DOI: 10.1002/anie.201301931

Femtochemistry

# Ultrafast Solvent-Assisted Electronic Level Crossing in 1-Naphthol**

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Nonadiabatic electronic transitions between potential energy surfaces play a dominant role in many photoinduced chemical reactions,[1–3] such as charge transfer,[1a–c] branching pathways in dissociation,[2] and cis/trans isomerizations.[3] Furthermore, nonadiabatic internal conversion (IC) to the ground state ($S_0$) is believed to protect photoexcited natural chromophores (e.g. nucleic acid bases of DNA.[4]) against UV radiation damage. The theoretical description of nonadiabatic level crossing (LC) dynamics is a highly active field of research for both gas phase and condensed phase molecular systems.[5] Importantly, in the condensed phase the solvent often provides more than just a heat bath for the reactive system, as it can strongly affect the outcome of different reaction products. Herein, we report the experimental observation of LC occurring in 60 fs between the two lowest electronic excited singlet states ($^1L_a$ and $^1L_b$) of 1-naphthol (1N).

Like other aromatic molecules such as benzene, naphthalene, or indole, the $^1L_a$ and $^1L_b$ electronic states of 1N have transition dipole moments (TDM) in the plane of the aromatic ring, pointing almost along the short ($^1L_a$) and long ($^1L_b$) molecular axes (Figure 1).[6] The energies of the two states depend on the nature of the aromatic structure and on the position of functional side groups, while their lifetimes depend on their energetic order. In line with Kasha's rule (i.e., fluorescence emission occurs only from the lowest-lying excited $S_1$ state), IC from the higher lying $S_2$ state must occur on ultrafast time scales (e.g., < 40 fs as shown for $^1L_a$-to-$^1L_b$ IC in 5-methoxyindole).[7] However, for some aromatic systems, a solvent-dependent fluorescence emission has been interpreted to arise from an inversion of the energetic order of the $^1L_a$ and $^1L_b$ states with increasing solvent polarity.[8,9] Here, we address the IC and LC mechanisms in 1N with ultrafast time resolution.

1N is a prototypical case for which the $^1L_a$ state is more polar than the $^1L_b$ state (Figure 1). In the gas phase, or in

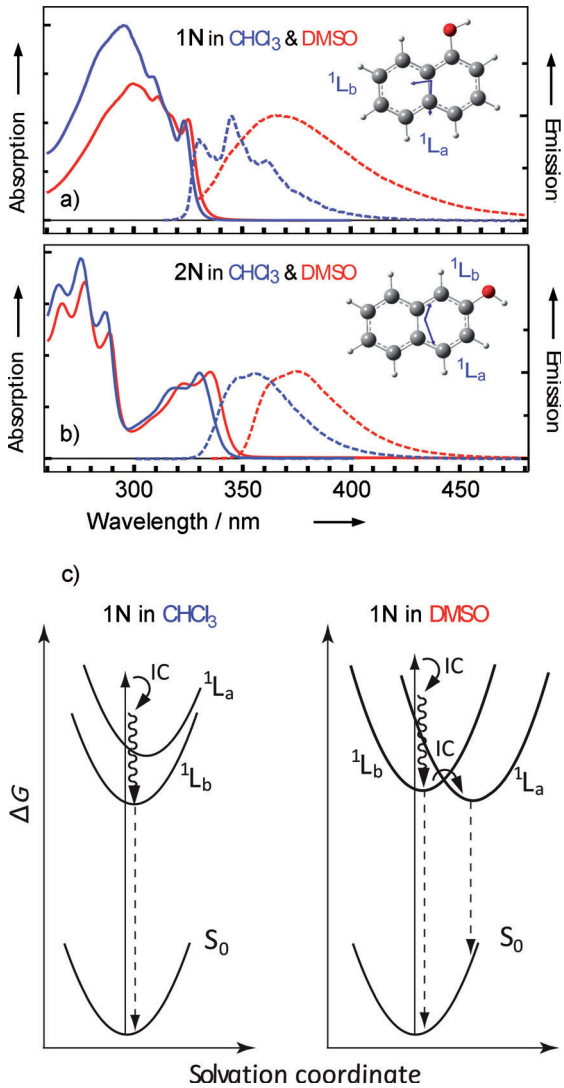


*Figure 1.* Normalized static optical absorption (solid lines) and emission (dashed lines) of: a) 1N and b) 2N. Insets: Molecular structures and transition dipole moments (blue arrows) of the $^1L_a$ and $^1L_b$ transitions of 1N and 2N, predicted by TDDFT for the molecules in gas phase. c) Scheme of the dynamics of 1N after photoexcitation.

