

Detecting Electronic Coherence in Excited-State Electron Transfer in Fluorinated Benzenes

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Photoinduced electron transfer (ET) in heavily fluorinated benzenes in solution has been studied with broadband transient absorption spectroscopy. Spectrally resolved kinetics exhibit oscillations with amplitude up to 70% of the signal. The oscillation frequency is specific for each probe; in addition, for pentafluorobenzene it markedly depends on solvent, being 86 cm^{-1} in hexane and 94 cm^{-1} in acetonitrile. We argue that the observed behavior is not related to vibrational coherences, but originate from coherent electronic motion between an optically excited and an ET state.

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The role of electronic coherence (EC) in photoinduced electron transfer (ET) has been theoretically discussed for the past decade [1–5]. The phenomenon can be explained with a two-level system which states 1 and 2 are isoenergetic and coupled by interaction V . When only state 1 is initially populated and there is no dissipation, the occupation probabilities P_1 , P_2 exhibit oscillations, $P_1 = \cos^2(Vt/2)$, $P_2 = \sin^2(Vt/2)$, caused by phase coherence between the corresponding wave functions [6]. When 1 and 2 correspond to vibrational modes of the same electronic term, the coherence effects have been experimentally demonstrated in the past [7]. Another case deals with different *electronic* states and the effect is then called electronic coherence. A known example of EC is Rabi oscillations between atomic states of different energy, detected first in gases [8] and recently in the solid phase [9]. Below we consider the case of degenerate vibronic states, which can be realized in molecular systems.

A scheme for observing EC in photoinduced intramolecular ET is sketched in Fig. 1. Here population is transferred from the ground g to excited state e by an ultrashort laser pulse. ET from e to e' proceeds along an intramolecular coordinate Q and is probed with transient excited-state absorption (ESA) or stimulated emission (SE). Electronic coherence, if it exists between an optically excited (OE) and an ET state, would be visible as large amplitude oscillations in both ESA and SE.

Two conditions must be met to detect EC. First, population at the intersection region of e and e' has to be large, otherwise oscillations in the signal will be weak. With conventional preparation schemes this means that ET should be nearly barrierless. Second, the oscillation frequency ν_{osc} must be faster than the relaxation rate $\gamma_{e'}$ in state e' , $\nu_{\text{osc}} > \gamma_{e'}$, to allow at least a few periods of oscillations. The frequency $\nu_{\text{osc}} = \sqrt{f_{ij}'} V_{ee'}$ equals the product of the bar electronic coupling $V_{ee'}$ and a Franck-Condon factor f_{ij}' between i and j vibrational levels of e and e' . For real systems ν_{osc} may be about 100 cm^{-1} [1–3], which gives an estimate $\gamma_{e'} < 3\text{ ps}^{-1}$. Note that the latter condition is difficult to satisfy. Indeed, as seen from

Fig. 1, a barrierless reaction requires a bias between e and e' . But in this case, ET results in vibrationally excited charge-transfer states which are known to undergo rapid relaxation. This may explain the failure of previous attempts to detect EC in complex systems such as biomolecules or mixed-valence compounds [2], for which fast, sub-50 fs, excited-state vibrational relaxation is expected.

In this Letter we test for the presence of EC heavily fluorinated benzenes. In spite of their simple structure, these molecules possess all the features characteristic for charge-transfer compounds. Their stationary spectra in solution are depicted in Fig. 2 [10]. A large, $12 \times 10^3\text{ cm}^{-1}$, emission Stokes shift clearly points out that the emitting state is different from the OE state. Besides, the emissive state is polar [11], which is recognized from a solvatochromic shift of the emission band, when comparing nonpolar hexane to polar acetonitrile. Recent calculations [12] do predict that this state of the $\pi\sigma^*$ character is

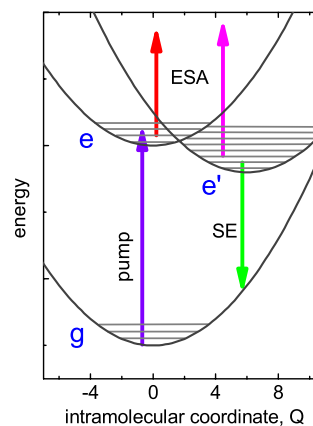


FIG. 1 (color online). Scheme of electron transfer (ET). Population is transferred from the ground g to optically excited (OE) state e by ultrashort pumping. ET from e to e' occurs along an intramolecular vibrational coordinate Q (reaction coordinate) and is probed with transient excited-state absorption (ESA) or stimulated emission (SE). Electronic coherence between the OE and the ET state may be observed as large amplitude oscillations in both ESA and SE.

