Vibrational Energy Relaxation of Selectively Excited Aromatic Molecules in Solution: The Effect of a Methyl Rotor and Its Chemical Substitution

J. Assmann, R. v. Benten, A. Charvat, and B. Abel*

Institut für Physikalische Chemie der Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany

Received: August 22, 2002; In Final Form: January 6, 2003

Transient femtosecond IR-pump−UV-probe spectroscopy is employed to investigate the intramolecular vibrational energy redistribution (IVR) and the intermolecular vibrational energy transfer (VET) of benzene, toluene ($CH_3-C_6H_5$), and α,α,α,-trifluorotoluene ($CF_3-C_6H_5$) selectively excited in overtones or combination bands of C−H stretch vibrations in solution. Global IVR and VET rate coefficients are derived from the measured transient absorption profiles using a simple kinetic model. The study reveals the effect of a methyl rotor and the effect of methyl rotor fluorination on the mechanisms and time scales of IVR and VET in aromatic model systems. For the present case, it turned out that the methyl rotor in toluene is not simply an enhancer for IVR; however, its fluorination accelerates IVR significantly. These results suggest that the methyl rotor effect on an aromatic ring in solution is more subtle than expected from previous gas-phase studies. In particular, the corresponding relaxation rates in this case are not simply governed by the number of lowest order resonances, such as found for aliphatic molecules. Instead, in aromatic molecules also, the very large number of higher order anharmonic resonances may play a pronounced role. Because the IVR rates are not at all correlated with the total density of states, we conclude that intramolecular vibrational energy relaxation of a zeroth order C−H stretch overtone or combination vibration in these molecules is not in its statistical limit and that hierarchical IVR, such as known for isolated molecules, still survives to some extent in solution. Our results further suggest that VET rates are not always simply correlated with the lowest frequency modes of the molecules.

I. Introduction

It is well-known that (vibrational) energy drives chemistry. In fact, chemistry requires not only energized molecules but also vibrational energy in specific degrees of freedom that project onto the reaction coordinate. Intramolecular vibrational energy redistribution (IVR) after selective vibrational excitation or chemical activation and intermolecular vibrational energy transfer (VET) play a central role in chemistry because they govern the rates, pathways, and efficiencies of chemical transformations.[1] IVR in competition to VET can be measured best in (vibrational) state specific experiments, where energy initially deposited in some degree of freedom of the molecule dissipates into combinations of lower energy vibrations and into the solvent degrees of freedom.[2−26] Several time-resolved techniques such as infrared absorption spectroscopy,[3,4,27−30] anti-Stokes Raman spectroscopy,[11−13,18,22,31−34] and electronic absorption spectroscopy[2,9,10,35,36] have been successfully applied to measure rates of IVR and VET of organic molecules. It is not surprising that the importance of these processes has also motivated theoretical work.[1,37−45]

IVR and VET of halogenated hydrocarbons,[4,25,30,36] benzene,[18] nitromethane,[13] acetonitrile,[11] alcohols,[19−22] and water[46,47] have been investigated successfully in the time domain employing different techniques of (more or less state selective) pump-and-probe spectroscopy. Each of these techniques opens a different observation window on the vibrational population distribution of an ensemble of relaxing molecules. In favorable cases, transient electronic absorption spectroscopy can provide information complementary to that from infrared or *anti*-Stokes Raman methods. Nevertheless, because almost all of the above (and other previous) experiments studied the relaxation in the fundamental, not much is known about IVR and VET at higher internal energies nor about its systematic structure, mode, and solvent dependence.[2,8−10] Moreover, despite the importance of IVR and VET for chemistry in solution a quantitative understanding of their mechanisms is still missing, such that a reliable prediction of their time scales and relaxation rates in general for molecules in solution appears to be not within reach at present.[1,45] Detailed experiments are therefore needed to guide theory and to develop theoretical models.

In a series of recent experiments, we have studied the effect of chemical substitution on intra- and intermolecular relaxation in solution for several aliphatic molecules.[2,9,10,48] The main focus of our studies was to find correlations between the molecules' chemical structure and the rates of IVR and VET, in particular the rates of intramolecular vibrational energy redistribution. Possible future applications may be the design of molecules in which IVR rates in solution can be controlled by (temporary) chemical modification.

Just recently, we extended our approach to aromatic molecules in solution. The experiments presented in this article focus on the influence of a methyl rotor on the intra(inter)molecular vibrational energy relaxation of aromatic molecules, a subject that has recently received much experimental and theoretical attention.[49−54] Most of the experimental results in the gas phase suggest that the methyl rotor acts as an IVR enhancer. The impact of chemical substitutions (deuteration) in the methyl

---

* To whom correspondence should be addressed. E-mail: babel@gwdg.de.

10.1021/jp026817r CCC: $25.00

group on IVR rates has been investigated for isolated molecules; however, the observed trends are not necessarily always well understood.

In this article, we report real-time measurements of intramolecular vibrational energy redistribution and subsequent intermolecular vibrational energy transfer in solution ($CF_2Cl-CFCl_2$) for benzene, toluene ($CH_3-C_5H_6$), and α,α,α,-trifluorotoluene ($CF_3-C_5H_6$), selectively excited in the two quanta overtone region or in combination bands of the CH stretch vibration.

The goal of this study is to elucidate the effect of methylation of the aromatic ring as well as chemical substitution (fluorination) in the methyl group. This study of molecules in solution may be compared with similar experiments in the gas phase where methyl rotors have been deuterated.[55,56]

II. Experimental Approach

Our experimental approach has been described in detail elsewhere.[2,9,10] Briefly, the technique has been employed first recently by Crim and co-workers to measure the relaxation of CH_2I_2 in organic solvents.[8] In the past two years, it has been further developed in their and our group to measure IVR and VET in fundamentals, in overtones, and in combination bands of several molecules containing C−I bonds.[2,8−10,36,48] In this article, we extend these studies to aromatic molecules showing that the experimental approach is very general and not limited to alkyl iodides.

For the selective excitation and probing of molecules in solution, we employ femtosecond (fs) IR-pump and UV-probe transient absorption spectroscopy. A special feature of the experiment is that the near-IR-laser pulse selectively excites molecules in overtones and combination bands of C−H stretch vibrations, whereas UV pulses monitor the excited-state populations of lower frequency modes which are Franck−Condon (FC)-active for the electronic transition. In other words, The near-IR pump laser creates a wave packet that resembles “excitation” of a zeroth-order vibration of a high-frequency C−H stretch mode (which is FC-inactive). The initially excited “state” is not an eigenstate of the molecule, but it evolves in time, and this process is correlated with IVR. Thus, vibrational energy in turn “flows” from the C−H bond to other degrees of freedom including the FC-active modes which were not excited initially. This energy redistribution process leads to an increased population of the FC modes. Unfortunately, we cannot probe the initial ultrafast time scale of IVR in the molecule; however, the measured time scales are likely a direct measure for the rate determining step in a relaxation cascasde. In addition, during and after IVR, vibrational energy transfer to the solvent takes place and in turn decreases the population of the FC-active modes. With a probe laser that is tuned to a wavelength where only vibrationally excited FC-active modes (i.e., a subset of all modes of the molecule) contribute to the absorption, both processes can be observed in real-time.

Specifically, in our experiments, the probe pulse is tuned to the red wing of the electronic absorption of the molecule in the near UV spectral range. The FC-active modes of this region can be identified via resonance Raman and dispersed fluorescence experiments. For molecules with a C−I bond, Raman experiments (in the gas and liquid phase) show that the dominant mode is the C−I stretch.[57−62] For molecules with an aromatic ring (chromophore), still only a limited number of low-frequency ring deformation modes are FC-active (see section III). The pump and probe schemes for C−I containing molecules (a) and aromatic molecules (b) are depicted schematically in Figure 1. The main difference in the two schemes is that the final state for the electronic absorption is repulsive (dissociative) in the case of C−I containing molecules and bound (although predissociative) in the case of aromatic molecules. For aromatic molecules, the aromatic ring and its FC-active modes play the role of the “C−I chromophore” in alkyliodides.

