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ARTICLES

Inner Sphere Reorganization Dynamics Accompanying Charge Transfer in Cyanoterphenyl

Gregory D. Scholes,*[†,‡] Pavel Matousek,[§] Anthony W. Parker,[§] David Phillips,[†] and Michael Towrie[§]

Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London SW7 2AY, United Kingdom, and Lasers for Science Facility, Central Laser Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

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Picosecond transient absorption studies of 4′-*n*-pentyl-4-cyanoterphenyl (CTP) suggest that the first excited singlet (S_1) state exhibits a solvent-dependent dynamic Stokes shift, attributed to intramolecular charge-transfer in the S_1 state (in polar solvents) followed by outer sphere reorganization. The degree of charge-transfer character attained by the CTP S_1 state is signaled in picosecond time-resolved resonance Raman (TR^3) measurements by a frequency shift of the CN-stretch band. No dynamics are observed for this mode frequency within the time resolution of the experiment (less than 1 ps). However, one of the bands in the 1200−1800 cm^{-1} region of the spectrum is reported to exhibit a solvent-dependent dynamic shift. Analysis of a spectral shift correlation function for this band reveals time constants of 45 ps in methanol, 36 ps in butanol, 21 ps in pentanol, and 18 ps in octanol. The evidence suggests that energy dissipation from the inner sphere coordinate to the solvent bath is affected by the dynamic Stokes shift (i.e., the outer sphere coordinate).

1. Introduction

The role of solvent effects on electron-transfer reactions has been the subject of a wide range of experimental[1−9] and theoretical investigations.[10−20] A huge range of photoinduced intramolecular charge-transfer reactions have been studied, by a wide variety of techniques.[1−9,21,22] In some systems a full electron is transferred from the donor to the acceptor part of a bichromophore; in other systems only partial charge is transferred. A well-known example of the latter reaction is often known as twisted intramolecular charge transfer (TICT), since it is thought that a significant structural change accompanies the charge transfer.[21−24] In solvents for which the intermolecular reorganization rate is much less than the rate of charge transfer, a frequency shift of the observed emission spectrum (a dynamic Stokes shift) is observed. This can be interpreted in terms of the relaxation of the polar and/or polarizable solvent to accommodate the change in dipole moment of the solute molecule and is often associated with the longitudinal relaxation time of the solvent. To observe this diffusive dielectric relaxation of the solvent, there must be a separation of time scales between the charge separation and the relatively slow solvent reorganization.

Theories for the rates of electron transfer and these subsequent relaxation dynamics have been developed and have been examined using methods such as time-resolved fluorescence, transient absorption, and echo peak shifts. In the present work we report our attempts to probe the *intramolecular* component of the reorganization accompanying a dynamic Stokes shift. To do this, we employ a type of pump−probe experiment (with

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[†] Imperial College of Science, Technology and Medicine.

[‡] Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

[§] Central Laser Facility, Rutherford Appleton Laboratory.

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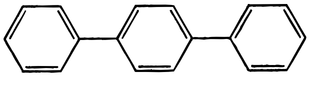
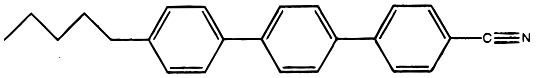
picosecond time resolution): time-resolved resonance Raman (TR^3) spectroscopy. In this experiment, a UV pump laser pulse creates a population of first excited singlet state (S$_1$) molecules at $t = 0$. We then probe this population at various time delays after the pump with a second laser pulse, tuned to resonance with an excited-state absorption band. The Raman scatter from this probe pulse is dispersed (in the frequency domain) across a CCD camera so that we measure the resonantly enhanced vibrational spectrum of an excited singlet state. Thus we obtain vibrational spectra of CTP at various time delays after the charge separation has been initiated (by the pump pulse). Moreover, this technique permits us to examine directly high-frequency intramolecular modes which would be obscured in a purely time-domain experiment owing to the limits of time resolution in ultrafast spectroscopies. It has been demonstrated recently by Mitambo and Loppnow[25] that Raman spectroscopy can be useful as a probe of solute−solvent interactions. They were able to correlate frequency shifts of certain vibrational modes with intermolecular interactions associated with dielectric and H-bonding stabilization of the solute molecule by solvent.

We investigate the molecule 4′-*n*-pentyl-4-cyanoterphenyl (cyanoterphenyl, CTP), which we found to have a large scattering cross section in the excited state. We report here transient absorption data, which suggest that the molecule exhibits a dynamic Stokes shift in the S$_1$ state on a (solvent-dependent) picosecond time scale. Hence, by satisfying these two criteria, the vibrational spectrum of the S$_1$ state of CTP can be measured using TR^3 spectroscopy at various times during the solvent reorganization. The results furnish a direct observation of the way in which each of the observed (Raman-active) vibrations are affected by the charge-transfer reaction and the concomitant dielectric relaxation of the solvent. The closely related molecule *p*-terphenyl (TP) is also examined. Since TP does not exhibit any solvent dependence of its S$_1$ state, nor any discernible dynamic Stokes shift (as suggested by the transient absorption data reported here), it provides a useful “standard” by which the CTP results may be compared.



