac{\langle E_{\mathrm{a}} \rangle}{E_i} \tag{5}$$

where $E_{\mathrm{i}} = \hbar\omega_0$ is the pulse carrier frequency energy and $\langle E_{\mathrm{a}} \rangle$ is the energy in the acceptor state.

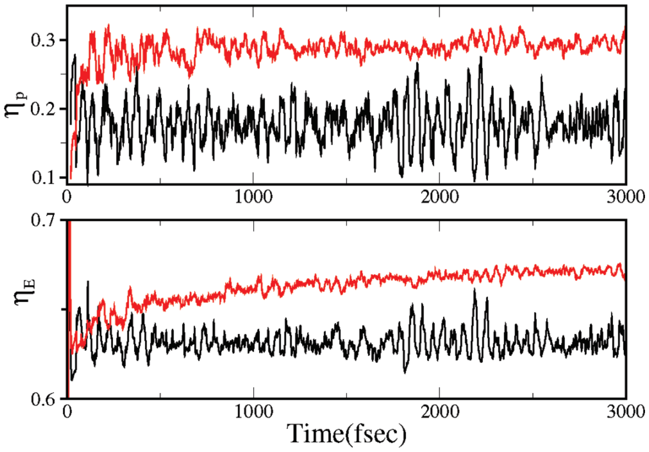

Figure 3. Top: population ratio η_p (eq 6) as a function of time, with (red) and without (black) relaxation/dephasing. Bottom: energy efficiency η_{E} (eq 5) as a function of time, with (red) and without (black) relaxation/dephasing. Results for scheme I (Cf. Tables 1 and 2).

Table 2. Propagation Parameters[a]

pulse parameters	typical values	units
ω_0	20600	cm^{-1}
τ_0	6.0	fs
Ω_0	0.2	eV
grid parameters	**typical values**	**units**
grid spacing, Δr	0.03125	bohr
number of grid points, N_r	128	
time steps, Δt	0.5	fs
order of Chebychev polynomials	128	
reduced mass m	16	amu
bath parameters	**typical values**	**units**
number of bath modes	12	
cutoff frequency ω_c	1.6	eV
system-bath coupling σ	1.945	bohr^{-1}
swap rate Γ_j/λ_j	1.05	

[a] The initial state is the vibrational ground state of $\hat{V}_{\mathrm{g}}(r)$ obtained by propagation in imaginary time.[22] The system wavefunction is represented on a Fourier grid of N_r points.[23] Propagation is carried out by the Chebychev method.[24] The system-bath coupling function is chosen to be linear $f(r) = \sigma(r - r_k)$ (eq 4). The spectral density $J(\omega)$ is chosen to be Ohmic with a cutoff frequency of ω_c.

The branching ratio between the bright and acceptor states is

$$\eta_{\mathrm{p}}(t) = \frac{p_{\mathrm{a}}}{p_{\mathrm{b}} + p_{\mathrm{a}}} \tag{6}$$

with p_{b} and p_{a} being the electronic states occupation probabilities.

Figure 3 presents the calculated population and energy ratio on the dark acceptor state with and without the bath, for the scheme I (Figure 1).

A physical system designed to optimize the process according to the first three principles should optimally contain a stiff bright state potential and a soft acceptor state potential. The proper positioning of the excitation is also essential. Figure 1 shows the potential energy surfaces for a system which has a large tunneling width and a

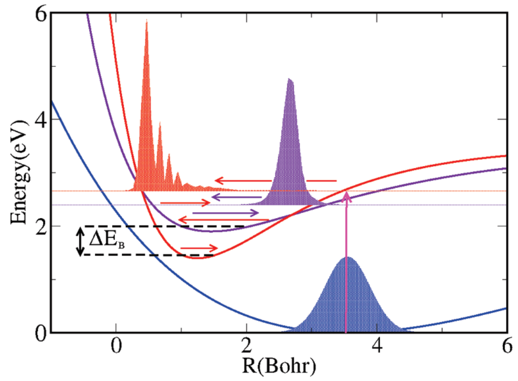

Figure 4. Scheme II (Table 1): Improved scheme of a system with a charge transfer acceptor state. The acceptor state is represented by an ion pair potential.

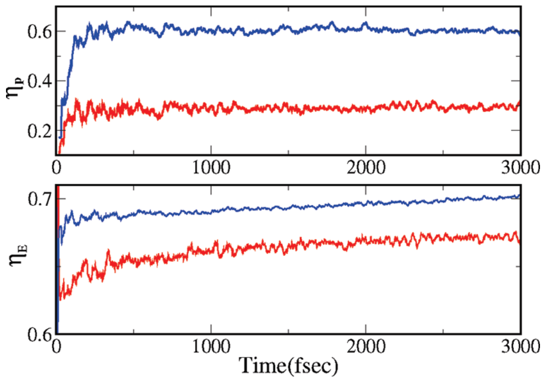

Figure 5. Comparison between the two schemes: direct, scheme I (red), and charge transfer acceptor, scheme II (blue). Bottom: Energy efficiency η_E (eq 5). Top: population ratio η_P (eq 6).