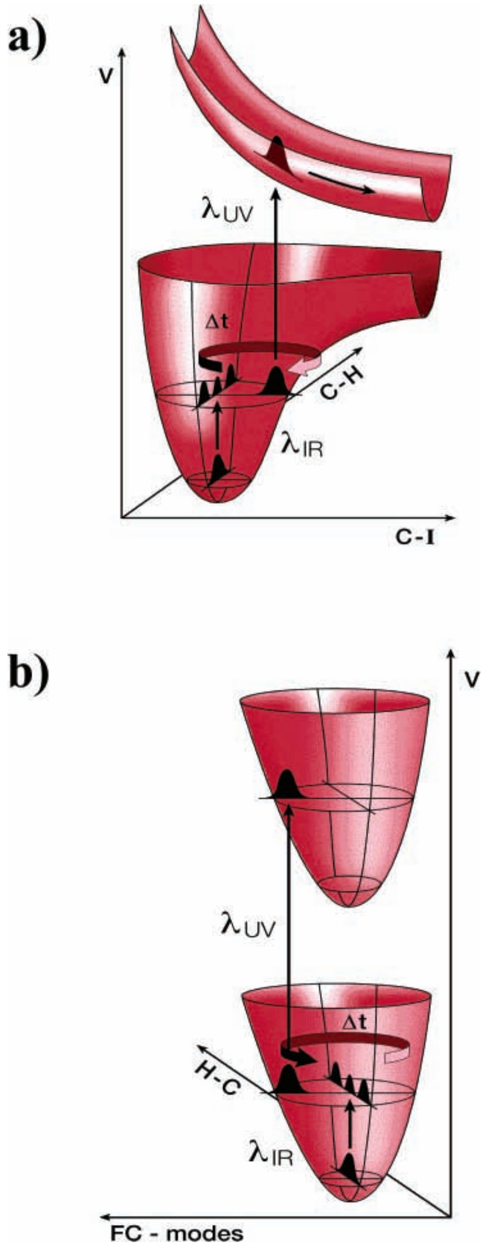

Figure 1. (a) Schematic visualization of the pump and probe process in alkyliodides where the final state in the electronic absorption is dissociative. Only two degrees of freedom of the molecules are considered. (b) Schematic visualization of the pump and probe process in aromatic molecules where the final state in the electronic absorption is bound. Only two degrees of freedom of the molecules are taken into account.

The characteristic features of the IR-pump−UV-probe measurements are (i) a fast nearly exponential increase and (ii) a nearly exponential decrease of absorption on a much longer time scale. We interpret the transients as intramolecular vibrational energy flow to FC-active modes in the molecule (IVR) and vibrational cooling due to intermolecular interactions with the solvent (VET). We want to point out at this point that an alternative speculative scenario, which would imply that the purely intramolecular IVR process could result in an initial rise and then decay of the population of these modes even in the absence of solvent, can be regarded to be unlikely. First, it can be shown that most of the density of states around the initially excited bright state is contributed by combination vibrations that contain quanta in the low-frequency FC-active modes. This is the reason we can assume that, to a good approximation, we probe the bath of states in the molecule and the redistributed energy E_{red}. Finally, the relative trends of the signal decays observed for the toluenes and benzene correlate with observed VET rates in the gas phase.[63]

Another distinct feature of our experiment is that transient absorption is converted into internal energy using high-temperature absorption spectra measured in separate shock-wave experiments.[10] It has been found that diffuse high temperature spectra of isolated molecules and corresponding spectra in weakly interacting solvents are very similar.[9] After an optimization of λ_{probe}, only one probe wavelength (and calibration) is sufficient to probe the internal energy of the molecules in this experiment.

In the experiments, we use laser pulses from a home-built regeneratively amplified Ti:sapphire system pumping two optical parametric amplifiers (TOPAS, Light Conversion, and a home build noncollinear optical parametric amplifier, NOPA) with a pulse width of ~50 fs and a bandwidth of ~300 cm^{-1}.[2,9,10] The excitation and delayed probe pulses are focused (f = 200 mm) and overlapped with perpendicular polarization in a thin (500 mm) fused silica flow cell containing the liquid sample (1−2 molar solutions). A concentration dependence of the signals has not been observed. During the experiments, laser pulse intensities were properly attenuated to avoid any nonlinear effects. The relatively weak transient difference absorptions with signal amplitudes in the range 50−1000 μOD (OD: optical density) were measured at 1 kHz with a noise level (after sufficient averaging) of about 5−10 μOD. For more details see refs 9 and 10.

III. Near-IR and UV Spectroscopy, Assignments, and Franck−Condon Active Modes

In this section, we discuss the near-IR and the UV absorption spectra of the model systems under investigation. In particular, we assign the (dominating) spectral features at the different excitation energies and identify the Franck−Condon active modes for the electronic transitions of the probe process. The corresponding spectra are displayed in Figures 2 and 3. In Table 1, the normal modes of the molecules are given and sorted with respect to the energy, which allows an easy comparison of the number of low-frequency modes in the molecules. The methyl groups of toluene and α,α,α,-trifluorotoluene are regarded as free rotors,[64,65] resulting in 30 + 9 − 1 = 38 vibrational degrees of freedom for these molecules. The eight normal modes correlated with the (trifluoro) methyl group are ν_{6-8}, ν_{13}, ν_{14}, ν_{16}, ν_{22}, and ν_{24} in the case of toluene and ν_{10}, ν_{14}, ν_{16}, ν_{25}, ν_{29}, ν_{31}, ν_{34}, and ν_{36} in the case of α,α,α,-trifluorotoluene.

For benzene, the IR spectrum needs to be discussed at wavelengths around 1664 and 2139 nm. The overtone spectrum of the C−H stretch modes was analyzed by Iachello et al.[66] These authors assigned the principal contributions in this regions as (pure) overtone exciations of the C−H stretch modes, in particular the overtone $2\nu_2$. In the complex spectrum around 2140 nm, numerous absorption lines of combination bands $1\nu_x1\nu_y$ (x = 1, 2, ..., 6, y = 7, 8, ..., 12) overlap. Symmetry allowed transitions are, e. g., $1\nu_1 1\nu_9$ or $1\nu_4 1\nu_7$.

The well-known UV spectrum for the electronic transition $^1A_{1g} \rightarrow {}^1B_{2u}$ of benzene contains the progressions (v',0) with $v' = nv'_{19} + v'_{27}$ (n = 1,2, ...).[67] In our experiment, UV pulses at 275 nm, however, probe (0,v'') transitions (mainly, $v'' = nv_{19} + mv_{27}$ [68]) that are red-shifted from the, symmetry forbidden, (0,0) band at 263 nm. The probe pulses are thus absorbed by

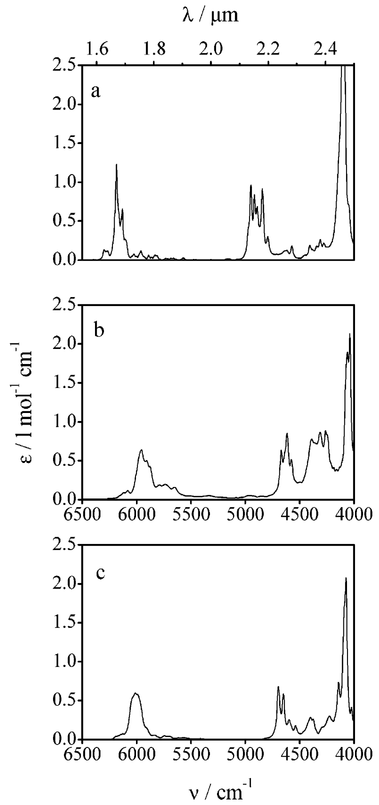

Figure 2. Near-IR absorption spectra of (a) benzene, (b) toluene, and (c) α,α,α,-trifluorotoluene in $CF_2ClCFCl_2$.

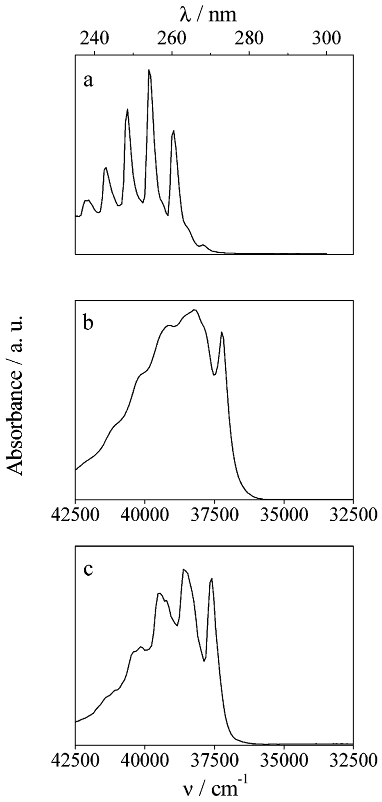

Figure 3. UV absorption spectra of (a) benzene, (b) toluene, and (c) α,α,α,-trifluorotoluene in $CF_2ClCFCl_2$.