TP



CTP

2. Experimental Section

The transient absorption measurements were carried out using two independently tunable and synchronized 150-fs pulses generated using a 40-kHz regenerative amplifier system as described in detail previously.[26] In this work, pump pulses were obtained at 277 nm by frequency tripling the regenerative amplifier fundamental, providing ca. 100 nJ after attenuation. A white light continuum (ca. 500−750 nm) generated in a sapphire crystal was used as the probe. The signal was focused into an optical fiber and dispersed across a CCD camera.

A modified configuration was used for the TR^3 measurements in which the regenerative amplifier was operating at a repetition rate of 1 kHz and the femtosecond pulse was spectrally filtered to 20 cm^{-1} inside the stretcher. The frequency-doubled output of the regenerative amplifier was used to pump two optical parametric amplifiers (OPAs), providing pump and probe pulses with typical energies of <100 nJ at the sample.[27] Pump and probe pulses (parallel polarization) were focused separately and combined using a dichroic mirror (spot size ca. 200 μm at the sample). The sample was flowed in a jet (550-μm diameter). The TR^3 signal was detected at right angles to both the direction of flow of the jet and the pump and probe beams using a single-stage spectrometer and a liquid-nitrogen-cooled CCD camera (Princeton Instruments). Further measurements used an improved detector, a back-illuminated liquid-nitrogen-cooled CCD detector (Princeton Instruments CSMALN/CCD-1024/TKB/I system). Scattered light was rejected using a holographic filter and a low-fluorescence cutoff filter.

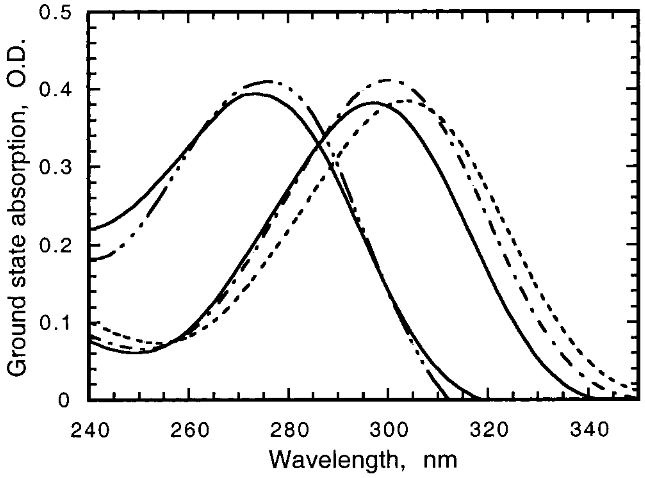


Figure 1. Ground-state absorption spectra of (a) TP, $\lambda_{\max} \approx 275$ nm, in hexane (solid line) and acetonitrile (dash−dots line); and (b) CTP, $\lambda_{\max} \approx 300$ nm, in hexane (solid line), octanol (dashed line), and acetonitrile (dash−dot line).

The time jitter between pump and probe pulses (<150 fs) was negligible compared to the 1-ps pulse duration. The TR^3 spectra were calibrated using the position of Ne lines at each spectrograph setting and assuming an approximate linear wavelength−channel relationship across the CCD. Additionally, the positions of nonresonant solvent bands were used to calibrate the 1200−1600 cm^{-1} range. The absolute frequency uncertainty is estimated to be about 5−10 cm^{-1}; however relative frequencies are accurate to within 1−2 cm^{-1}.

Ground-state (classical) Raman spectra were recorded in various solvents using a similar experimental setup. The 514.5-nm line from an Ar ion laser was used as the scattering source. These signals were detected with a Spex Triplemate 1877 spectrograph and a diode array or CCD detector.

The sample was obtained from Merck and used without further purification. Solutions were made to a concentration of ca. 1 mM in spectroscopic grade solvents. The background signal (mainly due to nonresonant solvent) was collected at a −10-ps “delay” for the probe pulse. The pump wavelength was 267 nm, the wavelength of the probe was varied, but a 600-nm probe was used for most of the data reported in the present work.

3. Results

3.a. Absorption Measurements. Ground-state absorption spectra of dilute solutions of CTP and TP in various solvents were recorded. Some of these data are shown in Figure 1. There is a large shift of the absorption maximum of CTP compared to that of TP (red-shift of ca. 2810 cm^{-1}); however, only a weak solvent dependence of the maxima of these absorption bands is evident.

