Femtosecond Spectroscopy of Heterogeneous Electron Transfer: Extraction of Excited-State Population Dynamics from Pump−Probe Signals

S. Ramakrishna* and F. Willig

Hahn-Meitner-Institut, 14109 Berlin, Germany

V. May

Institut für Physik, Humboldt-Universität, 10117 Berlin, Germany

A. Knorr

Institut für Theoretische Physik, Technische Universität Berlin, 10623 Berlin, Germany

Numerical calculations of pump−probe signals corresponding to excited-state absorption of the molecular state are presented. The molecular excited-state decays due to ultrafast electron injection into a continuum of electronic states (semiconductor levels) and the model calculations take into account the consequent molecular reorganization. A time-dependent Schrödinger wave equation approach is utilized to model the pump−probe dynamics. The continuum of semiconductor states, namely, its conduction-band levels, is described by an expansion in terms of orthogonal polynomials. It is shown that excited-state dynamics, including information on the modulation of population transfer due to vibrational coherences, can be unambiguously deduced from the pump−probe signals.

1. Introduction

In the last few years, a number of experimental studies have focused on time resolving the ultrafast photoinjection step from an attached molecular donor into a nanocrystalline semiconductor.[1−4] Time resolution has improved because of shorter laser pulses, and it has been shown that transfer times are typically below 100 fs for the dominant channel or in some cases the only channel of injection. Also, oscillations seen in the signal probing the formation of the molecular product state are indicative of vibrational coherences persisting during the course of electron transfer (ET)[2]. This establishes for a fact that in these cases heterogeneous ET proceeds from a thermally hot or vibrationally unrelaxed donor-molecular state.[4] Although in some cases experimental evidence points to the modulation of population transfer from the excited state to semiconductor conduction-band levels[2], a proper theoretical basis for interpreting excited-state dynamics from pump−probe signals is currently unavailable.

On the theoretical side, progress has been made in modeling the ultrafast injection from molecules to surfaces by taking into account the role played by coherent vibrational oscillations in the transfer process[5,6] and also when the transfer is mediated by off-resonant bridging states.[7] Earlier, expressions for pump−probe signals pertaining to excited-state absorption had been obtained via a density matrix approach.[8] In deriving the analytical expression for the signal, the interaction between the molecule and the laser fields had been treated perturbatively, which resulted in a third-order representation of the polarization ($\chi^{(3)}$).[8] However, this first attempt to model pump−probe signals

in the context of ultrafast heterogeneous electron transfer neglected the role played by the shift in the nuclear equilibrium position of the molecule that occurs when it is ionized. This displacement is related to the reorganizational energy, and its effects have been shown to be important when the energetic position of the injecting molecular donor level is close to the band edge and also when the density of states varies sharply with energy in the neighborhood of the injecting level.[6] When reorganizational effects are unimportant, the excited-state vibrational wave packet no longer modulates or participates in ET but shows up in the signal as oscillations.[8] In such a case, the excited-state population shows a smooth exponential decay. However, when reorganizational effects become important (i.e., the energetic difference between the position of the injecting level and the band edge is less than or comparable to the reorganizational energy), the vibrational wave packet modulates the decaying excited-state population, and the decay shows characteristic steps.[6] Currently, no calculations of the transient absorption, for the case when population transfer to the continuum levels of the semiconductor is modulated, are available. Such simulations would be vital in interpreting recent pump−probe signals wherein such oscillations have been reported.[2]

As a continuation of our previous work on excited-state probe absorption signals,[8] we now include effects of reorganization and explore the signals for two cases of population decay, namely, (i) when the decay is smooth (wide-band limit) and (ii) when the decay is modulated by a vibrational wave packet (injecting position closer to the band edge). Furthermore, by systematically changing the probe wavelength, we demonstrate that it is in principle possible to reconstruct the excited-state population dynamics completely from the pump−probe signal.