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[**] This work was supported by the German Science Foundation (ETJN; DFG NI 492/11.1), the U.S. National Science Foundation (Grant CHE 0911520 to V.S.B.), and partly by the NCCR-MUST of the Swiss National Science Foundation. M.C. is grateful to the Humboldt Foundation for support during his sabbatical at the MBI-Berlin. The authors acknowledge stimulating discussions with Prof. Ehud Pines. DMSO = dimethyl sulfoxide.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201301931.


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nonpolar/weakly polar solvents like $CHCl_3$, the $^1L_a$ state is higher than the $^1L_b$ state and only $^1L_b$-state emission is observed.[9] However, in polar solvents like dimethyl sulfoxide (DMSO), or alcohols and water, a red-shifted and broad fluorescence is ascribed to $^1L_a$-state emission. This inversion is currently explained as an effect of differential solvation of the two states during the lifetime of the excited state.[9] Figure 1 compares the optical absorption (OA) and emission spectra of 1N (panel a) to the corresponding spectra of 2-naphthol (2N; panel b) for which the emitting state is $^1L_b$ both in $CHCl_3$ and in DMSO.

The acidity of hydroxyarenes, and other molecules containing a weak Brønsted acidic group, can be up to several orders of magnitude higher in the electronic excited state compared to the ground state. This general property is called photoacidity and is typically sensitive to the position of substitutional groups in the ring. For example, 1N has a thousand-fold higher photoacidity than 2N, even though both photoacids have similar $pK_a$ values in the ground state, a behavior attributed to dynamical level inversion in 1N.[10] In addition, photoacidity is sensitive to the solvent environment. For instance, the excited-state proton transfer (ESPT) of naphthol molecules in aqueous solution proceeds with characteristic time constants of 35 ps for 1N, and 10 ns for 2N. On the other hand, no quantifiable ESPT reaction occurs within their excited-state lifetimes for either photoacid in DMSO. Thus, level inversion of 1N can be studied in DMSO without interference from ESPT during the ensuing early dynamics after photoexcitation. Although the 1N level inversion hypothesis has long been suggested,[9b,c] no study has yet resolved the nature or timescale of the dynamics. We find that the characteristic LC time for 1N in DMSO is 60 fs, as probed by polarization-resolved femtosecond fluorescence. The observed solvent-dependent anisotropy values are compared to ab initio time-dependent density functional theory (TDDFT) calculations, from which we draw conclusions about the occurrence of electronic mixing of the $^1L_a$ and $^1L_b$ states. We use ultrafast infrared (IR) spectroscopy to conclusively show that LC is complete within 200 fs in DMSO, while the subsequent dynamics only arises from solvent rearrangements. We propose that the vibrational mode, effectively coupling the $^1L_a$ and $^1L_b$ states, is related to motions of the hydrogen bond between 1N and DMSO.

Excitation at 290 nm of 1N and 2N dissolved in DMSO gives rise to fluorescence in the 330–450 nm range within the time resolution of the instrument (Figure 2). Further, 1N exhibits a Stokes shift of $900 \pm 50\ cm^{-1}$ occurring with an exponential time constant of $\tau_S = 2.5 \pm 0.3$ ps, in agreement with the value of 2.3 ps previously found for solvation in DMSO.[12] In contrast, the time-dependent emission of 2N does not show any spectral evolution. In principle, the emission from the $^1L_a$ state is expected to exhibit a much more significant Stokes shift than the emission from the comparatively apolar $^1L_b$ state. In this sense, the small Stokes shift observed in 2N agrees with a predominantly emission from the $^1L_b$ state of 2N. In contrast, the large Stokes shift of 1N suggests significant $^1L_a$ character for the 1N emission even at early ($\ll \tau_S$) times.