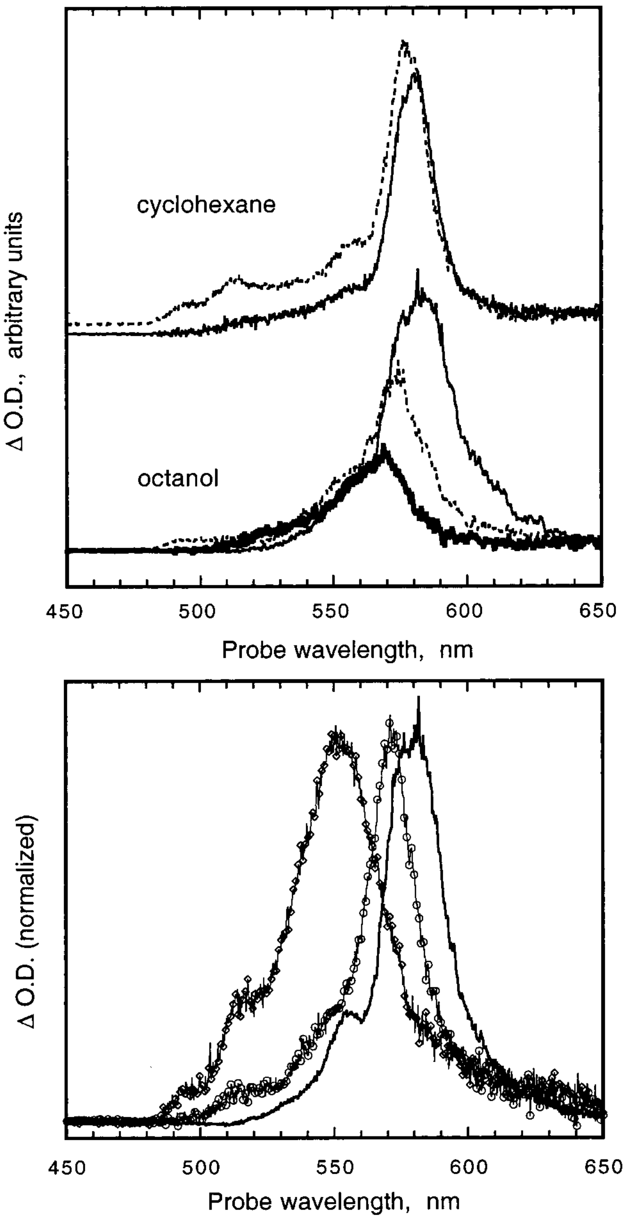


Figure 2. Upper panel: Transient absorption spectra of CTP in (a) cyclohexane at delays of 2 ps (solid line) and 50 ps (dashed line); and (b) octanol at delays of 2 ps (thin solid line), 20 ps (dashed line), and 500 ps (thick solid line). Lower panel: Transient absorption spectra of CTP in (a) dodecane (50-ps delay); (b) dioxane (20-ps delay); and (c) acetonitrile (50-ps delay).

Typical transient absorption spectra for CTP are shown in Figure 2. No stimulated emission or background fluorescence contributions to the signal should be present at these wavelengths. The signal in the region 500−550 nm (seen at later delay times) has been assigned previously to triplet−triplet absorption.[28] In nonpolar solvents such as cyclohexane, *n*-hexane, or dodecane the transient absorption spectra did not display any significant time-dependent shifts. In polar solvents the peak of the transient absorption spectrum shifts to the blue with time. The largest shift was observed for acetonitrile solvent, but the dynamics were too fast to be resolved. Fast shifts were observed also in dioxane and tetrahydrofuran solvents. The dynamics of the Stokes shift (a red-shift of S_1 relative to S_0, and therefore a blue-shift of the S_1-S_n energy gap) were well-resolved in alcohol solvents. No similar solvent dependence of the transient absorption spectra was observed for TP in either polar or nonpolar solvents. The transient absorption measurements were exploratory only. Quantitative measurements were undertaken only recently.