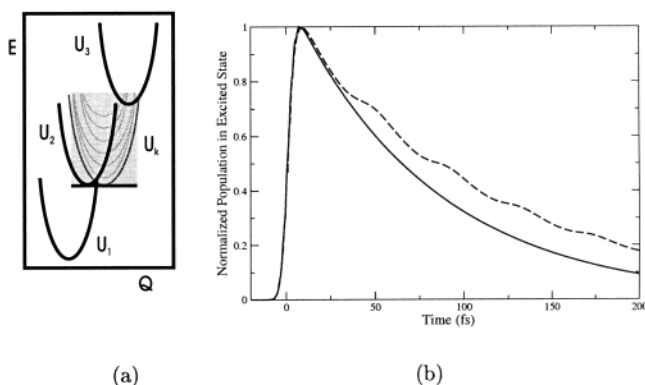* To whom correspondence should be addressed. E-mail: ramakrishna@hmi.de.

Figure 1. (a) PESs (U_a) of a molecular three-level system where the first excited state is coupled to the conduction-band continuum levels of a semiconductor are shown schematically. The continuum of the final PES of the ionized molecule is shown as the shaded region, and the donor molecular level is positioned close to the lower edge of the conduction band. (b) Decay of the normalized first excited state population due to a transfer to the continuum of electronic levels after excitation by a Gaussian pump pulse (pulse duration 10 fs). Injecting level positioned (i) 1 eV above the band edge (—) and (ii) 0.35 eV above the band edge (- -).

2. Hamiltonian and Basic Equations of Motion

The electronic Hamiltonian consists of three molecular states $|\varphi_j\rangle$ ($j = 1-3$): the ground $|\varphi_1\rangle$, the first excited $|\varphi_2\rangle$, and the next higher excited state $|\varphi_3\rangle$. The two time-dependent laser pulses are assumed such that the pump pulse couples only the ground state $|\varphi_1\rangle$ and the first excited state $|\varphi_2\rangle$, whereas the probe pulse excites only the first excited state to the next higher excited state $|\varphi_3\rangle$. This is valid for physical systems where the transition energies between the two sets of electronic states are sufficiently far apart. For instance, with modified perylene as a chromophore attached to a TiO$_2$ surface, there is very little spectral overlap between the pump and probe pulses while investigating excited-state absorption[2]. The interaction V_{2k}, between the excited state of the molecular donor level $|\varphi_2\rangle$ and the continuum states $|\varphi_k\rangle$ is assumed to be uniform (independent of k) and a constant. Although this particular choice of a band shape assumed for the forthcoming calculation, namely, a boxlike uniform level density, does not describe a TiO$_2$ conduction band,[9] the band shape that basically determines the dynamics of population decay in the excited state[6] is not essential to the general question of extracting the time-dependent population from pump−probe signals. Thus, the model Hamiltonian of a molecular three-level system interacting with a substrate (shown in Figure 1a) is similar to the one adopted in our previous work.[8]

$$H = \sum_{j=1}^{3} H_j(Q)|\varphi_j\rangle\langle\varphi_j| + \sum_k H_k(Q)|\varphi_k\rangle\langle\varphi_k|$$
$$+ (E_{pu}(t)\,\mu_{12}|\varphi_1\rangle\langle\varphi_2| + E_{pr}(t)\,\mu_{23}|\varphi_2\rangle\langle\varphi_3| +$$
$$\sum_k V_{2k}|\varphi_2\rangle\langle\varphi_k| + h.c.) \quad (1)$$

where E_{pu} and E_{pr} are the pump and probe pulses, respectively, and $\mu_{jj'}$ are the electronic transition dipole moments. The vibrational part of the Hamiltonian in terms of a harmonic oscillator model, for a single mode of vibrational frequency ω_o

($\hbar\omega_o$ is taken to be 0.1 eV in the calculations), has the usual form

$$H_a = T + U_a^{(0)} + \hbar\omega_o g_a^2 \quad (2)$$

where a represents the electronic states, namely, the various j and k values. The nuclear kinetic energy operator is given by T. The displacement term g_k is assumed to be the same for all of the ionized potential energy surfaces (PESs). The reorganizational energy λ of the molecule upon being ionized because of electron transfer is given as $\lambda = \hbar\omega_o(g_2 - g_k)^2$. The relative displacement between the excited and the higher excited molecular level, which will be varied in the coming calculations, is given as $g = (g_3 - g_2)$. This quantity determines the Franck−Condon matrix elements for the optical transitions between these two molecular states. The eigenvalues of H_a are written as

$$\epsilon_{av} = \epsilon_a + v\hbar\omega_o \quad (3)$$

where the first term reads

$$\epsilon_a = U_a^{(0)} + \frac{1}{2}\hbar\omega_o \quad (4)$$

It is given by the minimum of the respective PES plus the total zero-point energy of the vibrational mode.