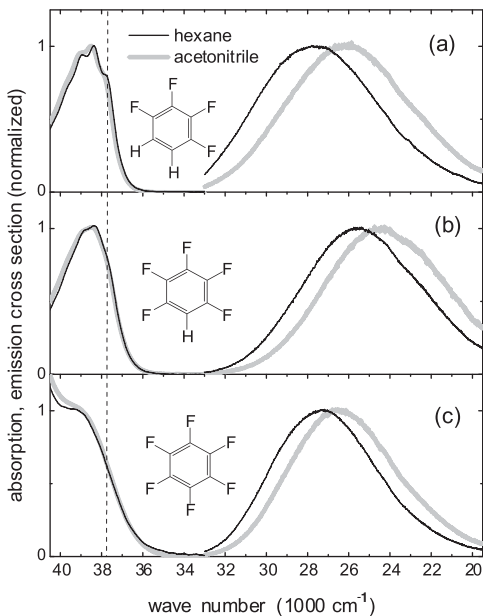


FIG. 2. Stationary spectra of 1,2,3,4-tetrafluoro- (a), pentafluoro- (b), and hexafluorobenzene (c) in hexane (black) and acetonitrile (gray). Absorption spectra of the probes are similar and nearly indistinguishable in both solvents. Emission spectra are strongly redshifted and show pronounced solvatochromism indicating ET and the polar nature of the emitting state. Dotted line marks excitation at 265 nm for transient absorption.

more polar than the $\pi\pi^*$ Franck-Condon state. Excited-state ET occurs from the benzene ring to the C-F bonds, being strongly coupled to out-of-plane bending of fluorine atoms [12]. Note that in this case the reaction mode is not optically active, which corresponds in terms of Fig. 1 to zero displacement between \mathbf{g} and \mathbf{e} . Hence, no wave packet along the reaction mode can be induced with optical excitation.

Our transient absorption setup has been described elsewhere [13]. Briefly, two noncollinear parametric amplifiers (NOPA, Clark) [14] were used to generate UV pump and supercontinuum probe pulses. A sample in a flowing optical cell (0.3 mm thick, absorbance $A \sim 0.7$) was excited at 265 nm (0.5 μJ pulse energy, 0.15 mm spot size) and probed at the magic angle in the range 334–1072 nm. The pump-probe cross correlation was about 100 fs over the whole spectrum. The experimental spectra $\Delta A(\nu, t)$ were corrected for the chirp of the supercontinuum and for the solvent signal [13].

Figure 3(a) shows the spectral evolution for pentafluorobenzene in acetonitrile. The main feature here is the strong oscillatory behavior ($\nu_{\text{osc}} = 94 \text{ cm}^{-1}$) of the signal, $\Delta A(\nu, t)$, seen across the full probe range. Note that at $\nu = 23 \times 10^3 \text{ cm}^{-1}$ the oscillation phase jumps by 180° . Figure 3(b) displays a kinetics at $14 \times 10^3 \text{ cm}^{-1}$, which exhibits large oscillations with a small background. It turns out that the first peak modulates the signal by 70% when the coherent pump-probe signal [15,16] is subtracted.