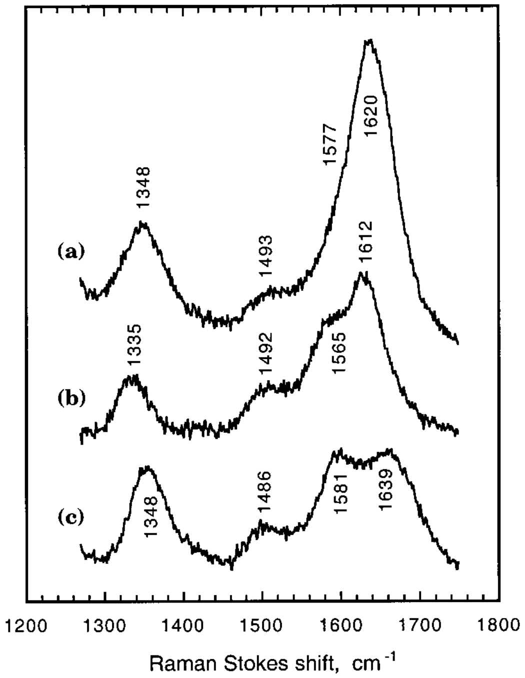


Figure 3. TR^3 spectra of (a) CTP in hexane, 200-ps delay; (b) CTP in octanol, 200-ps delay; and (c) TP in hexane, 50-ps delay. Peak positions (from fits) are indicated in cm^{-1}.

3.b. Raman Spectra. Classical Raman spectra of the ground state of CTP were measured. In the 1300−2400 cm^{-1} spectral region two strong bands were detected, at around 1610 cm^{-1} and 2230 cm^{-1}. In addition, a weak band was observed at 1509 cm^{-1} in hexane solvent. These data exhibited slight solvent dependencies (for example, hexane 1611, 2231 cm^{-1}; octanol 1611, 2231 cm^{-1}; methanol 1604, 2230 cm^{-1}; acetonitrile 1609, 2231 cm^{-1}).

The C−C regions of the TR^3 spectra of CTP and TP at long time delays between pump and probe are shown in Figure 3. One expects that at such time delays the molecule and solvent are for all intents and purposes fully equilibrated (orientationally and thermodynamically). Four bands were resolved by fitting the spectra with Lorentzian line shapes, as indicated in Figure 4. These bands have been better resolved in higher resolution spectra of TP reported in a previous study.[29] The observed frequency differences for CTP between polar and nonpolar solvent are notable (Table 1). It is reasonable to assign the frequencies as various aromatic ring modes. There is no band reported in the ground-state Raman spectrum[30] of TP in the region of 1486 cm^{-1}, nor was a progression in this mode observed in absorption or emission spectra.[31] Iwata and Hamaguchi[29] observe a mode at 748 cm^{-1} with high intensity and large excited-state displacement in the TR^3 spectrum of TP. It is likely that the 1486-cm^{-1} mode of S_1 TP is an overtone of this mode, in accord with the assignment of the analogous mode of quaterphenyl.[32] Accordingly, we assign the 1493-cm^{-1} mode of CTP S_1 state (1509 cm^{-1} in the ground state) as an overtone band.

The TR^3 spectra of CTP also have a band in the 2200-cm^{-1} region, absent from the TP spectrum, which we assign to the C≡N stretch. The frequency of this band was found to be solvent-dependent (much more strongly than the corresponding

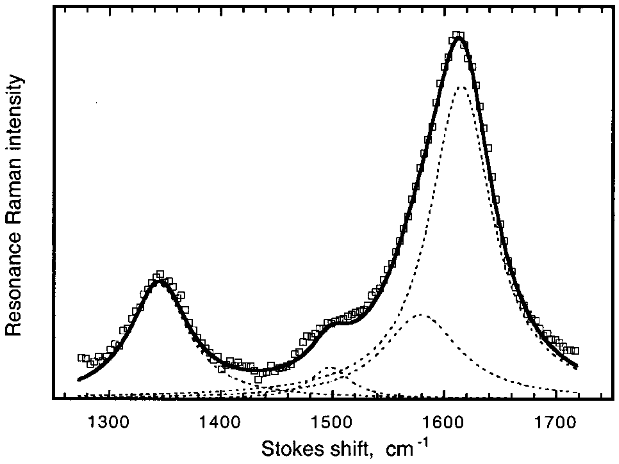


Figure 4. Illustration of TR^3 data for CTP in hexane, 20-ps delay (squares, every third data point) and the corresponding fit (solid line) of four Lorentzian components (dashed lines).

TABLE 1: Long-Time-Delay Band Positions (cm^{-1}) Observed for the S$_1$ State of CTP

hexane[a]	octanol[a]	butanol[b]	acetonitrile[c]
1348	1335	1341	1329
1493	1492	1496	1491
1577	1565	1571	1575
1620	1612	1616	1618
2159	2149	2144	2132

[a] Time delay of 200 ps. [b] Time delay of 100 ps. [c] Time delay of 50 ps.

ground-state frequency), as summarized in Table 1, but dynamic shifts were not observed within the time resolution of our experiment.