TABLE 1: Normal Mode Energies and Symmetry of Benzene, Toluene, and α,α,α-Trifluorotoluene (Gas Phase)

	benzene[82]		toluene[75]		trifluorotoluene[95,96]	
mode	sym	energy/ cm^{-1}	sym	energy/ cm^{-1}	sym	energy/ cm^{-1}
ν_1	a_{1g}	3073	a_1	3087	a_1	3096
ν_2	e_{1u}	3064	a_1	3063	b_1	3096
ν_3	e_{1u}	3064	a_1	3055	a_1	3076
ν_4	b_{1u}	3057	b_1	3039	b_1	3076
ν_5	e_{2g}	3056	b_1	3029	a_1	3022
ν_6	e_{2g}	3056	b_2	2979	b_1	1614
ν_7	e_{2g}	1600	b_1	2952	a_1	1593
ν_8	e_{2g}	1600	a_1	2921	a_1	1459
ν_9	e_{1u}	1483	a_1	1605	b_1	1459
ν_{10}	e_{1u}	1483	b_1	1586	a_1	1328
ν_{11}	a_{2g}	1350	a_1	1494	b_1	1328
ν_{12}	b_{2u}	1309	b_1	1494	b_1	1253
ν_{13}	e_{2g}	1177	b_1	1460	a_1	1187
ν_{14}	e_{2g}	1177	b_2	1460	b_1	1179
ν_{15}	b_{2u}	1149	b_1	1455	b_1	1161
ν_{16}	e_{1u}	1038	a_1	1379	b_2	1152
ν_{17}	e_{1u}	1038	b_1	1312	a_1	1072
ν_{18}	b_{1u}	1010	a_1	1208	b_1	1072
ν_{19}	a_{1g}	993	a_1	1175	a_1	1028
ν_{20}	b_{2g}	990	b_1	1154	a_1	1004
ν_{21}	e_{2u}	967	b_1	1080	b_2	990
ν_{22}	e_{2u}	967	b_2	1040	a_2	970
ν_{23}	e_{1g}	847	b_1	1040	b_2	923
ν_{24}	e_{1g}	847	a_1	1030	a_2	844
ν_{25}	b_{2g}	707	a_1	1003	a_1	770
ν_{26}	b_{2u}	673	b_2	978	b_2	770
ν_{27}	e_{2g}	608	a_2	964	b_2	695
ν_{28}	e_{2g}	608	b_2	893	a_1	657
ν_{29}	e_{2u}	398	a_2	843	b_1	657
ν_{30}	e_{2u}	398	a_1	784	b_1	618
ν_{31}			b_2	728	b_2	596
ν_{32}			b_2	695	b_2	485
ν_{33}			b_1	623	a_2	398
ν_{34}			a_1	521	b_1	398
ν_{35}			a_2	464	a_1	336
ν_{36}			a_2	408	b_2	317
ν_{37}			b_1	344	b_1	169
ν_{38}			b_2	217	b_2	139

molecules having significant vibrational energy in the FC-active modes of the electronic ground state.

Toluene was excited with fs pulses at 1678 (5959), 2165 (4619), and 2340 nm (4274 cm^{-1}) in our experiment. The absorption spectra in the spectral region around 1678 nm are mainly due to the absorption of pure overtones of the aromatic C−H stretch modes.[69−74] The C−H stretch overtones of the methyl group appear between 1715 and 1800 nm with significantly lower intensities. A broadband IR-pump pulse of 1678 nm will thus deposit energy mainly in overtone vibrations of the aromatic ring. From the three prominent bands that are visible in the spectral region of the IR pump pulse at $\lambda_{\mathrm{pump}} =$ 2165 nm, Fuson et al. [75] assigned the peaks at 2142 (4669) and 2167 nm (4615 cm^{-1}) as transitions to $1\nu_2 1\nu_9$ and $1\nu_5 1\nu_{10}$, respectively. The shoulder on the blue side of the second peak might arise from a transition to $1\nu_5 1\nu_9$. The energy of the third peak in this complex at 2185 nm (4577 cm^{-1}) corresponds to a transition to the combination vibration $1\nu_1 1\nu_{11}$ (the transition to the isoenergetic vibration $1\nu_1 1\nu_{12}$ is symmetry-forbidden). Finally, in the region from 2250 to 2380 nm, Fuson et al. assigned the prominent peaks at 2278 (4390) and 2320 nm (4310 cm^{-1}) as vibrations of the methyl group $1\nu_7 1\nu_{13}$ and $1\nu_8 1\nu_{16}$.[75] The position of the third maximum showing a double structure corresponds to the vibrations $1\nu_1 1\nu_{19}$ (2347 nm, 4261 cm^{-1}) and $1\nu_2 1\nu_{19}$ (2356 nm, 4244 cm^{-1}). In this region, vibrations of the methyl group can be excited.

In the UV spectrum of toluene, the (0,0) band is located at 266.8 nm.[69] The absorption of the UV-probe pulse, $\lambda_{\mathrm{probe}} =$ 280 nm, thus requires a vibrational energy of 1766 cm^{-1} in the FC-active modes for the $S_0 \rightarrow S_1$ transition. Assuming that only $(0,v'')$ transitions are initiated in this region of the absorption spectrum, the FC-active modes can be obtained from an analysis of the laser-induced fluorescence at these wavelengths.[76] In the listing of Table 1, the FC-active modes of toluene are the mainly total-symmetric deformations of the aromatic ring ν_{24}, ν_{25}, ν_{30}, ν_{34}, and ν_{36} and, to a smaller extent, ν_{18} and ν_{19}.

The near-IR spectrum of α,α,α,-trifluorotoluene shows a nearly symmetric spectral band around 1664 nm. According to the assignments for the overtone spectra of other monosubstituted benzenes in the literature,[73,77−79] this peak can be attributed to pure overtones of the C−H stretch modes $2\nu_x$ ($x = 1, 2, ...,$ 5). In the spectral region of the second IR excitation wavelength, $\lambda_{\mathrm{pump}} = 2130$ nm (4695 cm^{-1}), two prominent bands appear. Taking into account exclusively the combination of vibrations with suitable symmetry, the positions of the first maximum corresponds to the states $1\nu_4 1\nu_7$, $1\nu_2 1\nu_6$, and $1\nu_4 1\nu_6$. The second peak might be attributed to the combination band $1\nu_5 1\nu_7$. As mentioned before, combination bands at this energy are due to vibrations that are strongly coupled, e.g., through Fermi resonances. Finally, the UV spectrum of α,α,α,-trifluorotoluene was investigated in absorption[80] and laser-induced fluorescence[81] experiments. For the electronic transition $S_0 \rightarrow S_1$, the Franck−Condon active modes at energies below the (0,0) band (266 nm) were identified as ν_{20}, ν_{26}, ν_{28}, ν_{30}, ν_{35}, and ν_{38} (see listing of Table 1).

IV. Results and Discussion

In the present set of experiments, we focused on the effect of chemical substitution on the mechanisms and time scales of IVR and VET of aromatic molecules. We have chosen benzene, toluene ($CH_3-C_5H_6$), and α,α,α,-trifluorotoluene ($CF_3-C_5H_6$) in $CF_2Cl-CFCl_2$ for the present study because this set of molecules enables us to study the effect of a methyl rotor on an aromatic ring on IVR and VET. Furthermore, the fluorination of toluene in the methyl group reveals the effect of chemical substitution on vibrational energy relaxation, as was done for aliphatic molecules just recently.[2,9,10,48] In the latter case, the excitation energies, the solvent, the structure, the number of atoms, and the degrees of freedom are the same for toluene and α,α,α,-trifluorotoluene such that the differences in the time scales should be directly related to the chemical substitution of atoms.

A. Global Rates for IVR and VET Derived from a Simple Analytical Model. The recorded UV-absorption profiles show a fast, but not instantaneous, rise and a subsequent slower decay, induced by the IR pump, for all three molecules on a picosecond (ps) time scale. To obtain "global" rate constants for energy transfer processes from these measurements, the absorption profiles have to be converted into energy profiles. Therefore, we calibrated the transient absorption against high-temperature absorption spectra measured in separate shock-wave experiments. Figure 4 displays the molar extinction coefficient $\epsilon(\lambda_{\mathrm{probe}})$ for benzene ($\lambda_{\mathrm{probe}} = 275$ nm), toluene ($\lambda_{\mathrm{probe}} =$280 nm) and trifluorotoluene ($\lambda_{\mathrm{probe}} = 279$ nm) as a function of the internal energy E. The functional forms of the fitting curves for the depicted energy dependence as well as for the temperature dependence of these absorption coefficients are listed in Table 2.

