

LETTERS

The Impact of a Solvent and a Methyl Rotor on Timescales of Intramolecular Vibrational Energy Redistribution in Aromatic Molecules

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Selectively excited benzene and toluene in the gas and solution phase have been investigated with ultrafast transient absorption spectroscopy to study the impact of a solvent on the time scales of intramolecular vibrational energy redistribution (IVR). It has been found that multiple time scales exist for isolated benzene (toluene) in agreement with theory. A comparison of gas-phase and solution experiments revealed the effect and magnitude of solvent assisted IVR. Although the ultrafast IVR component is hardly influenced by the solvent, the picosecond time scale of IVR appears to be contracted in solution with respect to the gas phase due to interactions (collisions) with the solvent and an overall acceleration of slower IVR components. In addition, we find that an internal rotor (i.e., a methyl group on an aromatic ring) accelerates IVR in the gas phase significantly whereas the effect appears to be largely concealed in solution.

1. Introduction

The flow of vibrational energy within a polyatomic molecule is a fundamental process that underlies chemical reactivity.¹ In the past decade intramolecular vibrational energy redistribution in isolated molecules has been investigated experimentally in the time and frequency domain as well as theoretically with some success.^{2–5} Because most of the chemically relevant reactions happen in solution, it would be desirable to also have a good understanding of IVR in solution. Many successful experimental approaches to measure vibrational energy transfer of molecules in liquids have been reported.^{5–9} Unfortunately, generalizable mechanisms and principles, such as known for isolated molecules, have not been clearly identified yet. Moreover, it has not even been identified how and to what extent

the solvent influences the intramolecular process that we call IVR for isolated molecules. The reason for this lack of knowledge is that IVR for a particular molecule could not be measured in the gas phase *and* in solution (with the same technique) yet. As a consequence, it was nearly impossible to correlate time scales of isolated and solvated molecules and to obtain a quantitative understanding of IVR and its underlying mechanisms in solution. Also the impact of chemical substitution on IVR remained largely unclear in solution. It is not by chance that benzene and toluene in the gas phase have become the benchmark systems for experimental¹⁰ and theoretical IVR studies^{11,12} during the past two decades (for a good overview, see ref 10 and literature cited therein).

Recently, we have measured intramolecular in competition to intermolecular relaxation in solution for a large number of molecules of different size and structure.^{1,13–17} In the present communication we want to address two topics that have been

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identified to be crucial in a quantitative understanding of IVR in solution. First, we demonstrate here that intramolecular vibrational energy redistribution for a particular molecule (i.e., benzene and toluene as an illustrative example) both in the gas phase and in solution can be measured with the same technique, namely, ultrafast pump–probe transient absorption spectroscopy. In these experiments the impact of the solvent on intramolecular vibrational energy redistribution should be clearly seen and a correlation of time scales in the gas and solution phase should be possible. Second, we address the hitherto unresolved question, how does chemical substitution, in particular, an additional methyl rotor on an aromatic ring, affect IVR (in the electronic ground state) in isolated molecules and in solution?^{17,18}

2. Experimental Section

Details of our experimental approach, which is similar to the technique recently introduced by Crim et al.,^{19,20} have been published elsewhere.^{14–17} The main feature of the approach is that the initially excited nonstationary “states” in the two quanta region of the C–H stretch vibration are Franck–Condon (FC) inactive, but as energy redistributes in the molecule, the population of isoenergetic (zeroth-order) combination vibrations having quanta in the FC-active modes causes an increase in the absorption at the long wavelength wing of the electronic absorption spectrum. The limited number of FC-active modes of the molecules can be identified by resonance Raman and dispersed fluorescence experiments.^{17,21,22} Subsequent intermolecular vibrational energy transfer (VET) to the surrounding solvent decreases the absorption again. As described in previous reports, absorptions can be converted into internal energy of the molecules via high-temperature absorption spectra.¹⁷