3.c. Time-Resolved Raman Spectra. The TR^3 spectra for CTP in octanol solvent at various time delays are shown in Figure 5. The dynamic shift of the band, which at long time delays has a frequency of 1612 cm^{-1}, is apparent. Such a marked shift was not observed for the corresponding band of TP. The intensity differences between the TR^3 spectra recorded in the different solvents are probably due mainly to the changes in the resonance Raman excitation profiles that arise from the solvent-dependent shift of the transient absorption spectra.[32] Solvent-dependent dynamics and/or relative intensity changes with time were not observed in the TP TR^3 spectra.

Anti-Stokes Raman spectra were recorded for CTP in both hexane and butanol solvents, wherein the 1612-cm^{-1} band was clearly evident. More recent data (collected with significantly improved signal-to-noise) suggest that the band shapes in the TR^3 spectra are not as simple as the fit shown in Figure 4 implies. However, we have found that an analysis involving more complex band fitting makes little difference to the results of the present work. We are quite confident that we are observing a real band shift rather than an apparent shift arising from amplitude changes of component bands. This was further checked by investigating the TR^3 spectra as a function of probe wavelength (since it is likely that component bands would have different resonance Raman excitation profiles).

4. Discussion

4.a. Charge Separation in CTP. Solvent reorganization is inexorably involved in electron-transfer reactions.[33] For reactions in which the rate of charge separation is significantly faster than the rate at which the solvent can reorganize to accommodate the change in dipole moment (like that reported here for CTP), the extent of the reaction (i.e., the charge transfer) is dictated by the solvent. Two primary reaction coordinates are identifiable: (i) an inner sphere coordinate accounting for configurational and frequency changes between reactant and product states within the first solvation layer; (ii) an outer sphere coordinate which denotes the diffusional reorientation response of the solvent polarization. The competition between electron transfer and dielectric solvent polarization can be described by writing the rate of electron transfer in terms of a nonadiabatic (NA) and an adiabatic (AD) contribution:[34] $k^{-1} = k_{\mathrm{NA}}^{-1} + k_{\mathrm{AD}}^{-1}$. If there is fast motion along the former coordinate such that there is a local equilibration between electronic states at any point along the solvent polarization coordinate, then the reaction is dominated by the latter coordinate. In the limit of long solvent longitudinal relaxation times $\tau_{\mathrm{L}} = (\epsilon_\infty/\epsilon_0)\tau_{\mathrm{D}}$ (where ϵ_∞ and ϵ_0 are the optical and static dielectric constants and τ_{D} is the solvent dielectric relaxation time), it is predicted that the rate of electron transfer becomes $k \propto \tau_{\mathrm{L}}^{-1}$ in the adiabatic limit and "normal region".

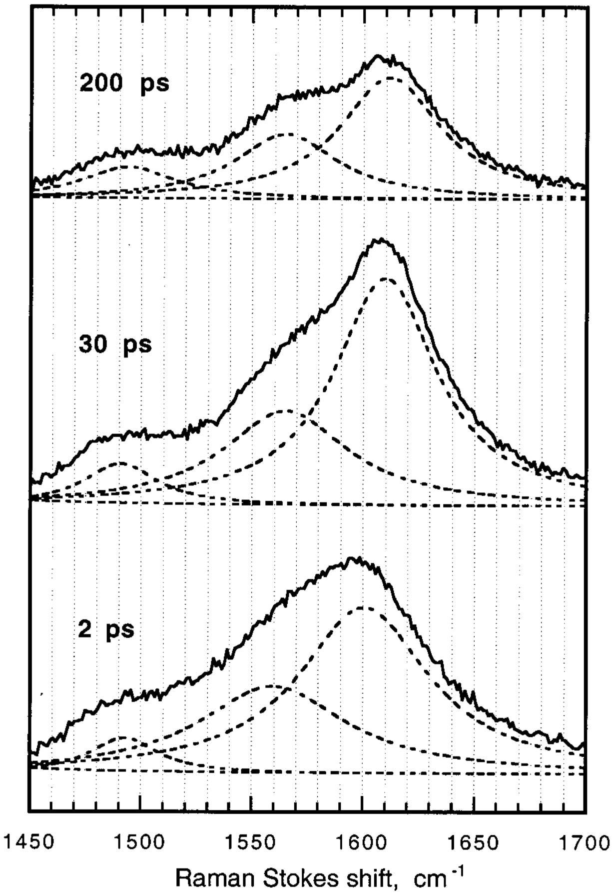


Figure 5. TR^3 spectra of CTP in octanol at various time delays between pump and probe (solid line). Dashed lines are the best-fit Lorentzian bands. Only the 1612-cm^{-1} band is seen to shift with time.