As vibrational relaxation is not crucial to the issues addressed in this article, a time-dependent Schrödinger equation is utilized to obtain the excited-state population dynamics as well as the probe absorption at different time delays. The electron vibrational wave function $|\Psi(t)\rangle$ is given as

$$|\Psi(t)\rangle = \sum_{jv}A_{jv}(t)|\chi_{jv}\rangle|\varphi_j\rangle + \sum_{k\mu}A_{k\mu}(t)|\chi_{k\mu}\rangle|\varphi_k\rangle \quad (5)$$

where $|\chi_{jv}\rangle$ and $|\chi_{k\mu}\rangle$ are the vibrational eigenfunctions of the discrete and continuum electronic states, respectively. The probe absorption signal I is usually given as[10]

$$I \propto - \int_{-\infty}^{\infty} dt\, \dot{E}_{pr}(t)\, P(t) \quad (6)$$

I is a function of the time delay between the pump and probe pulses and the central frequency of the probe pulse. Usually, $P(t)$ is the difference in polarization between preparing and not preparing the sample by the pump pulse (prior to the probe pulse) that radiates in the direction of the probe pulse. For the model Hamiltonian assumed, $P(t)$ is essentially what is obtained after irradiation with the pump pulse since there is no initial population in the excited states. Also, it is important to note that the dipole operator responsible for transitions between the ground and first excited states (μ_{12}) does not contribute to the probe signal in a three-level system, unlike the case in a two-level system.[10] Therefore,

$$P(t) = \langle\Psi(t)|\mu_{23}|\varphi_2\rangle\langle\varphi_3|\Psi(t)\rangle + c.c. \quad (7)$$

Since the expression for the pump−probe signal (eq 6) is numerically obtained, the calculations fully include the molecule−field interactions to all orders as well as the temporal overlap between the pump and the probe pulses. The continuum of states is expanded in terms of energy-dependent coefficients and orthogonal polynomials as a basis set for efficient numerical computations of the population and signals as outlined earlier.[7]

In the forthcoming model calculations, a transfer time of 80 fs is used. This is close to the value of 75 fs reported for the perylene chromophore attached as molecule DTB−Pe via the
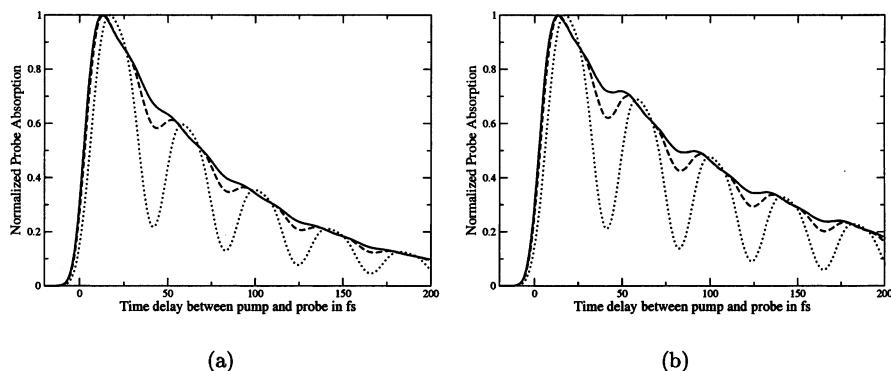
Femtosecond Spectroscopy of Electron Transfer

J. Phys. Chem. B, Vol. 107, No. 2, 2003 **609**

Figure 2. Normalized excited-state probe absorption vs the time delay between pump and probe pulses of same pulse duration (10 fs). Probe energy corresponds to the 0−0 transition. (··) $g = 1.0$, (- -) $g = 0.5$, and (—) $g = 0.3$. Two injecting positions: (a) 1 eV (smooth population decay) and (b) 0.35 eV (modulated decay of population) above the band edge.