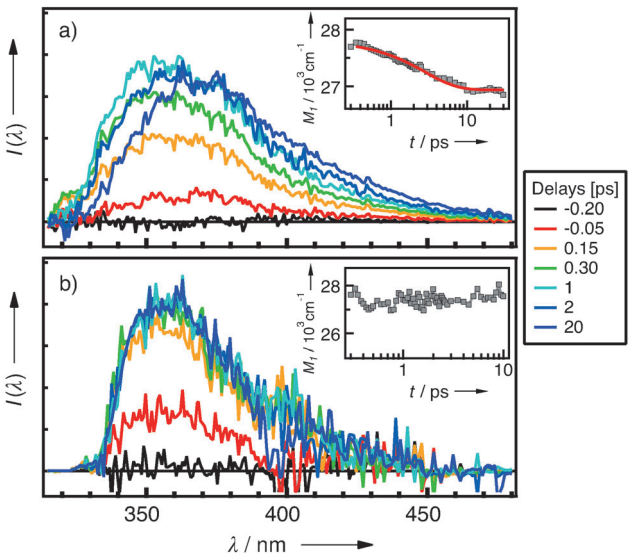


***Figure 2.*** Ultrafast polychromatic fluorescence spectra of a) 1N and b) 2N in DMSO, after photoexcitation at 290 nm. Insets: first moment ($M_1$) of the emission band and best fit (for 1N) with an appropriate expression representing exponential dynamics convoluted with the instrument response function.[11]

We measured the ultrafast fluorescence anisotropy, $r(t)$, of 1N and 2N to elucidate the early dynamics of the electronic states. The anisotropy is related to the angle, $\phi(t)$, between the absorption and emission TDMs, as follows: $r = 0.2\,(3\cos^2\phi - 1)$.[13] Ultrafast polarized transient absorption[14] and fluorescence[7,11] are sensitive probes of the non-adiabatic dynamics, because of their sensitivity to the orientation of the TDMs. Anisotropy was measured in single-wavelength detection mode (at the peak of the respective emission bands), allowing for better (140 fs) time resolution than in the polychromatic fluorescence measurements (250 fs) already shown in Figure 2. Excitation was carried out at 266 nm, which populates only the $^1L_a$ state in the Franck–Condon region for both 1N and 2N.[9c,d] Thus, before the onset of dynamics, $r(t)$ should be 0.4 as for any electronically non-degenerate molecule.[13] Because of their near perpendicular TDMs, a pronounced time dependence of $r(t)$ is expected upon IC from the $^1L_b$ to the $^1L_a$ state. From our measurements (Figure 3a) it is clear that within our time resolution an anisotropy value well below 0.4 is reached for 2N in DMSO and 1N in $CHCl_3$ (both expected to emit from the $^1L_b$ state), which remains constant for 0.6 ps. This means that IC from $^1L_a$ to $^1L_b$ is faster than what can be measured after applying a deconvolution procedure to the data (< 40 fs). As a matter of fact, the complete lack of dynamics suggests IC to be significantly faster than this limit, that is, to be practically instantaneous on the time scale of the experiment as also observed in Ref. [11]. The angle $\phi$ between the initially excited $^1L_a$ state and the emitting state, has a well-resolved value (i.e., $\phi_{2N\text{-}DMSO} = 49 \pm 2°$ and $\varphi_{1NgtingtCHCl_3} = 52 \pm 2°$).