To extract rate constants for IVR and VET, we adopted the simple model introduced and discussed in refs 9 and 10. Briefly,

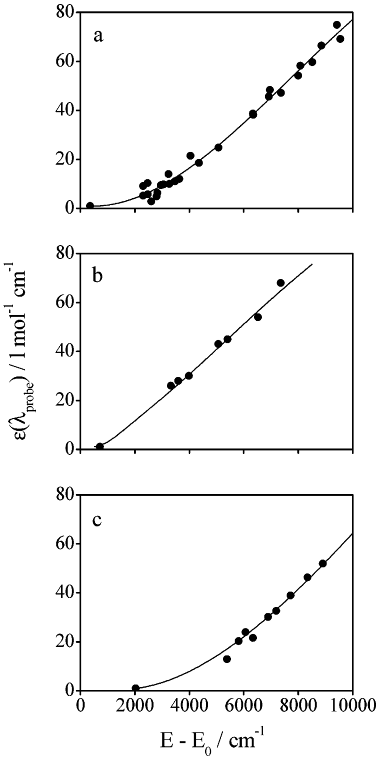

Figure 4. Energy dependence of the molar exctinction coefficient $\epsilon(\lambda_{\text{probe}})$ of (a) benzene ($\lambda_{\text{probe}} = 275$ nm), (b) toluene ($\lambda_{\text{probe}} = 280$ nm), and (c) α,α,α,-trifluorotoluene ($\lambda_{\text{probe}} = 279$ nm). The coefficients of the polynomial fits (solid lines) are summarized in Table 2.

TABLE 2: Polynomial Expressions for the Temperature and Energy Dependence of the Absorption Coefficient $\epsilon(\lambda_{\text{probe}})$ of Benzene ($\lambda_{\text{probe}} = 275$ nm), Toluene ($\lambda_{\text{probe}} = 280$ nm), and α,α,α,-Trifluorotoluene ($\lambda_{\text{probe}} = 279$ nm)[a]

benzene
$\epsilon(275\text{ nm})/\text{L mol}^{-1}\text{ cm}^{-1} = -6.440 + 9.187 \times 10^{-2}\, T/K - 3543 \times 10^{-4}\, T^2/K^2 + 5.143 \times 10^{-7}\, T^3/K^3 - 1.9104 \times 10^{-10}\, T^4/K^4$
$\epsilon(275\text{ nm})/\text{L mol}^{-1}\text{ cm}^{-1} = 1.242 - 1.41 \times 10^{-3}\, \delta E + 1.273 \times 10^{-6}\, \delta E^2 - 6.728 \times 10^{-11}\, \delta E^3$
$\delta E = (E - E_0)\text{ cm} = (E - 21\,389\text{ cm}^{-1})\text{ cm}$
toluene
$\epsilon(280\text{ nm})/\text{L mol}^{-1}\text{ cm}^{-1} = 1.186 - 669\, e^{2000K/T}$
$\epsilon(280\text{ nm})/\text{L mol}^{-1}\text{ cm}^{-1} = 1.186 + 200\, e^{14286/\delta E} + 55\, e^{3333/\delta E}$
$\delta E = (E - E_0)\text{ cm} = (E - 27\,182\text{ cm}^{-1})\text{ cm}$
α,α,α-trifluorotoluene
$\log(\epsilon(279\text{ nm})/\text{L mol}^{-1}\text{ cm}^{-1}) = 3.28 - 1420K/T + 145107K^2/T^2$
$\epsilon(279\text{ nm})/\text{L mol}^{-1}\text{ cm}^{-1} = 0.5000 - 6.616 \times 10^{-4}\, \delta E + 1.225 \times 10^{-6}\, \delta E^2 - 3.835 \times 10^{-11}\, \delta E^3$
$\delta E = (E - E_0)\text{ cm} = (E - 22\,494\text{ cm}^{-1})\text{ cm}$

[a] E_0 is the zero-point energy.

we assume a first-order energy decay process of an energy E_{loc} which is "localized" in the initial excitation (i.e., a wave packet that resembles the zeroth order bright state) to background states. The sum of the energies of the background states we termed "redistributed" energy E_{red}. The intramolecular vibrational energy redistribution process is followed by a significantly slower transfer of vibrational energy to the solvent. For the VET process, we also assume a simple first order decay. Because the initially prepared degrees of freedom are FC-inactive the measured absorption is a probe of the redistributed energy E_{red} of the molecule. The justification for such a simple model is given in refs 9 and 10. The time dependence of E_{red} is then given by

$$E_{\text{red}} = E_0\left(\frac{1/\tau_{\text{IVR}}}{1/\tau_{\text{IVR}} - 1/\tau_{\text{VET}}}\right)(\exp(-t/\tau_{\text{VET}}) - \exp(-t/\tau_{\text{IVR}})) \tag{1}$$

where τ_{IVR} and τ_{VET} are global phenomenological IVR and VET rate constants and E_0 is the initial excitation energy of the solute molecules which is determined by the photon energy $E_0 = h\nu_{\text{pump}}$ of the near-IR pump pulse. τ_{IVR} and τ_{VET} in eq 1 are adjustable parameters; however, E_0 is not a free parameter in this case[9,10] Using the expressions for $\epsilon(E)$ given in Table 2, the absorption profile is then calculated from

$$\Delta\text{OD}(t) \propto \epsilon(E_{\text{red}}(t)) - \epsilon(E_{\text{room temp}}) \tag{2}$$

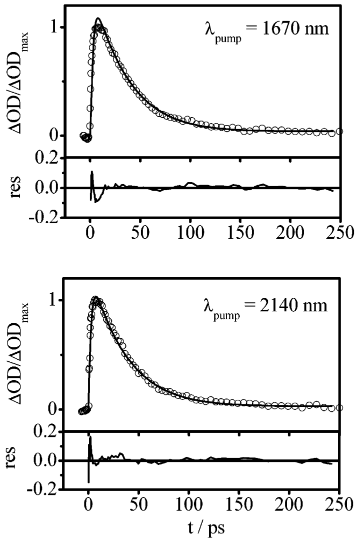

Figure 5. Normalized transient absorption time profiles for benzene (○) in $CF_2Cl-CFCl_2$ solution at different excitation wavelengths λ_{pump} for $\lambda_{\text{probe}} = 275$ nm. Also shown is a fit using the model described in the text (—). Residuals (res) are displayed to show the quality of the fits.

This model was used to fit the experimental traces presented in Figures 5−7 and to determine overall time constants for the intramolecular vibrational energy equilibration and intermolecular energy transfer. The overall fits are very satisfying and leave little uncertainty in the determination of the global rate constants τ_{IVR} and τ_{VET}, respectively, which are summarized in Table 3. Although for all molecules the overall features of the transients are similar, the corresponding time constants for IVR and VET are significantly different. Comparing, e.g., toluene and α,α,α,-trifluorotoluene, τ_{IVR} is significantly smaller for the fluorinated molecule whereas τ_{VET} is somewhat larger. For benzene, the relaxation rates of the IVR process are similar to toluene; however, the VET process takes place on a significantly longer time scale. Finally, changing the initial excitation from overtones ($\lambda_{\text{pump}} = 1660$ nm) to combination bands of C−H stretch modes (e.g., $\lambda_{\text{pump}} = 2130$ nm) slightly accelerates the IVR-process in all model systems.

B. Benzene: The Benchmark System for Studies of IVR. It is not by chance that benzene has become the benchmark system for IVR studies in the gas phase and to some extent in the liquid phase. It is difficult to compare the present experimental results with other data in the literature, because comparable data obtained with different or similar techniques do hardly exist. In fact, of the molecules presented here, only IVR and VET of benzene has been studied in solution so far.[18]

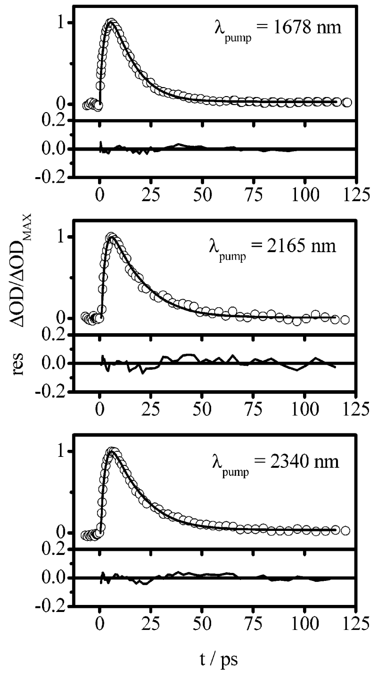

Figure 6. Normalized transient absorption time profiles for toluene (○) in $CF_2Cl-CFCl_2$ solution at different excitation wavelengths λ_{pump} for λ_{probe} = 280 nm. Also shown is a fit using the model described in the text (—). Residuals (res) show the quality of the fits.