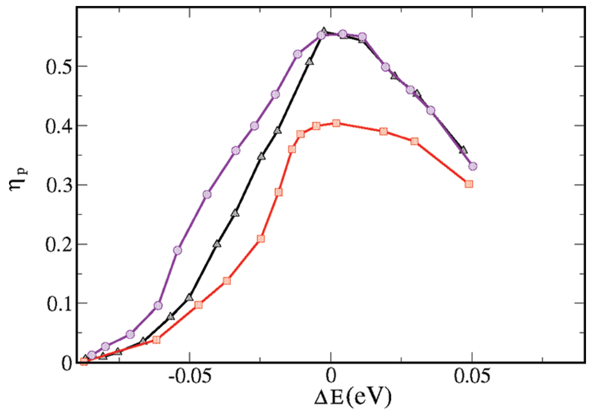

Figure 6. Population efficiency η_p (eq 6) in the long time limit for the direct, scheme I (red squares), and ion pair acceptor, scheme II (black triangles), as a function of ΔE. $\Delta E = E_i - E_c$ is the difference between the excitation energy and the energy at the curve crossing point E_c. Enhancement of reaction probability is obtained at energies below E_c by softening the repulsive part α by 5% (purple circles).

narrow near-resonance energy regime. The drawback of this design is that the nonadiabatic crossing probability is low.

An improved design is presented in Figure 4 where the electronic acceptor state is an ion pair state with a long-range coulomb attraction. Such an electronic state has a soft vibrational mode with a steep repulsion regime. In this system the transition is designed to occur at the inner turning point where the tunneling width is very narrow; we then expect a sort of single-event transition from bright to acceptor states. This leads to improved population and energy efficiency, Figure 5. This design permits a more efficient use of the pulse width, as shown in Figure 6. Softer repulsion at the inner turning point enhances the curve crossing probability below the curve crossing energy point. The nonadiabatic coupling to the charge transfer state is chosen to have an exponential decay with the internuclear distance, and has a very low crossing probability at the outer crossing point. Additional efficiency can be achieved by further optimizing the system-bath coupling as is demonstrated in Figure 7. A turnover is seen when the coupling to the bath leads to an energy relaxation rate T_1 which is comparable to the time-scale defined by $\hbar/\Delta E_a$ where ΔE_a is full width at 3/4 height of the population transfer spectrum (Cf. Figure 6). Further optimization can be achieved if by molecular design the bath is weakly coupled to the bright state and strongly coupled to the acceptor state. In the present calculations the coupling to both states is comparable.

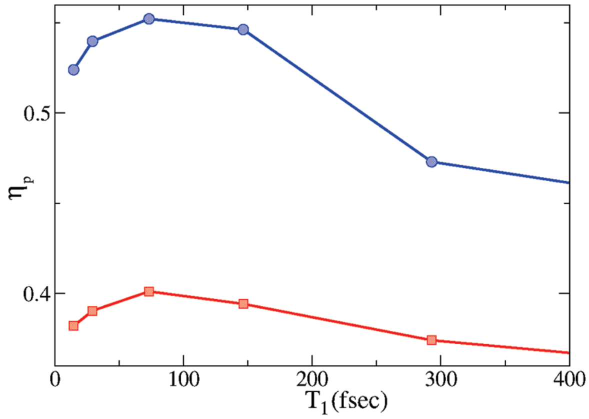

Figure 7. Asymptotic population efficiency η_P (eq 6) as a function of the system/bath energy relaxation time T_1. Direct, scheme I (red squares), and charge transfer, scheme II (blue circles). The value of T_1 corresponds to the system bath parameters used in Table 1. Cf. ref 12.

■ CONCLUSIONS

There are several examples of the failure of the so-called Vavilov rule that vibrational relaxation occurs before reaction in any photoexcited structure. The particular idea of "hot injection", that is, capturing the vibrational excitation contained in a vertically excited state before it can undergo "vibrational relaxation", is of particular interest because of its possible implications for increasing the efficiency of solar photovoltaic applications. In this paper, we suggest that such hot injection can be facilitated by very rapid decoherence processes in the acceptor (or dark state) that is accessed from the photophysically obtained bright state. Depending on the details of the curve crossings, the decoherence rates, and the energetics, it is possible to capture much of this initial vibrational energy.

The particular model used here works because of decoherence; that is, the decoherence traps the initial excited species in the acceptor state. This requires vibrational decoherence of the order of 1 ps. Other decoherence mechanism may work as well. The fact that control works due to decoherence is a bit unusual.

For the particular examples used here, which involve only one reaction coordinate, the performance is not remarkable. It seems clear that a richer vibrational manifold will be needed to capture energy more efficiently. Such a model is slightly more complicated, but will almost certainly produce far more experimentally attractive mechanisms for trapping initial vibrational excitations. Work on the higher dimensionality problem is ongoing.

Of the two trial potentials used for the current one-dimensional model, the inner crossing point of scheme II of Figure 4 provides higher efficiencies for capturing vibrational excitation than the more traditional structure of scheme I of Figure 1. The disadvantage of scheme II is that the amount of vibrational energy trapped is very small, because of the relatively weak bonding by this Coulombic ion pair potential in the acceptor. Once again, using several dimensions could amplify the possibilities for vibrational capture.

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