−CH$_2$− phosphonic acid group to anatase TiO$_2$ in ultrahigh vacuum.[2] The energy of the single mode of vibration is assumed to be 0.1 eV since it is known that modes around this energy exist in perylene.[11] A pulse width of 10 fs is chosen for the pump pulse so as to excite this mode coherently. In recent experiments, only modes around 0.052 eV and below could be coherently excited since the laser pulses were of 20-fs duration.[2] For the probe pulse, a finite pulse width that is short enough to time resolve the decay is needed (so a pulse width of 10 fs has been employed) to be able to explore excited-state population extraction with such *finite* pulse widths. This is because it has already been shown that excited-state population dynamics can be obtained with *ultrashort* probe pulses in the context of two-level systems.[12] Some of the displacements can be inferred only in an approximate manner from experimental spectra. For instance, for the mode of energy at 0.16 eV that is the most Franck−Condon-active in the perylene chromophore, the displacement between the ground and the first excited state $g_{12} = (g_1 − g_2)$ can be estimated as $g_{12} < 1$ in a solvent environment and as $1 < g_{12} < 1.5$ on the TiO$_2$ surface.[2] For $g = (g_2 − g_3)$, experimental spectra suggest that $0 < g < 0.5$.[2] In calculations for the mode of energy at 0.1 eV, values of $g_{12} = 1$ and $g = 0.5$ have been used in the final set of calculations. Since no information is available regarding the displacement between the excited state and the ionized ground state of the molecule, namely, the k levels, a value of $g_{2k} = (g_2 − g_k) = 1.5$ has been chosen to obtain a value of 0.225 eV for the reorganization that occurs upon ionization. The pump energy used in the experiments is around 2.8 eV, and the probe energy for excited-state absorption is around 1.7 eV.[2] Here, in the model Hamiltonian, as the pump and probe pulses interact with their own electronic transitions, even if their energies were to overlap in the numerical calculations the obtained signals would still correspond to a physical situation of spectral nonoverlap between them. Therefore, for the differences between the molecular electronic energies, namely, $\epsilon_2 − \epsilon_1$ and $\epsilon_3 − \epsilon_2$, a value of 2.0 eV has been assumed. Experiments have located the excited-state molecular donor level in perylene to be 1 eV above the conduction-band edge of TiO$_2$.[13] In the calculations, two positions for the excited state, as mentioned earlier, are considered. However, what is essential for the coming results is that the system must be definable as a three-level system, and a specific choice of parameters does not alter the generality of conclusions reached thereby.

3. Results and Discussion

The Gaussian pump pulse of duration 10 fs and energy 2.0 eV creates a vibrational wave packet in the first excited state,

and the population in this state decays because of its coupling to a 2-eV-wide continuum of electronic levels. The excited-state population dynamics for two different positions of the injecting level (first excited molecular donor level) is calculated, and a schematic is shown in Figure 1a when the injecting level is positioned close to the band edge. For an injecting position that is 1 eV above the band edge, the solid curve in Figure 1b shows the excited-state population to be decaying smoothly on a time scale of around 80 fs. This indicates that the transfer rate is almost solely determined by the electronic coupling strength. Thus, reorganization plays no role in the excited-state decay since the energy difference between the position of the donor molecular excited state and the band edge is much larger than the reorganizational energy (0.225 eV).[6] However, if the density of states is not uniform, as is usually the case, reorganization can modify the transfer process even when the above-mentioned energy difference is larger than the reorganizational energy.[6] The Franck−Condon factors that describe the overlap between the first excited molecular state and the ionized state appear as a summation in the rate of electron transfer, and their summation is close to unity when the position of injection is sufficiently far from the band edge (wide-band limit).[6] For the case when the injecting position is lower (0.35 eV above the band edge), the population decay is clearly modulated by the presence of the vibrational wave packet (time period around 40 fs) and shows steps due to insufficient crossings between the donor PES and the continuum of the PES of the final state. Similar conclusions have been made in earlier works while considering the effect of the continuum boundary in electron−molecule collisions.[14] The scheme shown in Figure 1a corresponds to such a situation. Also, the decay is slower in this case since the summation over the Franck−Condon factors that appears in the rate is less than unity for this position of injection.[6]