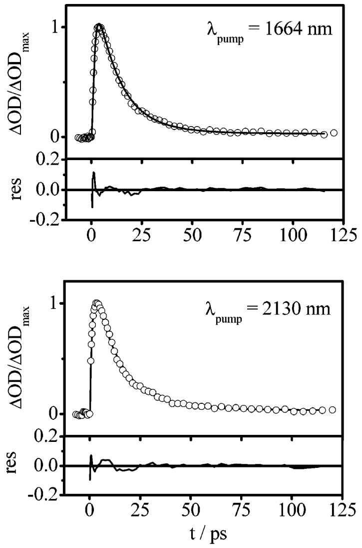

Figure 7. Normalized transient absorption time profiles for α,α,α,-trifluorotoluene (○) in $CF_2Cl-CFCl_2$ solution at different excitation wavelengths λ_{pump} for λ_{probe} = 279 nm. Also shown is a fit using the model described in the text (—). Residuals (res) indicate the good overall fit.

In these IR−Raman experiments, benzene, dissolved in CCl_4, was excited in the fundamental C−H stretch, and the energy transfer to the modes ν_{19} and ν_{27} as well as to the solvent was measured in real-time. The population of the modes ν_{19} and ν_{27} was found to rise with a time constant of 8 ps, and in the case of ν_{27}, a second time constant of 40 ps was observed. As mentioned above (section III), our IR-pump−UV-probe experiments are also sensitive to the population of the (FC-active) modes ν_{19} and ν_{27}, and the results of our study can thus be directly compared with the data of Dlott et al.[18] The IVR time constants for the excitation of the CH-stretch fundamentals and overtones in benzene differ by a factor of 4. It is interesting to note that the same differences have been reported for CH_2I_2 in CCl_4 [9,36] with a time constant of τ_{IVR} = 40ps for the excitation of the CH-stretch fundamentals and a time constant of τ_{IVR} = 10ps for the corresponding overtones. We attribute enhanced IVR for overtones and higher excitation energies to larger anharmonic couplings and/or a larger number of background states being correlated with a larger number of potential low-order coupling partners.

TABLE 3: Relaxation Rate Coefficients τ_{IVR} and τ_{VET} for Different Aromatic Molecules Dissolved in $CF_2ClCFCl_2$ as Determined from the Model Described in the Text

	τ_{IVR}/ps	τ_{VET}/ps
	Benzene	
λ_{pump} = 1664 nm	2.2 ± 0.5	70 ± 5
λ_{pump} = 2139 nm	1.8 ± 0.5	69 ± 5
	Toluene	
λ_{pump} = 1668 nm	2.9 ± 0.5	13 ± 2
λ_{pump} = 2165 nm	2.0 ± 0.5	18 ± 2
λ_{pump} = 2340 nm	2.3 ± 0.5	17 ± 2
	α,α,α,-Trifluorotoluene	
λ_{pump} = 1664 nm	1.2 ± 0.3	20 ± 3
λ_{pump} = 2130 nm	1.1 ± 0.3	21 ± 3

The molecular systems studied in this work, benzene in particular, are important model systems for understanding intramolecular vibrational energy redistribution. The reference for IVR of benzene in the condensed phase is the isolated molecule. Therefore, we will discuss the isolated molecules' dynamics first and then compare with the present results in the condensed phase. From an analysis of the eigenstate resolved spectrum of benzene in the first C−H stretching overtone and other ealier studies it is known that the IVR processs in the isolated molecule consists of at least two steps.[82] In the first step (≈100 fs), the initial excitation is rapidly redistributed among a first tier of states, which includes the $n\nu_1 + 2\nu_6$ ring modes, producing the spectrum observed by Page and coworkers.[83] Then, in a second, slower step (≈ 10−20 ps), further redistribution occurs into a larger bath of available states[82] thus producing the line widths observed by Nicholson and Lawrance[84] for the low-frequency ring modes of the molecule in the C−H overtone range. It is tempting to identify the first tier of states with the high frequency in-plane vibrations of benzene and to assume that the second tier of states contains also lower frequency ring modes. It is also tempting to speculate about a similar scenario in the liquid phase. If mechanisms of IVR of the isolated molecule survive in solution, it may be that similar (relative) time scales exist as well, although the solvent may accelerate the overall IVR to some extent. In any case, it is clear that the first ultrafast time scale cannot be observed in our experiment. The time scale we observe, i.e., a few picoseconds, may be correlated with the secondary time scales observed in high-resolution experiments.[82,84]

C. Effect of a Rotor and Its Fluorination on the Rate of IVR. As far as the effect of chemical substitution on the dynamics of the intramolecular energy transfer is concerned, it is interesting to compare our results obtained in solution with data for isolated molecules. It is well-known that a methyl rotor can accelerate IVR in molecules in the gas phase (see ref 85 and references therein). For instance, Parmenter et al.[53] attributed the significant acceleration of IVR rates in the S_1 excited state of *p*-fluorotoluene as opposed to difluorobenzene to an interaction of the methyl rotor hydrogens with the ring hydrogen atoms leading to mixing of states.

If we inspect the obtained data in Table 3, we realize that IVR in aromatic molecules in solution is not as simple as one might have expected on the basis of gas phase studies. In particular, if we consider benzene and toluene, we find that IVR is not significantly accelerated. Interestingly, VET is much faster for toluene as opposed to benzene. In the latter case, the maximum of the signals appears to be shifted somewhat toward shorter times, but the time constant for IVR remains nearly unaffected. This situation changes for the comparison of toluene and α,α,α,-trifluorotoluene. In this case, the IVR time constant decreases by a factor of 2.5 (whereas τ_{VET} is only slightly larger than in the case of toluene). It should be emphasized that this comparison is only valid if the decay of the signal is exclusively governed by VET. An alternative scenario would be the following: in our experiment, the population of several FC-active modes are measured. In particular, for toluene and trifluorotoluene, some of these modes have a relatively high frequency compared to the other modes of the system. One may speculate that the purely intramolecular IVR process could result in an initial rise and then decay of the population of these modes even in the absence of solvent. In such a case, these modes are only intermediates in the isolated-molecule IVR pathway. Therefore, the fall rate would include two contributions: IVR and VET with the measured rate being, in the simplest model, the sum of the two rates. For benzene, the effect would be less significant because the FC modes are among the lowest frequency normal modes. A conclusion from this argumentation is that the faster decay measured in toluene and trifluorotoluene (compared to benzene) could be due to the presence of the additional IVR rate, whereas the VET rate must be assumed to be essentially unchanged from benzene. In this case, the slower decay for trifluorotoluene, compared to toluene, would be attributed to a smaller IVR rate contribution for the fluoro compound. Although, only a similar experiment for the isolated molecule can unambiguously proof the interpretation, we strongly favor the first for several reasons: First, in all cases, several low-frequency modes of the molecules are probed. For benzene, these modes belong to the lowest frequency normal modes of the system. For toluene and trifluorotoluene, a few higher frequency modes are among a number of low frequency modes with FC factors assumed to be equal. The key point is now that in the experiment we probe a density of zeroth states, i.e., combination modes (at energy *E*), containing quanta in these FC-active modes. In this case, the statistical weight for the probed low frequency modes is expected to be much larger than that of the higher frequency modes. It can be shown that the majority of states around the initially excited bright state contain quanta in the lowest frequency FC-active modes. This is the reason we assume to probe the bath of states in the molecule and why we may not be sensitive to "transient populations". Finally, the relative trends of the signal decays observed for the toluenes and benzene correlate with observed VET rates in the gas phase.

Martens et al.[50] have examined the effect of large amplitude internal rotation on the rate and extent of IVR. They find that the full high-dimensional vibrational phase space of the system can be approximately decomposed into two subsystems. The first consists of the methyl rotor and the low-frequency ring modes, which interact strongly with the methyl rotor. The second subsystem consists of the remaining high-frequency modes, which do not strongly couple to the methyl rotor directly. The strong effect of changes in the relative ring-rotor frequency on the relaxation dynamics suggests an interesting isotope effect. Isotope substitution (deuteration or tritiation) of a methyl group will lower its rotational frequency. If this brings the rotor dynamics out of resonance with the ring vibrations, the interactions and in turn IVR should be weaker, despite the fact that the internal rotor contribution to the overall density of states is increased by isotopic or chemical substitution.

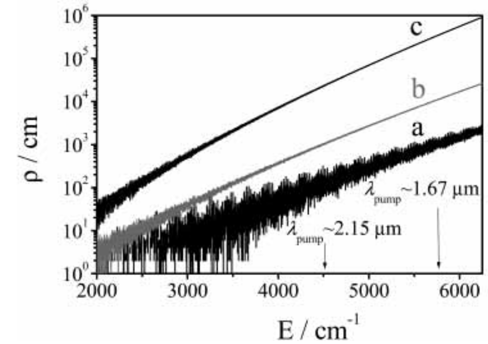

Figure 8. Densities of states $\rho(E)$ for (a) benzene, (b) toluene, and (c) α,α,α,-trifluorotoluene (direct harmonic count).