The adiabaticity parameter, eq 1, can be useful for characterizing the mechanism of charge-transfer reactions,

$$\kappa = 4\pi V^2\langle\tau\rangle/\hbar\lambda \tag{1}$$

where V is the electronic coupling, λ is the reorganization energy, and the medium reorganization time $\langle\tau\rangle = \tau_{\mathrm{L}}$ for polar Debye solvents. In the solvent-controlled adiabatic limit $\kappa \gg 1$ and the rate of outer sphere electron transfer is given by eq 2.

$$k = \tau_{\mathrm{L}}^{-1}(\lambda/16\pi k_{\mathrm{B}}T)^{1/2}\exp(-\Delta G^{\ddagger}/k_{\mathrm{B}}T) \tag{2}$$

where $\Delta G^{\ddagger}$ is the free energy of activation for the electron transfer, k_B is the Boltzmann factor, and T is the temperature. This limit is expected to describe appropriately the CTP charge separation in alcohol solvents owing to their long dielectric relaxation times.

The transient absorption data (Figure 2) reveal that the S_1 state of CTP exhibits strongly solvent-dependent dynamics, not observed as marked solvatochromism in the ground-state absorption spectra. This suggests that the CTP molecule undergoes charge transfer after photoexcitation (that is, the initially excited state is not a charge-transfer state). In contrast, the S_1 state of TP shows no evidence of a dynamic Stokes shift, which we attribute to the absence of the electron-withdrawing CN substituent.

The frequency of the C≡N stretch has been observed previously to be sensitive as an indication of the charge-transfer character for the molecule 4-dimethylaminobenzonitrile. Using transient infrared spectroscopy, it was found by Hashimoto and Hamaguchi[35] that the frequency of this mode shifts from 2216 to 2096 cm^{-1} on going from the ground state to the intramolecular charge-transfer state in butanol solvent. Moreover, Mitambo and Loppnow[25] have reported a similar observation for Raman frequencies of such an electron-withdrawing group in a related molecule (4-dimethylaminobenzoate) in the ground state. For the S_1 state of CTP we find there to be a solvent dependence of the C≡N-stretch frequency, Table 1. Such a solvent dependence of the frequency of this mode was not observed in the ground-state Raman spectra. Any dynamics of this Raman frequency shift in the S_1 state were not resolved for any of the solvents studied. If the frequency of the CN-stretch band does indeed signal the change in electron density on the C≡N group (as suggested by other studies[25,35]), and hence signals the charge transfer, then the fast dynamics of the shift (<1 ps in all solvents studied) suggests that there is a definite separation of time scales for CTP between a fast charge transfer and the subsequent solvent reorganization (i.e., the dynamic Stokes shift).

Hence we conclude that in polar solvents the excited CTP molecule undergoes rapid charge transfer, followed by solvent reorientation to accommodate the increased dipole moment (which we observe in the transient absorption spectra as a dynamic Stokes shift for solvents with long enough dielectric relaxation times). It thus seems that CTP is an archetype for studying intramolecular (inner sphere) reorganization accompanying the dynamic dielectric stabilization [intermolecular (outer sphere) reorganization] about an excited charge-transfer state.

4.b. Observations Connected with the Inner Sphere Coordinate. For the S_1 state of CTP we observe some mode-specific band shifts in the 1200−1800-cm^{-1} (C=C stretch) region of the TR^3 spectrum which exhibit a clear solvent dependence. Moreover, we are able to resolve the dynamics of these shifts for some of the solvents. Our observations suggest that the time scales of these frequency shifts are strongly correlated with solvent dielectric properties. It follows that these shifts are influenced by either the extent of the Stokes shift (i.e., the magnitude of the Stokes shift itself) or the rate of the dynamic Stokes shift. The CN-stretch mode exhibits an equilibrium (long time delay) frequency which depends upon solvent, red-shifting for more polar solvents. However, no time dependence was observed. The 1612-cm^{-1} mode displays little solvent dependence of the equilibrium frequencies (Table 1) and an overall dynamic shift of about 8−12 cm^{-1} in polar solvents. The shift must be viewed in terms of its relationship to the Stokes shift and, hence, a changing Raman excitation profile, which could affect the band intensities.

The dynamics of the 1612-cm^{-1} band may be examined and compared directly with those of the Stokes shift using a normalized spectral correlation function, $C(t)$, which accounts for the time-dependent reorganization energy, and is defined as[36,37]

$$C(t) = \frac{\nu(t) - \nu(0)}{\nu(\infty) - \nu(0)} \tag{3}$$

where ν is the nonequilibrium frequency of the transient absorption maximum or Raman band. The results of such an analysis for CTP in octanol indicate that the time scale of the Raman shift is shorter than that of the Stokes shift (in this case). By fitting the correlation function data to a single-exponential decay, we retrieve time constants of 18 ps versus 27 ps for the Raman shift and the Stokes shift, respectively. We note that in the transient absorption measurements we observe a rate for the dynamic Stokes shift on the order $k^{-1} \approx 27$ ps, whereas for octanol $\tau_L = 356$ ps[38] (associated with rotational relaxation of clustered molecules). We are presently undertaking more detailed transient absorption and TR^3 studies to establish the significance of the differences in kinetics between TR^3 and TA.