A Gaussian probe pulse of 10-fs duration is introduced at various time delays, and the calculated probe absorption is shown in Figure 2. The amplitude of oscillations (due to vibrational coherences) in the probe absorption signal, seen in both parts of Figure 2, is clearly sensitive to the displacement between the first excited and the higher excited state.[8] By decreasing the displacement between the two molecular PESs, the amplitude of the oscillations appears to be attenuated due to the increased diagonal character of the Franck−Condon matrix for the transition between the excited state and the higher excited molecular states.[8] The oscillations in the signal are due to a periodic displacement of the vibrational wave packet within the excited-state PESs. Thus, while probing the excited state with a specific central frequency of the probe pulse (0−0
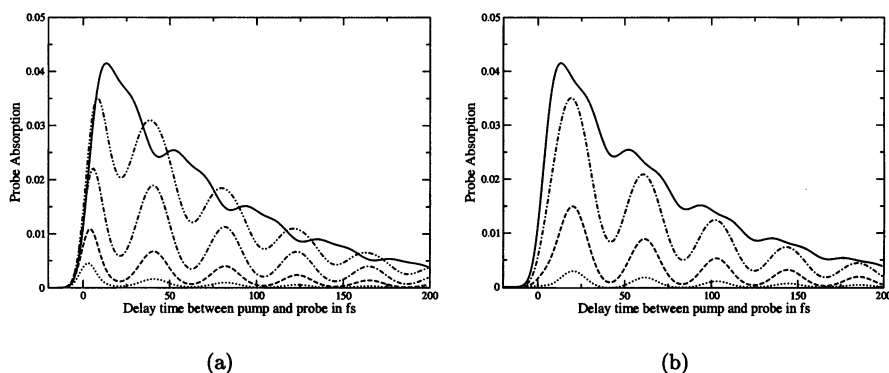
(a)   (b)

Figure 3. (a) Excited-state probe absorption vs the time delay between pump and probe pulses of Gaussian pulse widths (10 fs) for different probe energies where $g = 0.5$. The various transitions are (—) 0−0, (••-••-) 0−1, (•-••-) 0−2, (- -) 0−3, and (••) 0−4. (b) Same as in Figure 3a. The various transitions are (—) 0−0, (•-••-) 0-(−1), (- -) 0-(−2), and (••) 0-(−3).

transition for both parts of Figure 2, which corresponds to 2 eV), one opens up a select window of optical transition within which the signal waxes and wanes because of wave packet motion and the decay of the overall signal is caused either by the smooth (Figure 2a) or by the stepped (Figure 2b) disappearance of the excited-state population due to electron transfer.

More importantly, by changing the displacement from $g = 0.5$ to 0.3, one observes that steplike features can appear in the probe absorption. The steps appear clearly in Figure 2b but only in a rather suggestive manner in Figure 2a. In the former case (Figure 2b), the population is truly modulated, whereas in the latter (Figure 2a), it is not (see Figure 1b). Obviously for the trivial case of $g = 0$, one can recover the entire population dynamics in the excited state. However, when $g \neq 0$, the signal can exhibit oscillations whether the population in the excited state in the process of undergoing ET is being modulated (steplike decay) or not (smooth decay). Although for a displacement of $g = 0.3$ both the population and signal can in principle show steplike features (as seen in Figure 2b), this turns out to be an insufficient criterion by which to determine whether population transfer from molecules to semiconductors is being modulated.[2] Obviously, one may not see steps in the signal when the population transfer is being modulated ($g = 0.5$ in Figure 2b), or near-step-like behavior is seen in the signal when the population is definitely not being modulated (the $g = 0.3$ case in Figure 2a). The problem, therefore, is to establish clearly with the help of pump−probe signals whether ET is being modulated by the presence of a vibrational wave packet.