The Ti:sapphire laser system (Coherent/Clark) pumping two optical parametric amplifiers (TOPAS, Light Conversion), and a home build noncollinear optical parametric amplifier) with pulse widths of about 50 fs and a bandwidth of $\sim 300\text{ cm}^{-1}$ and most of the experimental setup is the same as that used in similar, earlier experiments.¹⁷ It should be noted that the actual time resolution (cross correlation of pump and probe pulses) in the experiments reported here is much poorer than the 50 fs pulse length (i.e., 500 ± 200 fs) due to the broadening of the laser pulses in time as they pass through a medium (cell windows, gas, liquid). The excitation and delayed probe pulses are focused ($f = 200$ mm) and overlapped in the sample cell. Gas-phase experiments were performed in a stainless steel cell equipped with quartz windows (2 mm) with an optical path length of 20 mm. The temperature of the cell was controlled by electrical heating elements and a thermocouple. The pressure for the gas-phase measurements was controlled with a pressure gauge attached to the cell. For the liquid-phase experiments performed in a quartz flow cell with a path length of 0.2 mm the concentrations of benzene and toluene in $\text{CF}_2\text{ClCCl}_2\text{F}$ solution was 1 mol/L. Transient difference absorptions were measured at 1 kHz for a particular time delay until an acceptable signal-to-noise level was reached (~ 8000 shots).

3. Results and Discussion

In the present experiments we excited both molecules, i.e., benzene and toluene, in the two quanta region of the CH-stretch vibration with a short femtosecond (fs) laser pulse centered at $1.7\ \mu\text{m}$. The recorded transient absorption profiles show a characteristic rise that we interpret as IVR and a subsequent slower decay on a picosecond (ps) time scale that we attribute to intermolecular vibrational energy transfer (VET). The assignment of the two processes is discussed in detail in refs 14

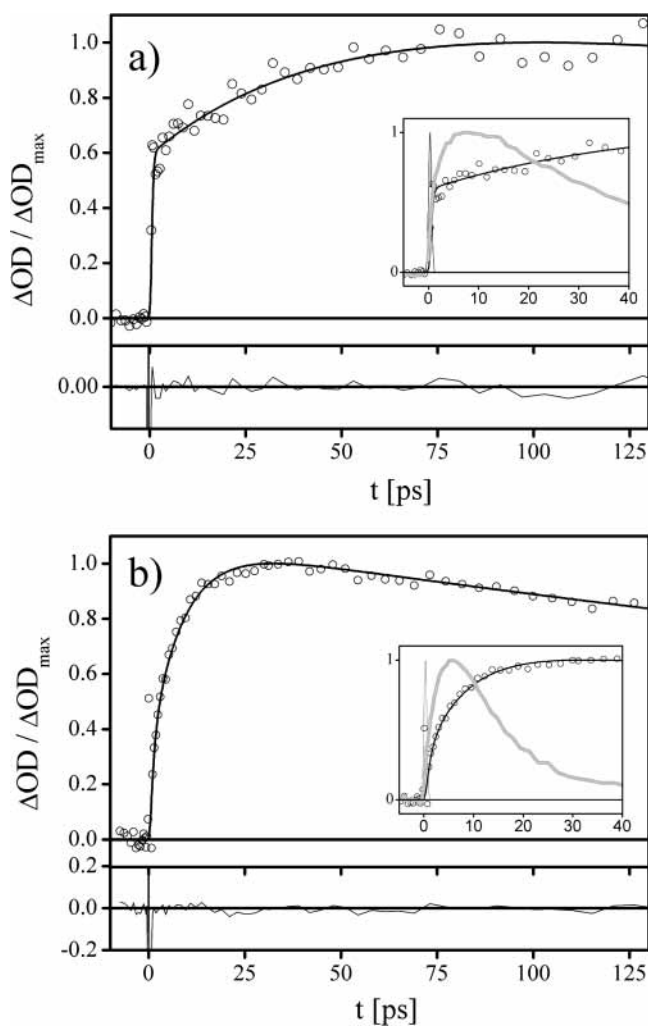


Figure 1. (a) Normalized transient absorption time profiles for benzene (○) in the gas phase (4 bar, $T = 408$) for $\lambda_{\text{pump}} = 1670$ nm and $\lambda_{\text{probe}} = 275$ nm. Also shown is a fit using the model described in the text (—). (b) Normalized transient absorption time profiles for toluene (○) in the gas phase (4 bar, $T = 421$ K) for $\lambda_{\text{pump}} = 1678$ nm and $\lambda_{\text{probe}} = 280$ nm. Also shown is a fit using the model described in the text (—). Residuals show the quality of the fits. The insets display the traces on a shorter time scale (○), the cross correlation (—) of the experiment and the comparison with the solution experiment in Figure 3 (gray line).