In Figure 6 analyses of TR^3 data of CTP in various other solvents are depicted. By employing a least-squares fitting of a linear function through these data, we obtain from the spectral shift correlation functions time constants for the TR^3 band shifts of (a) 45 ps in methanol; (b) 36 ps in butanol; and (c) 21 ps in pentanol. Thus, a trend is observed: for alcohol solvents, the time constant associated with the spectral shift correlation function for the Raman band is inversely proportional to the solvent dielectric relaxation time.

In large polyatomic molecules in solution, much of the excess excitation energy is absorbed into high-frequency modes and is redistributed internally on a sub-picosecond time scale by IVR. This is evident in the anti-Stokes TR^3 spectra of CTP, as indicated by the dynamic data shown in Figure 7. These data suggest IVR time scales of 1.8 ps for CTP in hexane and 1.2 ps in BuOH. This excess energy is subsequently transferred to the solvent bath on a longer time scale, rate-limited in part by thermal diffusion.[39−43] Using TR^3 spectroscopy, various workers[44−47] have observed time-dependent shifts for the 1570-cm^{-1} band of the S_1 state of *trans*-stilbene, which have been connected to dissipation of excess excitation energy. This observation is not reported to be dependent on solvent dielectric constant. However, before this can be clearly established, an excitation energy dependence must be undertaken. This will be the subject of our next publication.

A detailed study of energy dissipation dynamics and their relationship to the Stokes shift dynamics for the molecule *p*-quaterphenyl has been reported recently in ref 32. It was found that the TR^3 spectra and the transient absorption spectra were very closely related, enabling detailed comparisons using transform theory. Changes in Stokes Raman band intensities with time were correlated with the Stokes shift and concomitant change in width of the 0−0 electronic transition in addition to changes in Franck−Condon displacements during the relaxation. The fast decay of the anti-Stokes Raman band was attributed to decay of the $v = 2$ (and higher) excitations through IVR. Finally, a slower (ca. 17 ps time scale) relaxation of all observed degrees of freedom took place, manifest as small blue shifts and bandwidth reductions of vibrational bands.

Hence, particularly in view of the close chemical homology between TP and *p*-quaterphenyl, it is reasonable to assume that

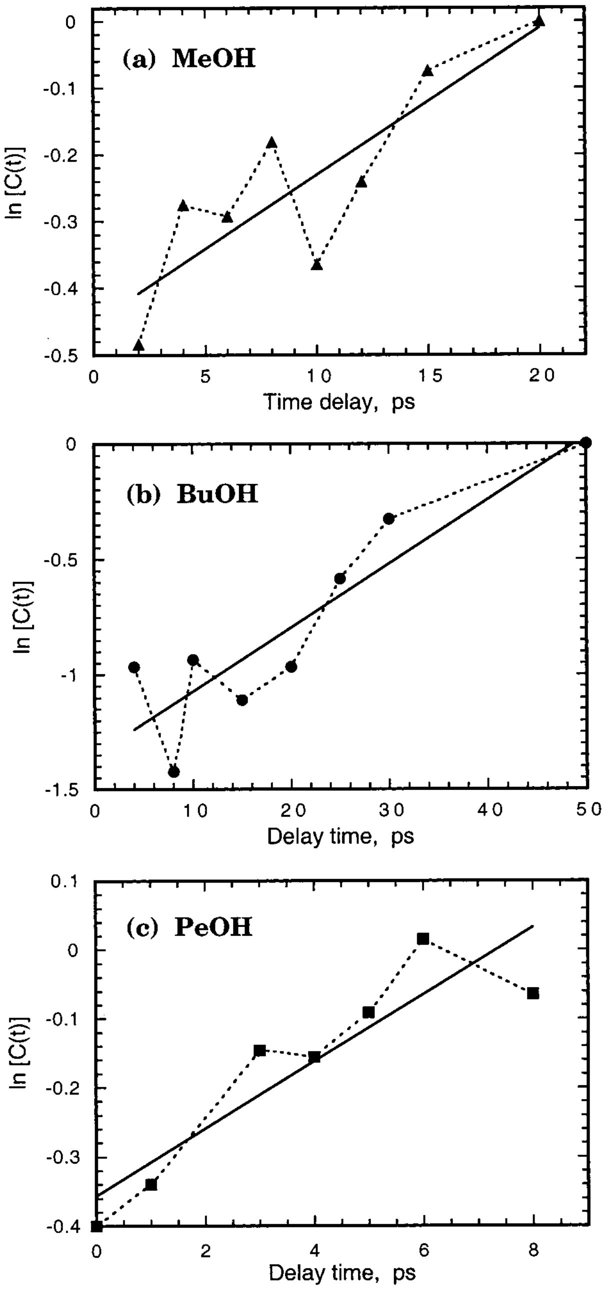


Figure 6. Plots of the ln of the initial spectral shift correlation function (eq 3) for the 1612-cm^{-1} Raman band as a function of time for CTP in various alcohol solvents. Solid lines are linear fits to the data points (filled shapes), from which time constants of (a) 45 ps, (b) 36 ps, and (c) 21 ps are retrieved.