To recover unambiguously the time-dependent excited-state population from the probe signal, one should either use an ultrashort probe pulse[12] or vary the central frequency of a *finite* probe pulse. In Figure 3, a collection of such probe signals when the molecular donor level is positioned 1 eV above the band edge is shown. The signal intensity predictably goes down as the probe energy is increased beyond the 0−0 excitation (2 eV), which corresponds to the resonance transition (Figure 3a). The changes in probe energy are always in steps of 0.1 eV, which corresponds to the energy of the vibrational mode. Similar behavior is seen in Figure 3b as one tunes to energies below the 0−0 transition, and more importantly, the phase of oscillations changes sign, as can be seen by comparing Figure 3a and b. The change of phase is simply the result of photon energy changing from being greater than to becoming less than the energy difference between the two molecular electronic levels. When these signals, calculated for about nine different probe energies, are summed, the summation yields a fairly accurate description of the excited-state population dynamics, as is seen from Figure 4. At a given central frequency of the probe pulse,
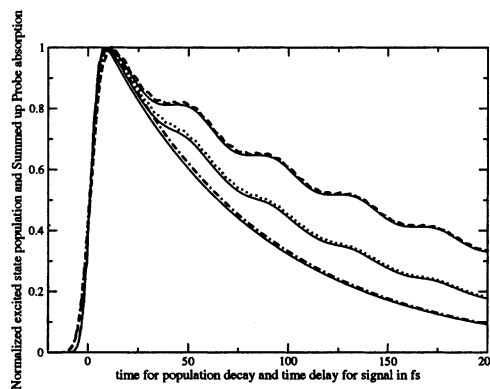

Figure 4. Normalized summed probe signals plotted alongside the respective population decay. (•-••-) Injecting position 1 eV above the band edge. (••) Injecting position 0.35 eV above the band edge. (- -) Same injecting position as for the dotted line but reorganization is 0.4 eV. (—) Population decay for the above three cases.

one samples the wave packet only in a particular region of the excited-state PES. By summing over all of the relevant variations of the probe frequency, one thus obtains the total sum of the population over the entire excited-state PES. Thus, one recovers from a summing of probe signals of different frequencies the smooth and modulated population decay curves of Figure 1a and, in addition, a slower decay curve due to increased reorganizational energy (0.4 eV) from the lower position of injection of 0.35 eV above the band edge.

One can conclude that even if population dynamics in the excited state is complicated by factors such as (i) a varying density of states (this issue has been explored in ref 6) (ii) a nuclear-coordinate-dependent electronic coupling to the continuum, (iii) a multidimensional PES, and (iv) even relaxation processes, one must be able to recover the population dynamics from a summation of probe signals over the relevant central frequencies. The range of relevant frequencies over which the probe pulse needs to be varied depends, of course, on the displacement between PESs of states $|\varphi_2\rangle$ and $|\varphi_3\rangle$. In most cases of donor−acceptor electron-transfer systems, where the modulation of electron transfer due to the vibrational wave packet has been reported,[15,16] one encounters a two-level electronic system instead of the three-level system considered here. In such systems, in the absence of spectral overlap with other excitations, one can in principle obtain excited-state population dynamics with only a single central frequency of the probe pulse, provided the pump and probe pulses are extremely short, which is termed the impulsive limit.[12] For pulses of finite duration, however, the probe absorption contains both excited-state (via stimulated emission) and ground-state (via stimulated Raman) population

dynamics.[10] Thus, in experiments where the physical system should be characterized by a two-level system or even a three-level system with considerable spectral overlap between the pump and probe pulses, it will not be easy to extract or isolate excited-state population dynamics via this summation procedure.[17] Experimental signals probing ultrafast heterogeneous electron transfer are usually connected with the rise of the product state. Since cationic ground-state absorption can also be described as a three-level system with negligible spectral overlap for the perylene−TiO$_2$ system[2], it is clear that when working with such signals excited-state population dynamics can also be obtained by the procedure outlined here. Instead of changing the probe frequency for a whole series of time delays,[18] it may be experimentally easier to have one probe pulse that is chirped so as to change its central frequency for a single time-delay setting. Well known as the pump−supercontinuum probe technique, it achieves the same purpose[19] and would therefore permit the reconstruction of the population dynamics once the time-zero correction function for the various central frequencies is known.