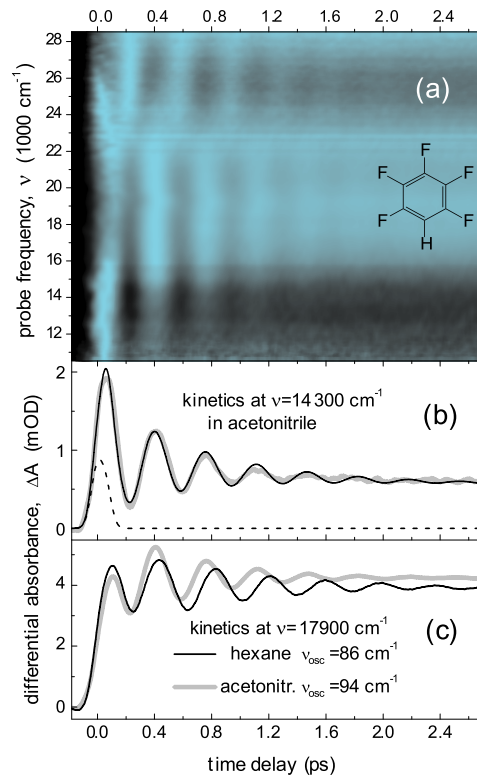


FIG. 3 (color online). (a) Spectral evolution for pentafluorobenzene in acetonitrile. Large oscillations in the signal indicate EC between optically excited and ET states. At $\nu = 23 \times 10^3 \text{ cm}^{-1}$ the oscillation phase jumps by 180° . (b) Kinetics at $14 \times 10^3 \text{ cm}^{-1}$ (gray) together with its fit (black); the first peak modulates the signal by $\sim 70\%$ if the coherent spike (dashed line) is subtracted. (c) A kinetics through $18 \times 10^3 \text{ cm}^{-1}$ for hexane (black line) and acetonitrile (gray line) displays a 9% difference in the oscillation frequency.

Another kinetics at $18 \times 10^3 \text{ cm}^{-1}$ is shown in Fig. 3(c). Here oscillations are also strong but overlaid with a higher background. For comparison, a similar kinetics in hexane is also shown. In hexane $\nu_{\text{osc}} = 86 \text{ cm}^{-1}$ differs by 9% from that in acetonitrile, a huge difference if the oscillations were due to intramolecular vibrations. These two features, a large oscillation amplitude and sensitivity of the frequency to solvent, indicate an unusual nature of the observed oscillations and imply, in light of the above discussion, that we may deal with EC between the OE and the ET state. We, however, postpone this crucial conclusion to consider other explanations.

An alternative source for the oscillatory behavior might be vibrational coherences (VC), which are common in femtosecond measurements [15–17]. Usually VC are due to optically active vibrational modes excited by ultrashort pumping. They may also appear because of vibronic coupling between the OE and the ET state [1,3]. VC modulate optical frequencies of electronic transitions, showing up in femtosecond kinetics as oscillations with frequencies of intramolecular vibrations. In transient spectra they are

recognized as *spectral* oscillations of the corresponding ESA and SE bands (with which these VC are coupled). These bands move back and forth along the probe frequency ν , thus mirroring the motion of the vibrational wave packet. An estimate for the oscillation amplitude a_{VC} due to VC is given as $a_{VC} = \nu_{osc}[d\sigma(\nu)/d\nu]/\sigma(\nu)$, where $\sigma(\nu)$ is the ESA/SE band shape [17]. The strongest oscillations are expected then for the region where $\sigma(\nu)$ is very steep, and weak oscillations (phase jump) will be at the band peak and in its far tail. To check these features of VC, we now turn to the transient spectra which underlie the evolution shown in Fig. 3.

Transient absorption spectra of pentafluorobenzene in acetonitrile are displayed in Fig. 4. Note that ESA and SE contribute to the total signal $\Delta A(\nu, t)$ with opposite sign, ESA being positive and SE negative. The spectra are dominated by two ESA bands peaked at $\nu = 20 \times 10^3 \text{ cm}^{-1}$ and $29 \times 10^3 \text{ cm}^{-1}$, but a growing SE band is also recognized as a local minimum at $25 \times 10^3 \text{ cm}^{-1}$ [compare with Fig. 2(b)]. The spectra are shown for such pump-probe delays that black and green (gray) colors correspond, respectively, to *maxima* and *minima* in the oscillation signal. The first green spectrum at 0.23 ps (minimum) is followed by black one at 0.4 ps (maximum), then goes again green at 0.57 ps and so on. The oscillatory part is given by the difference between subsequent green and black spectra. Considering the ESA band at $20 \times$