In DMSO, in contrast to 2N, 1N exhibits a time-dependent anisotropy. Within our time resolution, $r(t)$ has a value of $-0.05$, followed by an exponential increase to 0.08 with a $60 \pm 10$ fs time constant. These values of $r(t)$ correspond to a time-

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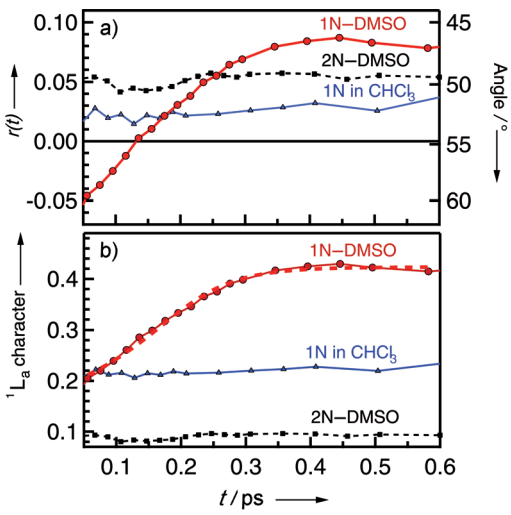


*Figure 3.* a) Fluorescence anisotropy measured in 1N (solid lines) and 2N (dashed line) after photoexcitation, and corresponding angle between absorption and emission transition dipole moments. b) $^1L_a$ character of the emission, $\rho(t)$ (see the Supporting Information), calculated from the data in panel (a). Data of 1N in DMSO are fitted (dashed red line) as described in the Supporting Information. The fit estimates the increase of $r(t)$ to occur with a $60 \pm 10$ fs time constant.

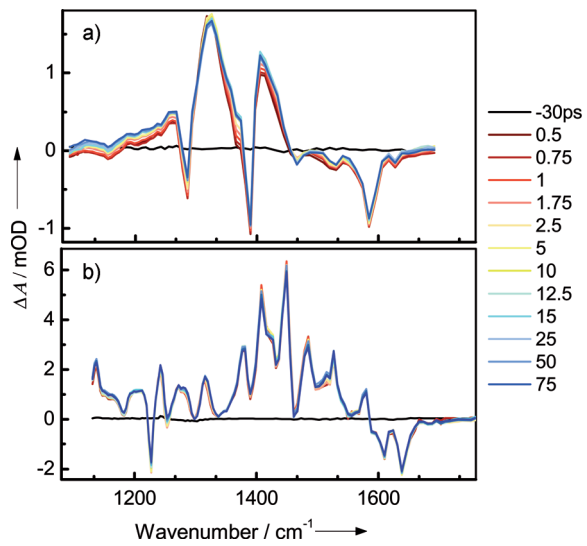


*Figure 4.* Transient IR measurements in the mid-IR spectral region of a) 1N and b) 2N in [D$_6$]DMSO measured after photoexcitation. The vertical axis represents the differential absorption in milliOD (mOD), where OD stands for optical density.

dependent angle, $\phi_{1N\text{-}DMSO}(t)$, changing from $60 \pm 2°$ at $t = 0$ to $47 \pm 2°$ at $t > 250$ fs. This important result shows that for 1N in DMSO the electronic excited-state dynamics is much more involved. Neither relaxation within the $^1L_a$ state with intramolecular vibrational redistribution and concomitant solvent rearrangement, nor a single IC from $^1L_a$ to $^1L_b$ can fully explain the observed behavior of the fluorescence anisotropy. Instead, multiple electronic LC dynamics must occur for 1N in DMSO. Since rotational diffusion strongly affects the absolute value of $r(t)$ at $t > 2$ ps (see Figure S1 in the Supporting Information), one must analyze whether the level dynamics is complete in the first hundreds of femtoseconds (as suggested by Figure 3) or if additional slower dynamics occur. To address this question, we used ultrafast IR measurements where electronic state crossings translate into changes of vibrational mode patterns.[15] Figure 4 shows that for both 1N and 2N in DMSO no significant dynamics of IR-active fingerprint patterns can be observed between 200 fs (time resolution in the transient IR experiments) and 1.3 ns. We conclude that no significant LC dynamics occur on picosecond time scales. This also agrees with the rigid shift of the emission band of 1N in DMSO with no accompanying shape changes (Figure 2a).