Our experimental data for toluene and α,α,α,-trifluorotoluene in solution appear to show the opposite trend; that is, the relaxation constant (τ_{IVR}) is markedly smaller for α,α,α,-trifluorotoluene (see Table 3). Unfortunately, there is a lack of similar data for molecules in solution such that comparisons can only be made with a limited number of gas-phase data. It is interesting to note that Lehmann et al. also found an increased rate of IVR for deuterated compounds as opposed to the undeuterated species.[49] They investigated line widths of *tert*-butylacetylene-d_9 and (trimethylsilyl) acetylene-d_9 in the gas phase. In addition, Parmenter and co-workers compared excited state (S_1) IVR lifetimes for *para*-fluorotoluene (pFT) and pFT-d_3 in the gas phase and found that the undeuterated and deuterated compound showed an IVR lifetime of 3.4 and 1.5 ps, respectively.[85] Although, these results have been obtained for isolated molecules and for excited states, we note that they appear to be in qualitative agreement to the results we obtain for similar molecules in weakly interacting solvents.

The molecules investigated in the present study are more complex than those we have investigated before.[2,9,10,48] Although we have found that specific low order interactions may survive in solution, which govern the intramolecular dynamics in aliphatic molecules, the total density of states of the molecules may be relevant in the limiting case of very strong couplings in larger molecules. The question to ask is: are aromatic molecules, excited in the overtone and combination band region of the CH-stretch, close to the statistical limit of IVR? According to Fermi's golden rule the IVR relaxation rate in this case should be proportional to the overall density of states. Chemical substitution in our case changes the total density of states, $\rho(E)$, significantly. We have calculated $\rho(E)$ for these molecules from the normal-mode frequencies listed in Table 1 employing a direct harmonic count (Figure 8). Given the state densities at an excess energy of 6000 cm^{-1}, which differ for benzene and toluene by a factor of 20, we conclude that for these molecules IVR is not yet statistical, if they are excited in the overtone and combination band region of the CH stretch.

This observation again provides evidence for our picture of IVR in solution in which hierarchical IVR can be still governed by specific (low-order) intramolecular interactions. It is the question, however, if the situation in the case of aromatic molecules can still be rationalized within a very simple low-order coupling model that we recently suggested to explain our results on IVR in aliphatic molecules.[2] To investigate this, we analyzed the number of low order resonances for benzene, toluene, and α,α,α,-trifluorotoluene according to the procedure described in ref 2. They are given in Table 4. It is obvious that in the present case the relaxation constants τ_{IVR} do not scale

TABLE 4: Intramolecular Relaxation Coefficients τ_{IVR} for Different Aromatic Molecules Excited in $v_{CH} = 2$ in $CF_2ClCFCl_2$ and Number of Low Order Interactions of the C−H Stretch ($v_{CH} = 2$, ± 100 cm^{-1}) to States in the First Tiers

		number of low-order resonances		
	τ_{IVR}/ps	3rd order	4th order	5th order
benzene	2.2	7	356	852
toluene	2.9	14	589	1962
α,α,α-trifluorotoluene	1.2	6	647	4562

simply with the number of lowest order resonances, which would indicate an early bottleneck of IVR found for some aliphatic molecules. Instead, in aromatic molecules also, the very high number of higher order (as opposed to the small number of strong lowest-order) anharmonic resonances may play a pronounced role (see Table 4). We anticipate that the strong (exponential) dependence of the individual interactions upon coupling order may be overcompensated by a large number of higher order interactions.[86] Upon comparing the experimentally determined (overall) relaxation coefficients, it should be kept in mind, however, that the obtained time constants are very likely a measure of the rate determining step in an extended relaxation cascade[2,9,10] over several tiers. Therefore, from the overall rate we measure, we cannot deduce specific relaxation pathways. It is important to note at this point that the global rate coefficients given in Table 4 very likely correspond to the intermediate time scales of the IVR process and that they are characteristic for the relaxation of zeroth order C−H stretch overtones, whereas intramolecular vibrational energy redistribution among the zeroth order C−H in plane vibrations in aromatic molecules such as benzene can be expected to be ultrafast.[82]

The development and application of a more sophisticated (quantitative) theoretical model which was suggested by Gruebele et al.[87] and Wolynes et al.[88] for IVR in isolated molecules, in which IVR is described as a quantum energy flow (diffusion) in quantum number space with scaling prescriptions for relevant low-order interactions, is in progress at present. It may be anticipated that such a model may be able to capture the trends we observe and to identify relevant relaxation pathways.

The small decrease of the overall relaxation time constant τ_{IVR} for the excitation of the combination bands of the molecules in comparison to τ_{IVR} for pure overtone excitation may be attributed to the delocalization of the pump energy already at the beginning or to an enhanced number of (low-order) coupling possibilities of combination modes to background states as opposed to pure (zeroth order) overtones. It is interesting, however, that we recently found the opposite trend for CH_2I_2.[9,10]

After we have discussed the variations in the global IVR relaxation coefficients (which are indeed all of the same order of magnitude), one may also pose the question why the observed relaxation rates do not vary dramatically and why they are not expected to do so. From work on isolated molecules in the gas phase, in particular from a series of experiments by Nesbitt et al.[89,90] and Lehmann and co-workers[91−93] who investigated a variety of molecules in the gas phase containing an acetylenic group, it is known that IVR lifetimes correlated with the C−H chromophore are remarkably insensitive to the nature of the substitution group. They vary no more than a factor of 2 when the state density is increased by a factor of 100, and even for an increase of the state density by a factor of 10^7, the observed IVR rates vary within 1 order of magnitude only for all acetylenic systems investigated.[55] From these studies, it is apparent that the huge reservoir of state density provided by the larger substitution groups has essentially little or no coupling with the zeroth-order bright C−H stretch state. It is an exceedingly important and simplifying result for efforts to model IVR dynamics theoretically and indicates that the state mixing in these systems is rate-limited to a highly restricted region of vibrational phase space.

For the present case of substituted aromatic molecules, we have argued that we excite preferentially zeroth order C−H stretch modes of the aromatic ring and probe FC-active modes of the ring chromophore. Therefore, we may consider the aromatic ring as a pumped and probed chromophore which is chemically substituted for the case of benzene, toluene, and trifluorotoluene. Obviously, IVR rates correlated with the IVR of zeroth order C−H stretches of the aromatic ring are quite insensitive to chemical substitution at the aromatic ring or in a side chain (methyl group). This result is maybe not surprising because we probe similar FC-active states in all molecules which are probably all in a similar distance away from the zeroth order bright state in state space. This insensitivity can probably be found for a series of systems in which the substitutions do not perturb the energy level structure of the aromatic ring too much and therefore do not change the pattern of (low-order) resonances significantly.

D. Effect of a Methyl Rotor and Its Fluorination on the Rate of VET. Just recently, we have reported on IVR and VET rates of the aliphatic model systems iodoethane and 2,2,2-trifluoro-1-iodoethane (CH_3CH_2I and CF_3CH_2I).[2] In that study, fluorinating the methyl group significantly decelerated VET (and IVR as well), although it increased the number of low-frequency modes. This might indicate that, for those aliphatic molecules, VET may take place before IVR is completed and before the low frequency modes are significantly populated.

Interestingly, we have found that a methyl group on the aromatic ring has a much more pronounced effect on the time scales of the VET than of the IVR process: for benzene and toluene, the rate constants τ_{VET} differ by a factor of 4. On the other hand, the fluorination of the methyl group in toluene has only little effect on the VET process; that is, τ_{VET} increases somewhat.

With classical Landau−Teller and energy gap type arguments, the first result is easy to explain. In the Landau−Teller approach, the VET rate of a molecule in solution is directly related to the frequency dependent friction $\xi(\omega)$ at the oscillator frequency ω, calculated from the time-correlation function of the solvent forces acting on the vibrational coordinate of the solute.[1,9] It is well-known that $\xi(\omega)$ has a maximum at very low frequencies and decays exponentially for increasing ω such that VET is dominated by low frequency modes of the solute. Because of the large number of high-frequency modes, benzene transfers much less energy in a collision to any bath (molecule) than other aromatic molecules, e.g., toluene. Because the rate of intermolecular energy transfer is expected to depend significantly on the number of low-frequency modes in the molecule, we had expected that the chemical substitution ($C_6H_5{-}CH_3 \rightarrow C_6H_5{-}CF_3$) introduces a significant number of "new" low-frequency modes such that the VET would be enhanced. Instead, an increase of τ_{VET} is observed.