4. Conclusions

The first calculations of probe absorption corresponding to ultrafast heterogeneous ET inclusive of molecular reorganizational effects have been presented. Consequently, it has been possible to address the crucial question of what may be the signature of modulation of population transfer in the pump−probe signal. Results have shown that it may not be possible to discern such a signature unambiguously for a given central wavelength of a finite probe pulse. However, it has been clearly demonstrated that by varying the central wavelength of a finite probe pulse over a relevant range it is possible, in principle, to extract excited-state population dynamics via pump−probe spectroscopy for three-level systems.

References and Notes

(1) Asbury, J. B.; Hao, E.; Wang, Y.; Ghosh, H. N.; Lian, T. *J. Phys. Chem. B* **2001**, *105*, 4545.

(2) Zimmermann, C.; Willig, F.; Ramakrishna, S.; Burfeindt, B.; Pettinger, B.; Eichberger, R.; Storck, W. *J. Phys. Chem. B* **2001**, *105*, 9245.

(3) Huber, R.; Moser J.-E.; Grätzel, M.; Wachtveitl, J. *J. Phys. Chem. B* **2002**, *106*, 6494.

(4) Benko G.; Kallioinen, J.; Korppi-Tommola, E. I.; Yartsev, A. P.; Sundström, V. *J. Am. Chem. Soc.* **2002**, *124*, 489.

(5) Ramakrishna, S.; Willig, F.; May, V. *Phys. Rev. B* **2000**, *62*, R16 330.

(6) Ramakrishna, S.; Willig, F.; May, V. *J. Chem. Phys.* **2001**, *115*, 2743.

(7) Ramakrishna, S.; Willig, F.; May, V. *Chem. Phys. Lett.* **2002**, *351*, 242.

(8) Ramakrishna, S.; Willig, F. *J. Phys. Chem. B* **2000**, *104*, 68.

(9) Petersson, A.; Ratner, M.; Karlsson, O. H. *J. Phys. Chem. B* **2000**, *104*, 8498.

(10) Seidner, L.; Stock, G.; Domcke, W. *J. Chem. Phys.* **1995**, *103*, 3998.

(11) Ong, K. K.; Jensen, J. O.; Hameka, H. F. *J. Mol. Struct.: THEOCHEM* **1999**, *459*, 131.

(12) (a) Domcke W.; Köppel, H. *Chem. Phys. Lett.* **1987**, *140*, 133. (b) Stock G.; Domcke, W. *Chem. Phys.* **1988**, *124*, 227.

(13) Hannappel, T. Ph.D. Thesis, Technische Universität Berlin, 1997.

(14) (a) Estrada, H.; Domcke, W. *Phys. Rev. A* **1989**, *40*, 1262. (b) Plöhn, H.; Thoss, M.; Winterstetter, M.; Domcke, W. *Phys. Rev. A* **1998**, *58*, 1152.

(15) Wynne, K.; Reid, G.; Hochrasser, R. M. *J. Chem. Phys.* **1996**, *105*, 2287.

(16) Engleitner, S.; Seel, M.; Zinth, W. *J. Phys. Chem. A* **1999**, *103*, 3013.

(17) Wolfseder, B.; Seidner, L.; Domcke, W.; Stock, G.; Seel, M.; Engleitner, S.; Zinth, W. *Chem. Phys.* **1998**, *233*, 323.

(18) Thomsen, C. L.; Thogersen, J.; Keiding, S. R. *J. Phys. Chem. A* **1998**, *102* 1062.

(19) Kovalenko, S. A.; Dobryakov, A. L.; Ruthmann, J.; Ernsting, N. P. *Phys. Rev. A* **1999**, *59*, 2369.