and 15. In previous reports from our lab we have explained how transient absorption profiles can be converted into energy profiles.¹⁷ Therefore, the measured absorption of a near UV-laser pulse following the excitation pulse is an observable for the time dependent energy content in the Franck–Condon (FC) active modes and for the redistributed energy in the molecule.^{14,15} The experimental traces for benzene in the gas phase ($p = 4$ bar, $T = 408$ K) are displayed in Figure 1a. Interestingly, a fast rise approximately within the time resolution of the experiment ($\tau_{\text{IVR}}^{(1)}$) and a slower rise on a 100 ps time scale ($\tau_{\text{IVR}}^{(2)}$) followed by a very slow decay (τ_{VET}) on a nanosecond (ns) time scale was observed. For many experiments in solution a simple model with two sequential first-order steps described by single-exponential expressions for the rise and the decay was sufficient for a quantitative understanding of the time profiles.¹ However, if several FC-active modes in differently fast populated tiers are probed such as displayed in Figure 2, the traces cannot be modeled with the simple ansatz described in ref 17. Such a situation is obviously encountered for benzene in Figure 1a. To process the observed time profiles and to determine the

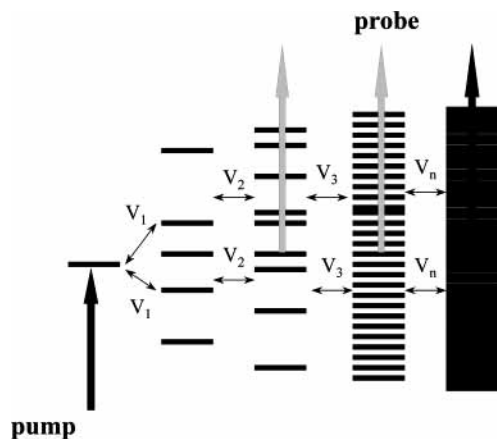


Figure 2. Pump and probe scheme within a tiers picture (schematic). The zeroth-order bright state, which is not Franck–Condon (FC) active in the electronic transition is excited via the near-IR laser pulse (V_i represents matrix elements between zeroth-order states). FC-active modes in later tiers having no population at $t = 0$ are probed, and their time dependent population is a measure for IVR in the molecule giving rise to an enhancement of the electronic absorption.

TABLE 1: Parameters of Eq 1 Used in the Model To Fit the Experimental Traces (See the Text for Details)

	$\tau_{\text{IVR}}^{(2)}$ (ps)	$\tau_{\text{IVR}}^{(1)}$ (ps)	τ_{VET} (ps)	A_{inst}
	Gas Phase			
benzene	50 ± 7	≤ 0.5	570 ± 90^a	0.52 ± 0.05
toluene	8.7 ± 0.9	≤ 0.8	500 ± 80^a	0.25 ± 0.05
	Solution ^b			
benzene	3.8 ± 0.8	≤ 0.5	55 ± 5	0.49 ± 0.06
toluene	4.7 ± 0.8	≤ 0.8	12 ± 2	0.22 ± 0.06

^a τ_{VET} calculated from energy transfer data in the gas phase (self-collisions) given by Toselli et al.²³ ^b Benzene and toluene in 1 M 1,1,2-trichlorotrifluoroethane solution ($\text{CF}_2\text{ClCCl}_2\text{F}$).

time constants for the different IVR and VET processes, the functional form of eq 1 was used (within the simple model outlined above).

$$S(t) \propto \exp\left(-\frac{t}{\tau_{\text{VET}}}\right) - \left[A_{\text{inst}} \exp\left(-\frac{t}{\tau_{\text{IVR}}^{(1)}}\right) + (1 - A_{\text{inst}}) \exp\left(-\frac{t}{\tau_{\text{IVR}}^{(2)}}\right) \right] \quad (1)$$

It implies two different IVR processes superimposed on each other (see Figure 2) and a subsequent slower VET process, all probed in the experiment. For a realistic comparison of experimental and modeled traces the simulation was convoluted with the cross correlation function of pump and probe pulses. It is displayed in the inset of Figure 1a. Good agreement between experiment and model was obtained when $\tau_{\text{IVR}}^{(1)} \leq 0.5$ ps, which was close to the time resolution (cross correlation function) of the experiment. The remaining parameters in this refined model are $\tau_{\text{IVR}}^{(2)}$, τ_{VET} , and the relative amplitudes, A_{inst} and $(1 - A_{\text{inst}})$, being correlated with the relative contributions of the IVR rate coefficients. All parameters are given in Table 1. The time constant for VET in the gas phase, τ_{VET} , was calculated from the gas-phase energy transfer data for benzene–benzene and toluene–toluene collisions reported by Barker and co-workers.²³ This procedure enabled us to obtain (fit) $\tau_{\text{IVR}}^{(2)}$ and A_{inst} with good accuracy.