Although the magnitude of the VET rate of benzene in comparison to toluene and trifluorotoluene is clear and easy to understand, the origin of the trend for the latter two molecules is not completely clear at present. They do not differ in the degrees of freedom nor in the number of atoms, such that they would represent an ideal pair of molecules to study the effect of chemical (atom) substitution and the change of intramolecular frequencies and intermolecular pair potentials keeping the structure of the molecules unchanged. In principle, there are two possibilities to qualitatively rationalize the VET rates of the two toluenes. It may be the case that IVR in these molecules is not complete and rate limited to a restricted region of vibrational phase space more or less excluding the low frequency modes connected mostly with the side chain of the aromatic molecule. On the other hand, the different intermolecular pair potentials for hydrogen and fluorine and the corresponding different spectral densities at the corresponding (changed) oscillator frequencies may be responsible for the observed effect. This is, however, difficult to judge because intermolecular pair potentials for the present molecules in solution are not known very precisely, such that it is difficult to make reliable (even qualitative) predictions. Further attempts to explain the observed trends have to wait for detailed molecular dynamics calculations on these systems. In addition, investigations of IVR and VET for molecules with other chemical substitutions, e.g., substitution directly on the aromatic ring,[94] may shed more light into the VET process of chemically substituted aromatic molecules.

Finally, our VET time constants for benzene can be directly compared with those from a recent IR−Raman experiment of Dlott and co-workers[18] in which C−H fundamentals are pumped and IVR as well as VET processes are observed in real time. In these experiments, the VET process to the solvent takes approximately 80 ps which is in good agreement with our results if we assume a small or negligible energy dependence of the VET.

V. Conclusions

In conclusion, in the present study, we used a mode specific experimental approach, employing near-infrared and near-ultraviolet fs-laser pulses, for the direct time-resolved measurement of IVR and VET of aromatic molecules in solution. In the present study, we have investigated the effect of a methyl rotor and its fluorination of the rates of IVR and VET. The reported overall IVR rates are very similar for benzene and toluene; however, a fluorination of the methyl group significantly enhances intramolecular vibrational energy redistribution. This trend does not correlate with the total density of states of the molecules nor clearly with the number of lowest-order resonances of the zeroth order bright state. The results from the present study may indicate that in aromatic molecules also the very high number of higher order (as opposed to the small number of strong lowest-order) anharmonic resonances may play a pronounced role. Our experimentally determined (overall) relaxation coefficients can be regarded as a measure of the rate determining step in an extended relaxation cascade over several tiers and being characteristic for the relaxation of a zeroth order C−H stretch overtone, whereas the first step in intramolecular vibrational energy redistribution in aromatic molecules can be expected to be ultrafast. Unfortunately, from the overall rate we measure, we cannot measure this initial ultrafast relaxation out of the zeroth order bright state nor deduce specific relaxation pathways.

At the same time, we did not find a simple correlation of the VET rates with the molecules' number of low frequency modes. Although the magnitude of the VET rate of benzene as opposed to toluene and trifluorotoluene can be understood in terms of energy gaps of involved energy levels, the origin of the trend for the latter two molecules is not completely clear at present. Explanations to qualitatively rationalize the VET rates of the two toluenes involve incomplete IVR on the time scale of relaxation and different intermolecular pair potentials for hydrogen and fluorine and the corresponding different spectral densities at the corresponding (changed) oscillator frequencies.

A more detailed understanding of the effect of chemical substitution on the intra- as well as intermolecular dynamics of selectively excited molecules in solution will require more experimental data on systematically varied model systems. It appears interesting to compare with molecules in which the substitution is made directly on the aromatic ring, e.g., with *p*-difluorobenzene. Studies on *p*-difluorobenzene and similar molecules are underway at present and will be published in a forthcoming article.

Acknowledgment. The authors enjoyed discussions of various aspects of this work with Prof. D. Schwarzer. We thank Dr. C. Kappel and R. Bürsing for the measurements of the absorption coefficients in shock-tube experiments and one of the referees for valuable comments on the paper. Financial support from the Deutsche Forschungsgemeinschaft within the SFB 357 ("Molekulare Mechanismen Unimolekularer Prozesse") and the Fonds der Chemischen Industrie is also gratefully acknowledged.

References and Notes

(1) Owrutsky, J. C.; Raftery, D.; Hochstrasser, R. M. *Annu. Rev. Phys. Chem.* **1994**, *45*, 519.

(2) Assmann, J.; Charvat, A.; Schwarzer, D.; Kappel, C.; Luther, K.; Abel, B. *J. Phys. Chem. A* **2002**, *106*, 5197.

(3) Bakker, H. J.; Planken, P. C. M.; Langendijk, A. *Nature* **1990**, *347*, 745.

(4) Bakker, H. J.; Planken, P. C. M.; Kuipers, L.; Langendijk, A. *J. Chem. Phys.* **1990**, *94*, 1730.

(5) Bakker, H. J.; Planken, P. C. M.; Langendijk, A. *J. Chem. Phys.* **1991**, *94*, 6007.

(6) Bakker, H. J. *J. Chem. Phys.* **1993**, *98*, 8496.

(7) Bakker, H. J. *J. Chem. Phys.* **1993**, *98*, 8496.

(8) Bingemann, D.; King, A.; Crim, F. F. *J. Chem. Phys.* **2000**, *113*, 5018.

(9) Charvat, A.; Assmann, J.; Abel, B.; Schwarzer, D. *J. Phys. Chem A* **2001**, *105*, 5071.

(10) Charvat, A.; Assmann, J.; Abel, B.; Schwarzer, D.; Henning, K.; Luther, K.; Troe, J. *PCCP* **2001**, *3*, 2230.

(11) Deak, J. C.; Iwaki, L. K.; Dlott, D. D. *J. Phys. Chem. A* **1998**, *102*, 8193.

(12) Deak, J. C.; Iwaki, L. K.; Dlott, D. D. *Chem. Phys. Lett.* **1998**, *293*, 405.

(13) Deak, J.; Iwaki, L. K.; Dlott, D. D. *Phys. Chem. A* **1999**, *103*, 971.

(14) Graener, H.; Lauberau, A. *Appl. Phys. B* **1982**, *29*, 213.

(15) Graener, H. *Chem. Phys. Lett.* **1990**, *165*, 110.

(16) Graener, H.; Seifert, G. *J. Chem. Phys.* **1993**, *98*, 36.

(17) Graener, H.; Zürl, R.; Hofmann *J. Phys. Chem. B* **1997**, *101*, 1745.

(18) Iwaki, L. K.; Deak, J. C.; Rhea, S. T.; Dlott, D. D. *Chem. Phys. Lett.* **1999**, *303*, 176.

(19) Laenen, R.; Simeonidis, K. *Chem. Phys. Lett.* **1999**, *299*, 589.

(20) Laenen, R.; Rauscher, C. *Chem. Phys. Lett.* **1997**, *274*, 63.

(21) Lauberau, A.; Kehl, G.; Kaiser, W. *Opt. Comm.* **1974**, *11*, 74.

(22) Lauberau, A.; Kaiser, W. *Rev. Mod. Phys.* **1978**, *50*, 607.

(23) Seifert, G.; Zürl, R.; Graener, H. *J. Phys. Chem. A* **1999**, *103*, 10749.

(24) Tokmakoff, A.; Fayer, M. D. *J. Chem. Phys.* **1995**, *103*, 2810.

(25) Hartl, I.; Zinth, W. *J. Phys. Chem. A* **2000**, *104*, 4218.

(26) Hamm, P.; Lim, M.; Hochstrasser, R. M. *J. Chem. Phys.* **1997**, *107*, 10523.

(27) Seifert, G.; Patzlaff, T.; Graener, H. *J. Chin. Chem. Soc.* **2000**, 667.

(28) Seifert, G.; Zurl, R.; Patzlaff, T.; Graener, H. *J. Chem. Phys.* **2000**, *112*, 6349.

(29) van den Broek, M. A. F. H.; Bakker, H. J. *Chem. Phys.* **2000**, *253*, 157.

(30) Bonn, M.; Brugmans, M. J. P.; Bakker, H. J. *Chem. Phys. Lett.* **1996**, *249*, 81.

(31) Iwaki, L. K.; Dlott, D. D. *Chem. Phys. Lett.* **2000**, *321*, 419.

(32) Iwaki, L. K.; Dlott, D. D. *J. Phys. Chem. A* **2000**, *104*, 9101.

(33) Hong, X. Y.; Chen, S.; Dlott, D. D. *J. Phys. Chem.* **1995**, *99*, 9102.

(34) Chen, S.; Hong, X. Y.; Hill, J. R.; Dlott, D. D. *J. Phys. Chem.* **1995**, *99*, 4525.