We calculated the absorption ($S_0 \rightarrow {}^1L_a$) TDM of 1N and 2N in the optimized $S_0$ molecular geometries at the TDDFT/B3LYP level, and the two emission TDMs, $^1L_a \rightarrow S_0$ and $^1L_b \rightarrow S_0$, in the $^1L_a$ and $^1L_b$ geometries, respectively. The calculations identify four (three) stable conformers (Figures S5–S6) of the 2N–DMSO (1N-DMSO) complex in DMSO solution, whereas uncomplexed 1N in $CHCl_3$ only exists in cis and trans form. Using an appropriate ensemble-averaging procedure accounting for the co-existence of these conformers, we calculated the distinctive anisotropy values $r_A$ and $r_B$ for pure $^1L_a$ and pure $^1L_b$ emission and the corresponding absorption–emission angles $\phi_A$ and $\phi_B$ (Table S4). These independent estimates can be compared to the experimental data allowing for an accurate interpretation of the results. Since the predicted angles $\phi_A$ are always close to zero, it is possible to confirm that the initial experimental values $r(t=0)$ well below 0.4 do not arise from structural relaxation in the excited $^1L_a$ state within the time scale of the pulse overlap.

For the 2N–DMSO complex, the experimental angle $\phi = 49°$ is fairly close to the calculated value of $\phi_B = 60.4°$ (whereas $\phi_A = 3.9°$). Thus, the emission is essentially of $^1L_b$-type character, already within time resolution. Such a fast IC from $^1L_a$ to $^1L_b$ is in line with the 30 fs time constant measured for gas-phase naphthalene,[16] and similar to IC rates observed for solution-phase 5-methoxyindole,[7] tryptophan, and also polypyridine metal complexes.[11b] Although the small deviation between $\phi$ and $\phi_B$ might be interpreted as an estimate of the uncertainty inherent to the calculation, we observe this effect to become more marked for 1N in $CHCl_3$, where TDDFT predicts $\phi_B = 84.6°$ (and $\phi_A = 3.1°$), against a measured value of $\phi = 52°$. Hence we infer that an ultrafast IC from $^1L_a$ to $^1L_b$ occurs also for 1N in $CHCl_3$, yet the emission is not strictly of $^1L_b$-type character. Instead, the influence of the energetically close $^1L_a$ state translates into a mixed nature of the fluorescence. To quantify this, one can estimate the $^1L_a$ type character of the emission $\rho(t)$ (with $0 < \rho(t) < 1$), by relating (see the Supporting Information) the experimental anisotropy with the two limiting values $r(\phi_A)$ and $r(\phi_B)$ predicted for pure emissions from the $^1L_a$ and $^1L_b$ states. Thus, we derive (Figure 3b) that the emission of 1N features a small, but appreciable ($\approx 22\,\%$) value of $\rho$ in $CHCl_3$. This effect is minor in 2N ($\approx 9\,\%$) where the energy separation of $^1L_a$ and $^1L_b$ is large enough for the two states to remain well apart even in very polar DMSO (see Figure 1). Finally, with the calculated angles of $\phi_B = 77.6°$ and $\phi_A = 2.2°$, the observed anisotropy of the 1N–DMSO complex implies that $\rho$ is initially close to what was found for 1N in $CHCl_3$, but it then

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rises to a value of about 43 % with a 60 fs time constant. This increase in $^1L_a$ character of the 1N fluorescence with increasing solvent polarity has been concluded in previous studies based on steady-state optical spectroscopy.[9b,c] Here, we provide for the first time a direct determination of the time-scale on which this occurs in DMSO.