such a picture holds also for TP and CTP in general. In fact, this picture is consistent with our observations of CTP in nonpolar solvents and TP in polar as well as nonpolar solvents. Hence, we conclude that the slower time-scale relaxation involving all degrees of freedom (identified in previous work[32]) is affected by the charge-transfer reaction. It is possible that in polar solvents the shifts we observe for CTP involve a contribution from the dissipation of the free energy change associated with formation of the charge-transfer state, in addition to the energy dissipation of excess excitation energy. In other words, owing to the long time scale of the Stokes shift, the thermal equilibration of the molecule is perturbed. Considering the lack of dynamics observed for the CN stretch, a two-coordinate decomposition of the charge-transfer dynamics could be reasonable,[12,48] for example, local high-frequency modes versus outer sphere dielectric relaxation and inner sphere (low-frequency) modes. A theory accounting for both longitudinal dielectric relaxation and vibrational dynamics has been reported by Loring et al.[49]

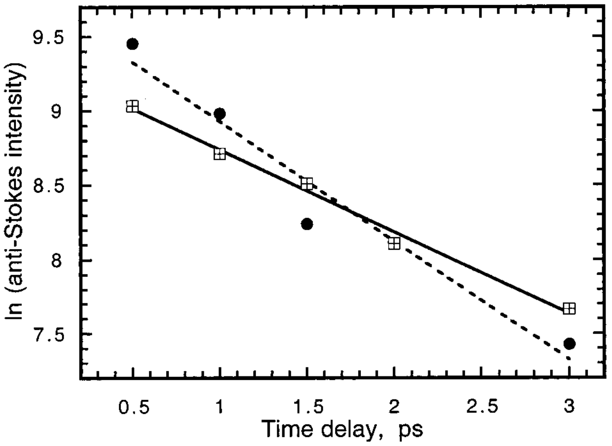


Figure 7. Plots of ln(anti-Stokes intensity) of the 1612 cm^{-1} band versus time for CTP in hexane (squares, solid fit) and butanol (circles, dashed fit).

At this stage we cannot rule out the possibility that the frequency shifts are directly associated with intramolecular reorganization between the initial S_1 state and the final charge-transfer state,[50] although intramolecular reorganization is normally assumed to be very rapid. Such a mechanism has been suggested as a possible contribution to the shifts observed for *trans*-stilbene. Intramolecular reorganization of the CTP molecule may accompany the Stokes shift; changes in structure and electron density should occur in any charge separation reaction and may be manifest as frequency shifts in certain modes. If this were the case, then the charge transfer would need to be described by theories for nonequilibrium solvation.[20,51,52]

5. Conclusions

Picosecond transient absorption studies of 4′-*n*-pentyl-4-cyanoterphenyl (cyanoterphenyl, CTP) revealed that the first excited singlet (S_1) state exhibits a solvent-dependent dynamic Stokes shift. This was not observed for terphenyl (TP). It was attributed to a fast intramolecular charge-transfer reaction in the S_1 state (in polar solvents) followed by outer sphere reorganization. The degree of charge-transfer character attained by the CTP S_1 state was also signaled in the time-resolved resonance Raman (TR^3) measurements with picosecond time resolution by a frequency shift of the CN-stretch band. No dynamics were observed for this mode frequency in the time resolution of the experiment (less than 1 ps). However, one of the bands in the C=C region of the CTP spectrum was observed to exhibit a solvent-dependent dynamic shift which was not observed for TP. Analysis of the spectral shift correlation function for this band revealed time constants of 45 ps in methanol, 36 ps in butanol, 21 ps in pentanol, and 18 ps in octanol. These time constants go as the inverse of the corresponding solvent dielectric relaxation times. The shift was within our time resolution for acetonitrile and tetrahydrofuran solvents. The data suggest that high-frequency intramolecular reorganization is fast (e.g., that involving the CN stretch), while reorganization involving low-frequency modes (i.e., the inner sphere coordinate) involves energy dissipation to the solvent bath which is affected by the dynamic Stokes shift (i.e., the outer sphere coordinate). In other words, owing to the long time scale of the Stokes shift, the molecule has a complex thermal equilibration time scale.

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