(35) Emmerling, F.; Lettenberg, M.; Lauberau, A. *J. Phys. Chem.* **1996**, *100*, 19251.

(36) Cheatum, C. M.; Heckscher, M. M.; Bingemann, D.; Crim, F. F. *J. Chem. Phys.* **2001**, *115*, 7086.

(37) Kaeb, G.; Schroeder, C.; Schwarzer, D. *Phys. Chem. Chem. Phys.* **2002**, *4*, 271−278.

(38) Larsen, R. E.; Stratt, R. M. *J. Chem. Phys.* **1999**, 1036.

(39) Ladanyi, B. M.; Stratt, R. M. *J. Phys. Chem. A* **1998**, *102*, 1068.

(40) Egorov, S. A.; Skinner, J. L. *J. Chem. Phys.* **1996**, *105*, 7047.

(41) Egorov, S. A.; Skinner, J. L. *J. Chem. Phys.* **2000**, *112*, 275.

(42) Oxtoby, D. W. *Adv. Chem. Phys.* **1981**, *47*, 487.

(43) Oxtoby, D. W. *Annu. Rev. Phys. Chem. 32* **1981**, *32*, 77.

(44) Stannard, P. R.; Gelbart, W. M. *J. Phys. Chem.* **1981**, *85*, 3592.

(45) Stratt, R. M.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 12981.

(46) Woutersen, S.; Emmerichs, U.; Bakker, H. J. *Science* **1997**, *278*, 658.

(47) Nienhuis, H.-K.; Woutersen, S.; Santen, R. A.; Bakker, H. J. *J. Chem. Phys.* **1999**, *111*, 1494.

(48) Assmann, J.; Charvat, A.; von Benten, R.; Abel, B. In *Springer Series in Chemical Physics, Ultrafast Phenomena XIII*; Miller, R. D., Murnane, M. M., Scherer, N. F., Weiner, A. M., Ed.; Springer-Verlag: Berlin, 2003; p 490.

(49) Gambogi, J. E.; L'Esperance, R. P.; Lehmann, K. K.; Pate, B. H.; Scoles, G. *J. Chem. Phys.* **1992**, *98*, 1116.

(50) Martens, C. C.; Reinhardt, W. P. *J. Chem. Phys.* **1990**, *93*, 5621.

(51) Moss, D. B.; Parmenter, C. S.; Ewing, G. E. *J. Chem. Phys.* **1987**, *86*, 51.

(52) Jasinski, J. M. *Chem. Phys. Lett.* **1984**, *109*, 462.

(53) Parmenter, C. S.; Stone, B. M. *J. Chem. Phys.* **1986**, *84*, 4710.

(54) Walters, V. A.; Colson, S. D.; Snavely, D. L.; Wiberg, K. B.; Janison, B. M. *J. Phys. Chem.* **1985**, *89*, 3857.

(55) Nesbitt, D. J.; Field, R. F. *J. Phys. Chem.* **1996**, *100*, 12735.

(56) Lehmann, K. K.; Scoles, G.; Pate, B. H. *Annu. Rev. Phys. Chem.* **1994**, *45*, 241.

(57) Kwok, W. M.; Phillips, D. L. *J. Chem. Phys.* **1995**, *104*, 2529.

(58) Kwok, W. M.; Phillips, D. L. *Chem. Phys. Lett.* **1995**, *235*, 260.

(59) Markel, F.; Myers, A. B. *Chem. Phys. Lett.* **1990**, *167*, 175.

(60) Phillips, D. L.; Lawrence, B. A.; Valentini, J. J. *J. Phys. Chem.* **1991**, *95*, 7570.

(61) Phillips, D. L.; Myers, A. B. *J. Chem. Phys.* **1991**, *95*, 226.

(62) Phillips, D. L.; Rodier, J. M.; Myers, A. B. *Chem. Phys.* **1993**, *175*, 1.

(63) Hippler, H.; Troe, J. In *Recent Direct Studies of Collisional Energy Transfer in Vibrationally Highly excited Molecules in the Ground electronic state*; Ashfold, M. N. R., Baggott, J. E., Ed.; Royal Society of Chemistry: London, 1989.

(64) Ogata, T.; Cox, A. P. *J. Mol. Spec.* **1976**, *61*, 265.

(65) Kreiner, W. A.; Rudolph, H. D.; Tan, B. *J. Mol. Spec.* **1973**, *48*, 86.

(66) Iachello, F.; Oss, S. *J. Chem. Phys.* **1993**, *99*, 7337.

(67) Atkinson, G. H.; Parmenter, C. S. *J. Mol. Spec.* **1978**, *73*, 22.

(68) Atkinson, G. H.; Parmenter, C. S. *J. Mol. Spec.* **1978**, *73*, 51.

(69) Burton, C. S.; Noyes, W. A. *J. Chem. Phys.* **1968**, *49*, 1705.

(70) Kjaergaard, H. G.; Turnbull, D. M.; Henry, B. R. *J. Phys. Chem. A* **1997**, *101*, 2589.

(71) Kjaergaard, H. G.; Turnbull, D. M.; Henry, B. R. *J. Phys. Chem. A* **1998**, *102*, 6095.

(72) Kjaergaard, H. G.; Rong, Z.; McAlees, A. J.; Howard, D. L.; Henry, B. R. *J. Phys. Chem. A* **2000**, *104*, 6398.

(73) Gough, K. M.; Henry, B. R. *J. Phys. Chem.* **1984**, *88*, 1298.

(74) Gosh, P. N.; Panja, P. K.; Pal, C. M. *Chem. Phys. Lett.* **1988**, *148*, 337.

(75) Fuson, N.; Garrigou-Lagrange, C.; Josien, M. L. *Spectrochim. Acta* **1960**, *16*, 106.

(76) Bass, A. M. *J. Chem. Phys.* **1950**, *18*, 1403.

(77) Gough, K. M.; Henry, B. R. *J. Phys. Chem.* **1983**, *84*, 3433.

(78) Gough, K. M.; Henry, B. R. *J. Am. Chem. Soc.* **1984**, *106*, 2781.

(79) Rospenk, M.; Leroux, N.; Zeegers-Huyskens, T. *J. Mol. Spec.* **1997**, *183*, 245.

(80) Cave, W. T.; Thompson, H. W. *Discuss. Faraday Soc.* **1950**, *9*, 35.

(81) Sastri, M. L. N.; Sponer, H. *J. Chem. Phys.* **1952**, *20*, 1428.

(82) Callegari, A.; Merker, U.; Engels, P.; Srivastava, H. K.; Lehmann, K. K. *J. Chem. Phys.* **2000**, *113*, 10583.

(83) Page, R. H.; Shen, Y. R.; Lee, Y. T. *J. Chem. Phys.* **1988**, *88*, 4621.

(84) Nicholsen, J. A.; Lawrance, W. D. *Chem. Phys. Lett.* **1995**, *236*, 336.

(85) Moss, D. B.; Parmenter, C. S. *J. Chem. Phys.* **1993**, *98*, 6897.

(86) Leitner, D. M.; Wolynes, P. G. *J. Chem. Phys.* **1996**, *105*, 11226.

(87) Gruebele, M.; Bigwood, R. *Rev. Phys. Chem.* **1998**, *17*, 91.

(88) Schofield, S. A.; Wolynes, P. G. *J. Chem. Phys.* **1992**, *98*, 1123.

(89) McIllroy, A.; Nesbitt, D. J. *J. Chem. Phys.* **1994**, *101*, 3421.

(90) McIlroy, A.; Nesbitt, D. J. *J. Chem. Phys.* **1989**, *91*, 104.

(91) Gambogi, J. E.; Lehmann, K. K.; Pate, B. H.; Scoles, G.; Yang, X. *J. Chem. Phys.* **1992**, *98*, 1748.

(92) Gambogi, J. E.; L'Esperance, R. P.; Lehmann, K. K.; Pate, B. H.; Scoles, G. *J. Chem. Phys.* **1993**, *98*, 1116.

(93) Kerstel, E. R. T.; Lehmann, K. K.; Mentel, T. F.; Pate, B. H.; Scoles, G. *J. Phys. Chem.* **1991**, *95*, 8282.

(94) Assmann, J.; von Benten, R.; Charvat, A.; Abel, B. *J. Phys. Chem. A* **2003**, submitted.

(95) Narasimham, N. A.; Nielsen, J. R.; Theimer, R. *J. Chem. Phys.* **1957**, *27*, 740.

(96) Scott, D. W.; Douslin, D. R.; Messerly, J. F.; Todd, S. S.; Hossenlopp, I. A.; Knicheloe, T. C.; McCullogh, J. P. *J. Am. Chem. Soc.* **1959**, *81*, 1015.