The quantity $\rho(t)$ is the fraction of 1N molecules in the $^1L_a$ state, estimated within a population equilibration scenario where the nature of the $^1L_a$ and $^1L_b$ states is assumed to be unchanged. However, the increasing $^1L_a$ character of the emission might alternatively be described as a solvent-dependent electronic state mixing, or a combination of the two effects. At least two arguments point to significant quantum-mechanical mixing between the $^1L_a$ and $^1L_b$ states (as defined for gas-phase 1N) when going to polar media such as DMSO: 1) The anisotropy is almost the same throughout the emission band (Figure S2), at least at long times. 2) In a pure population equilibration scenario, the solvation dynamics we found occurring with a 2.5 ps time constant (Figure 2) should result in a further increase of $^1L_a$ population as its energy decreases further below that of the $^1L_b$ state by solvation. In contrast, LC is completed within 250 fs and $\rho$ never exceeds 0.5. For these reasons, we can discount a pure crossing scenario, and significant state mixing is inferred. Regardless of the actual degree of mixing, we emphasize that our results demonstrate the sequential $^1L_a \rightarrow {}^1L_b \rightarrow {}^1L_a$ dynamics proposed in Ref. [9a–e] after IC from $^1L_a$ (Franck–Condon) to $^1L_b$ within time resolution, 1N-DMSO undergoes a delayed second electronic LC from the weakly polar $^1L_b$ state to the emissive state assigned as the polar $^1L_a$ state equilibrated by the solvent shell (Figure 1 c).

The observed LC of the 1N–DMSO complex with a $\tau_{LC} =$ 60 fs time constant is clearly faster than the shortest time component of nonspecific solvation dynamics reported for DMSO ($\approx 0.2$ ps[12,17]). However, the value of $\tau_{LC}$ is typical of reported hydrogen bond readjustment/cleavage processes,[18] or intramolecular hydrogen transfer.[19] For instance, the photoinduced rearrangement of the hydrogen bond linking a strong photoacid to DMSO was found to occur in 55 fs.[17] Therefore, we argue that LC is controlled by the photo-triggered local readjustment of the hydrogen bond donated by 1N to DMSO. Such a readjustment along the hydrogen bond coordinate tunes the relative energy of the two states until their ordering is reversed and level inversion occurs. Once the levels become degenerate, or nearly so, nonadiabatic couplings induce a certain degree of mixing between the two unperturbed electronic states. The role of hydrogen bonding is strongly supported by our IR data. Indeed, a close inspection of the steady-state IR-active fingerprint pattern reveals that a particular transition located around 1280 $cm^{-1}$ can be assigned (see the Supporting Information) to a mode with C–O stretching character, the frequency up-shift of which can be correlated with the frequency downshift of the O–H stretching mode with increasing hydrogen bond strength. Upon electronic excitation of different hydrogen-bonded complexes of 1N, this mode exhibits a frequency increase (Figure S3), which reflects an increase in strength of the hydrogen bond from the ground to the excited state and also, most important, from the $^1L_b$ to the $^1L_a$ state. This is fully in line with the traditional photoacidity ansatz, whereby photoexcitation results in a partial charge transfer from the O–H group into the ring, strongly enhanced upon level inversion. Indeed, this mechanism weakens the O–H bond linking the proton to the parent molecule, to the advantage of the bond between the proton and the solvent. In water, these effects are expected to be even stronger and eventually cause a full proton transfer to the solvent, that is, the photoacidity of 1N.

In summary, we have presented an ultrafast spectroscopic study of the electronic excited-state dynamics of 1-naphthol (1N), as a prototype system undergoing nonadiabatic transitions with level inversion induced by solvation in a polar medium. We have determined the nature and the time scale of the relaxation dynamics, providing compelling arguments for a solvent-assisted nonadiabatic coupling between the electronic states through a vibrational mode of the hydrogen-bonded 1N–DMSO complex. Since LC of the photoacid 1N is complete within 250 fs, whereas the fluorescence continues to undergo a large Stokes shift on a picosecond time scale because of solvation, we infer a substantial state mixing between the first two excited states. These findings may shed light on the excited-state dynamics common to molecules with two close-lying excited states, and on the excited-state dynamics of other photoacids.[20] Moreover our results should stimulate further studies based on quantum dynamical simulations of these ultrafast nonadiabatic solvent-assisted crossing mechanisms of electronic states.[5]

Received: March 7, 2013
Published online: June 12, 2013

**Keywords:** femtochemistry · kinetics · naphthol · photoacids · ultrafast dynamics

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