In Figure 3a an experiment is shown in which benzene has been measured in $\text{CF}_2\text{Cl}-\text{CFCl}_2$ solution. This experiment is compared with the gas-phase result in the inset of Figure 1a.

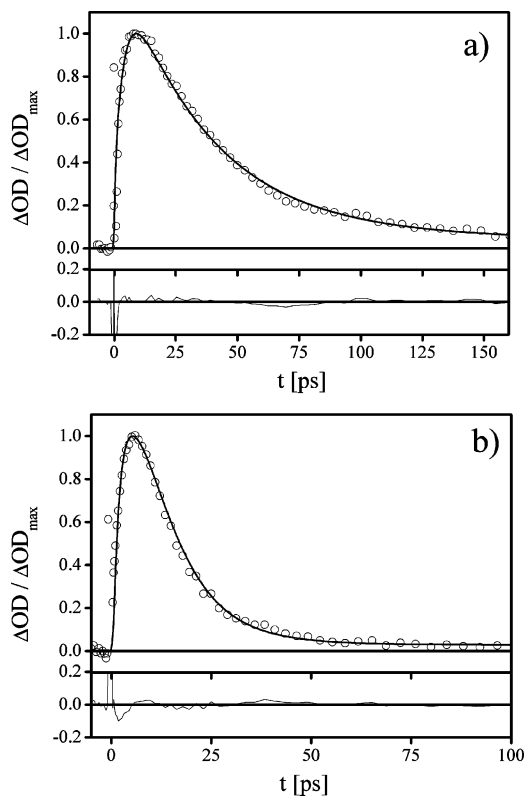


Figure 3. (a) Normalized transient absorption time profiles for benzene (O) in $\text{CF}_2\text{Cl}-\text{CFCl}_2$ solution for $\lambda_{\text{pump}} = 1670$ nm and $\lambda_{\text{probe}} = 275$ nm ($T = 295$ K). Also shown is a fit using the model described in the text (—). (b) Normalized transient absorption time profiles for toluene (O) in $\text{CF}_2\text{Cl}-\text{CFCl}_2$ solution for $\lambda_{\text{pump}} = 1678$ nm and $\lambda_{\text{probe}} = 280$ nm ($T = 295$ K). The solid line is a fit using the model described in the text. Residuals show the quality of the fits.

For the determination of the kinetic parameters the same model has been used as described above but now τ_{VET} was fitted. Again a good fit is obtained for $\tau_{\text{IVR}}^{(1)} \leq 0.5$ ps being close to the time resolution of the experiment. The obtained parameters have also been summarized in Table 1. The residues in Figures 1a and 3a leave little uncertainty in the determination of the IVR parameters. These data imply that, in the case of benzene in the gas phase, IVR dynamics proceeds on at least two distinct time scales, i.e., one on a subpicosecond and one on a much longer time scale. The similarity of parameters A_{inst} and $\tau_{\text{IVR}}^{(1)}$ for the gas- and liquid-phase experiments suggests that the ultrafast time scale is probably not influenced significantly by the solvent.

From an analysis of the eigenstate resolved frequency domain spectra of benzene in the first C–H stretching overtone region it is expected that the IVR process in the isolated benzene molecule consists of at least two phases.¹⁰ In the first step (≈ 100 – 200 fs), the initial excitation is rapidly redistributed among a first tier of states that is observable in the spectrum observed by Page and co-workers.²⁴ Then, in a second, slower step (≥ 10 – 20 ps), further redistribution occurs into a larger bath of available states being responsible for the line widths and the time scales observed by Nicholson and Lawrance²⁵ and others.¹⁰ In fact, in our direct time domain experiments, we observe an ultrafast time scale and a slower one with an overall effective time constant of $\tau_{\text{IVR}}^{(2)} = 50 \pm 7$ ps, which is somewhat larger than reported from studies in the frequency domain.¹⁰ It should be noted, however, that $\tau_{\text{IVR}}^{(2)}$ in the present case may be an average of more than one time constant, and that the data in refs 10 and 25 are likely only sensitive to the

intermediate time scales or provide lower bounds for $\tau_{\text{IVR}}^{(2)}$. Also the temperature in both types of experiments is somewhat different.