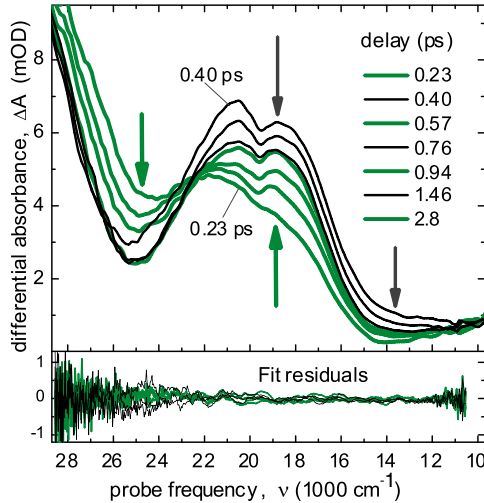


FIG. 4 (color online). Top panel: Transient spectra of pentafluorobenzene in acetonitrile. ESA and SE contribute to the signal $\Delta A(\nu, t)$ with opposite sign, ESA positive and SE negative. A growing SE band is recognized at $25 \times 10^3 \text{ cm}^{-1}$. Black and green (gray) spectra correspond, respectively, to maxima and minima in the oscillatory signal. Arrows point to the evolution of the signal. The difference between subsequent spectra gives the oscillation amplitude; it changes sign (phase jump) at 22800 cm^{-1} where all the spectra intersect. The spectral bands do not show horizontal oscillations characteristic for vibrational coherences. Bottom panel: Residuals between the spectra on top and their fit to Eqs. (2) and (3).

10^3 cm^{-1} , it is seen that the oscillations are very strong at the band peak, contrary to what is expected if VC were involved. Accordingly, there are no “horizontal” spectral oscillations, instead the evolution proceeds along the vertical axis as indicated by the arrows. Last, the above estimate for a_{VC} results in the amplitudes $a_{VC} < 10\%$, well below those experimentally observed. We can conclude that VC are insignificant in our experiment, and what we observe should be related to EC.

With this result at hand, we can go a step further to develop a theoretical model of the ET process. Referring to Fig. 1 we model our system with only three states. State 1 is the OE lowest vibrational state at the bottom of **e**. ET occurs from 1 to 2 due to coupling V_{12} , 2 representing an excited vibrational state belonging to **e'**. We consider 1 and 2 to be nearly degenerate, $E_1 - E_2 < V_{12}$. Our quantum-chemical calculations show that the vibrational frequency ν_{vib} of the reaction mode associated with **e'** is below 100 cm^{-1} ; therefore this condition is satisfied. Upon ET state 2 undergoes vibrational relaxation to result in state 3 at the bottom of **e'**. We neglect coupling and coherences between 1 and 3 [18]. The equation of motion reads $\partial \rho_{mn} / \partial t = -i[H, \rho]_{mn} - \rho_{mn} \gamma_{mn}$, with $H_{11} = E_1$, $H_{22} = E_2$, $H_{12} = H_{21} = V_{12}/2 = V/2$, $H_{33} = E_3$, $\gamma_{11} = 0$, $\gamma_{12} = \gamma_{\perp}$, $\gamma_{22} = -\gamma_{33} = \gamma_{\parallel}$. Assuming $E_1 = E_2$, $\gamma_{\parallel} \ll V$ the solution is

$$\begin{aligned} \rho_{11} &= [\exp(-\gamma_1 t) + \exp(-\gamma_2 t) \cos(Vt)]/2, \\ \rho_{22} &= [\exp(-\gamma_1 t) - \exp(-\gamma_2 t) \cos(Vt)]/2, \\ \rho_{12} &= \rho_{21}^* = \exp(-\gamma_{\perp} t) + i \exp(-\gamma_2 t) \sin(Vt)/2, \\ \rho_{33} &= 1 - \exp(-\gamma_1 t), \quad \gamma_1 = \gamma_{\parallel}/2, \quad \gamma_2 = \gamma_{\parallel}/4 + \gamma_{\perp}/2. \end{aligned} \quad (1)$$

The transient absorption signal $S(\nu, t) = S_I + S_{II}$ consists of two parts. The S_I term is proportional to the populations ρ_{jj} , $S_I = \text{Im} \sum_{kj} \mu_{kj}^2 \rho_{jj} L(\nu - \nu_{kj})$, where μ_{kj} are the transition dipoles, and $L(\nu - \nu_{kj}) \sim \gamma_{kj}/(\nu - \nu_{kj} + i\gamma_{kj})$ are the ESA/SE line shapes for the transitions $j \rightarrow k$. With (1), S_I can be written as

$$\begin{aligned} S_I &= [\sigma_1(\nu) + \sigma_2(\nu)]/2 \exp(-\gamma_1 t) \\ &\quad + [\sigma_1(\nu) - \sigma_2(\nu)]/2 \exp(-\gamma_2 t) \cos(Vt) \\ &\quad + \sigma_3(\nu)[1 - \exp(-\gamma_1 t)], \end{aligned} \quad (2)$$

where $\sigma_j(\nu) = -\sum_k \mu_{kj}^2 \text{Im}[L(\nu - \nu_{kj})]$ are the spectra associated with the states 1, 2, and 3. These spectra are recognized in Fig. 4 where $\sigma_1(\nu)$, $\sigma_2(\nu)$ correspond to the first black and green spectra (at 0.4 and 0.23 ps), respectively, and $\sigma_3(\nu)$ is the last green spectrum at 2.8 ps. One sees from (2) that the oscillation amplitude is given by the difference $\sigma_1(\nu) - \sigma_2(\nu)$; it changes sign at the intersection point $\sigma_1(\nu) = \sigma_2(\nu)$. This explains the phase jump in Fig. 3(a). Next, the oscillations are overlaid with a background which has a growing incoherent contribution from σ_3 and decaying coherent one from $(\sigma_1 + \sigma_2)/2$.

TABLE I. Fit parameters of the signal $\Delta A(\nu, t)$ to Eqs. (2) and (3). Accuracy for ν_{osc} is $\pm 1 \text{ cm}^{-1}$ and for $\gamma_{\parallel}, \gamma_{\perp}$ is $\pm 0.15 \text{ ps}^{-1}$.

	$\gamma_{\parallel} (\text{ps}^{-1})$	$\gamma_{\perp} (\text{ps}^{-1})$	$\nu_{\text{osc}} (\text{cm}^{-1})$
Pentafluorobenzene,			
Hexane	2.6	1.4	86
Acetonitrile	2.6	1.9	94
Hexafluorobenzene,			
Hexane	4.2	2.9	103
Acetonitrile	5.2	4.2	104
1,2,3,4-tetrafluorobenzene,			
Hexane	2.6	1.3	80
Acetonitrile	3.8	2.9	87

The second term $S_{II} = \text{Im}\{\mu_{a1}\mu_{a2}[\rho_{12}L(\nu - \nu_{a1}) + \rho_{21}L(\nu - \nu_{a2})]\}$ represents the signal due to coherences ρ_{12}, ρ_{21} . It may contribute if 1 and 2 are optically coupled to the *same* molecular state, say, a . With $\mu_{1a} \approx \mu_{2a}$ it can be evaluated as

$$S_{II} = [\sigma_1(\nu) + \sigma_2(\nu)] \exp(-\gamma_{\perp} t) - \left(\frac{\gamma_{a1}}{2\sigma_1} \frac{d\sigma_1}{d\nu} - \frac{\gamma_{a2}}{2\sigma_2} \frac{d\sigma_2}{d\nu} \right) \mu_{1a}^2 \exp(-\gamma_{\parallel} t) \sin(Vt), \quad (3)$$

where the first nonoscillating part adds to the background, and the oscillatory contribution is seen to be out of phase with the population oscillations (2). We then fit the experimental signal $\Delta A(\nu, t)$ to Eqs. (2) and (3) with parameters γ_1, γ_2 , and ν_{osc} . The residuals are displayed at the bottom of Fig. 4, while a typical fit in the time domain is shown in Fig. 3(b). In this fit the S_{II} contribution was about 15%. Recall that although γ_1, γ_2 , and ν_{osc} were allowed to vary, they were *identical* for all probe frequencies. We conclude that the model is in reasonable agreement with the experiment.

The fit results for three probes in two solvents are collected in Table I. The frequency ν_{osc} varies with the probe by 20%. Besides, it markedly depends on solvent polarity for penta- and tetrafluorobenzene, while for hexafluorobenzene its change is within the experimental error. A reason for this different behavior could be that ν_{osc} is affected by at least two contributions which may compensate each other. These are the detuning $E_1 - E_2$ (set to zero) and the bar electronic coupling $V_{ee'}$. At present, however, we cannot measure or calculate these quantities, leaving this problem for future work.

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- [18] Assume $\nu_{\text{vib}} = 100 \text{ cm}^{-1}$ both for \mathbf{e} and \mathbf{e}' , $\Delta Q_{ee'} = 5$, $V_{ee'} = 300 \text{ cm}^{-1}$, $E_1 - E_3 = 1000 \text{ cm}^{-1}$. Then 2 is the tenth vibrational level of \mathbf{e}' , $f_{12} = 0.1$, $V_{12} = 100 \text{ cm}^{-1}$, $f_{13} = 5 \times 10^{-5}$, $V_{13} \ll V_{12}$.