Wyatt et al.^{26,27} have calculated IVR in 30-mode benzene and projected the energy flow in time onto the normal modes. Their analysis is actually in good agreement with our picture, assumptions, and the observed time scales. Because we assume^{17,21,22} that we observe combination modes of the E_{2g} FC-active mode at 608 cm^{-1} and likely also the A_{1g} mode at 994 cm^{-1} (possibly as a superposition) the agreement between theory and experiment can be regarded to be quite satisfactory.

A comparison of gas-phase and solution experiments in the case of benzene unambiguously reveals the existence, the effect, and the magnitude of solvent assisted IVR. Although the ultrafast IVR component seems to be unaffected by the solvent, the picosecond time scale of IVR is shorter in solution and appears to be contracted with respect to the gas phase, which is likely caused by the interactions (collisions) with the solvent and an overall acceleration of slower IVR components. This effect is also seen clearly in our recent experiments in supercritical CO_2 .²⁸ That appears to be the reason the traces for experiments in solution could be modeled with one effective (average) exponential for the IVR in earlier studies¹⁷ and why the visible impact of chemical substitution on the rates of IVR in solution is only moderate. In the latter case the effect may be simply concealed in solution even if it is pronounced for isolated molecules.

For the case of toluene experiments in the gas phase and in $\text{CF}_2\text{Cl}-\text{CFCl}_2$ are displayed in Figures 1b and 3b. In the inset of Figure 1b the gas-phase signal is shown on a shorter time scale together with the solution experiment and the cross correlation function of pump and probe pulses. The time-resolved traces have been modeled as in the case of benzene, and the obtained parameters are also summarized in Table 1. For toluene the initial fast rise is less pronounced (A_{inst} is smaller in general in comparison with benzene; see Table 1). This is likely a consequence of the different FC-factors of the different FC-active modes involved, which also may depend somewhat upon the probe wavelength. $\tau_{\text{IVR}}^{(1)}$ in the gas phase and in solution was again found to be close to the cross correlation function of the experiment. Due to the rather similar values for A_{inst} (and $\tau_{\text{IVR}}^{(1)}$) in both experiments, we conclude that also for toluene the ultrafast IVR time scale is hardly influenced by the solvent. The secondary time scale, however, is again significantly “squeezed” in solution with respect to the gas phase, which is the reason the rise of the signal attributable to IVR in solution looks like a single exponential.

Beyond the changes of the dynamics going from gas phase to solution for both molecules it is very exciting to see a change of the time scale for secondary IVR when benzene and toluene are compared in the gas phase (Figure 1). Interestingly, such an effect cannot be clearly identified in solution (Figure 3), possibly due to the shortened picosecond IVR time scale in general. For the slower IVR component in the gas phase we observe a significant acceleration by a factor of roughly 5–6 (see Table 1), which appears to be a direct consequence of the additional internal rotor at the aromatic ring. As was first shown by Parmenter and co-workers,¹⁸ the interaction of this degree of freedom with the vibrational motions of the ring can induce rapid intramolecular vibrational energy redistribution. Moss et al. have proposed that this effect has its origin in the van der Waals interactions between the methyl hydrogen atoms and the carbon and hydrogen atoms of the ring—interactions that may be modulated by the relative motion of the two groups.^{29,30}

However, direct spectroscopic evidence for the validity of this or other possible models is lacking in the gas phase and in particular in solution.¹⁷

In summary, selectively excited benzene and toluene in the gas and solution phase have been investigated to study the impact of a weakly interacting solvent on the time scales of intramolecular vibrational energy redistribution (IVR). It has been found that multiple time scales exist for isolated benzene (toluene) in agreement with theory. A comparison of gas-phase and solution experiments nicely revealed the effect and magnitude of solvent assisted IVR. Although the ultrafast IVR component appears not to be influenced by the solvent (in the simplest picture we assume the process to be faster than the average time between collisions with the solvent), the picosecond IVR time scale is contracted in solution as opposed to the gas phase, which we attribute to interactions (collisions) with the solvent and an overall acceleration of slower IVR components.

In addition, the hitherto unresolved question has been addressed whether an internal rotor (i.e., a methyl group on an aromatic ring) accelerates IVR in the gas phase and in solution. We find that a methyl rotor in fact accelerates IVR in the gas phase (factor of $\sim 5-6$) whereas the effect appears to be concealed in solution due to an overall contraction of the (secondary) time scales of IVR. To our knowledge the present investigation is the first direct time-resolved study that shows this effect in toluene and benzene both in their electronic ground state.

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