Intra- and Intermolecular Vibrational Energy Relaxation of C−H Overtone Excited Benzonitrile, *para*-Difluorobenzene, and Pyrazine in Solution

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

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

Received: November 1, 2002; In Final Form: March 11, 2003

Femtosecond IR-pump−UV-probe spectroscopy allows us to directly observe the intramolecular vibrational energy redistribution (IVR) and the intermolecular vibrational energy transfer (VET) of selectively excited aromatic molecules in solution ($CF_2ClCFCl_2$). In this article, we report global IVR and VET rate coefficients for benzonitrile, *p*-difluorobenzene, and pyrazine in a weakly interacting (nonpolar) solvent which are excited in overtones or combination bands of C−H stretch vibrations. The experimental findings are compared with recent results for benzene, toluene, and α,α,α-trifluorotoluene. While we have found a characteristic variation of the relaxation dynamics of the aromatic systems upon chemical substitution, the remarkable similarity of the time scales of IVR for a large group of molecules investigated is striking. Furthermore, the intermolecular vibrational relaxation is characteristically different for different chemical substitutions; however, the correlation of VET rates with the presence of low-frequency modes in the molecules is poor.

I. Introduction

Excited molecules play a major role in chemical transformations in solution. Since rearranging bonds requires moving nuclei, vibrational energy is often the most important form of energy that drives it. Vibrational energy may redistribute within the molecule or relax when molecules interact. Therefore, intramolecular vibrational energy redistribution (IVR) and intermolecular vibrational energy transfer (VET) are most important for chemical reactions because both govern the rates, pathways, and quantum yields of chemical transformations in solution.[1] A detailed understanding of these processes is thus prerequisite for an understanding of chemistry in solution.[2,3] Calculations with a direct comparison to experiments have been reported.[4] However, despite their importance for the outcome and the success of a chemical reaction, a general detailed mechanistic understanding of IVR and VET, which has been achieved for systems in the gas phase, is still missing in solution.

In the present article, we focus on the relaxation dynamics of overtones of C−H stretch vibrations of aromatic molecules in their ground electronic state. Several time-resolved experimental techniques such as infrared absorption spectroscopy,[5−10] anti-Stokes Raman spectroscopy,[11−19] and electronic absorption spectroscopy[20−27] have enabled a more or less detailed—often vibrational state selective—observation of IVR and VET of small molecules in solution. They open up distinct but different observation windows that can monitor different populations of selectively highly excited states of molecules in solution as a function of time. With a few exceptions, most of the experimental work in the past has been focused on relaxation in fundamentals, mostly of C−H and O−H stretch vibrations, in halogenated hydrocarbons,[9,28] nitromethane,[16] acetonitrile,[14] alcohols,[19,29−31] benzene,[12] and water.[32,33] Recently, femtosecond (fs) IR−pump−UV−probe spectroscopy has become a powerful tool for studying the relaxation in overtones or combination modes of high-frequency vibrations in alkyl iodides.[21−26,34,35]

This method measures changes in the electronic absorption spectrum after selective overtone excitation as relaxation populates Franck−Condon (FC) active vibrational modes in the ground state. This aspect of IR/UV transient absorption spectroscopy makes the technique complementary to infrared absorption and anti-Stokes Raman spectroscopy. In comparison to the techniques above, transient electronic absorption spectroscopy can be regarded to be selective because it is only sensitive to the FC active modes of the molecule; however, it is also nonspecific to some extent because it cannot distinguish among them. A significant advantage over other techniques is its overall sensitivity, which permits studies of dilute solutions[1,21−26,34−36] and supercritical fluids such as CO_2.[37]

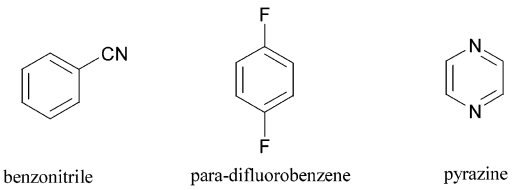
In a recent series of experiments, we employed the technique to study the relaxation of selectively excited CH_2I_2,[23] allyl iodide,[24] iodoethane, 2,2,2-trifluoro-iodoethane,[25] and iodoethanol.[26] Just recently, we demonstrated that this approach is very general and can be applied to aromatic molecules as well.[27] Our results suggest that IVR in solution is dominated by interactions via specific low-order resonances. This implies that mechanisms that dominate IVR in isolated molecules survive, at least to some extend, in solution. The fact that VET rates do not necessarily correlate with the number of low-frequency modes in the molecules[25,27] may indicate that VET competes with IVR in the molecule.

Very recently, we have studied the impact of a methyl rotor and its chemical substitution on the rates and time scales of IVR and VET in solution (benzene, toluene, and α,α,α-trifluorotoluene).[27] In the present study, we continue these investigations, that is, we studied the effect of chemical substitution of the aromatic ring on IVR and VET relaxation rates more systematically (benzonitrile, *p*-difluorobenzene (pDFB), and pyrazine, see Scheme 1 for chemical formulas), and provide more experimental data on aromatic model systems in weakly interacting solvents to shed some light on the relaxation mechanisms in this family of molecules.

* E-mail: babel@gwdg.de.

10.1021/jp027368y CCC: $25.00
Published on Web 06/14/2003

SCHEME 1: Substituted Aromatic Systems Investigated in This Study



benzonitrile para-difluorobenzene pyrazine

II. Experimental Section

Details of our experimental approach have been described elsewhere for alkyl iodides[23] and aromatic molecules.[27] The technique is an extension of a concept recently introduced by Crim and co-workers[21] to measure the relaxation of selectively excited CH_2I_2 molecules in solution. The main idea of this approach is that the initially excited nonstationary "states" in the two quanta region of the C−H stretch vibration are 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. Subsequent intermolecular vibrational energy transfer to the surrounding solvent brings the initially excited molecule back to equilibrium with the solvent, which *decreases* the absorption again. It has been known for some time that the temperature or internal energy dependence of a molecule's electronic spectrum depends on the population of very few FC active modes only. In the present experiment, we use the FC active modes as intramolecular probes for the internal energy. The FC active modes of the molecules can be identified by resonance Raman and dispersed fluorescence experiments (see following section). For molecules with an aromatic (ring) chromophore also, only few modes are FC active. A special feature of our experiments is that we convert the absorptions into internal energy of the molecules via high-temperature absorption spectra measured in separate shock-tube experiments.[24] Our approach does not imply that the energy flow from the excited to the FC active degrees of freedom is measured. They may be spectators and may not even be involved in the IVR directly. However, it can be shown that most of the density of (zeroth order) 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}. At the same time, our approach does imply that the energy we detect is redistributed nearly statistically.

The signals of the IR-pump−UV-probe measurements are characterized by (i) a fast nearly exponential increase and (ii) a nearly exponential decrease of absorption on a longer time scale. We interpret the rise as intramolecular vibrational energy flow in the molecule (IVR) and the subsequent decay as vibrational cooling due to intermolecular interactions with the solvent (VET). After converting the absorption into internal energy of the molecule, we use a simple model to derive rate coefficients for the two energy transfer processes from the recorded transient absorption profiles.

The (overall) relaxation coefficients we derive from the experiment must be regarded as a measure of the rate-determining step in an extended relaxation cascade over several tiers of the molecule and characteristic for the relaxation of a zeroth order C−H stretch overtone. The intramolecular vibrational energy redistribution among the zeroth order in plane C−H stretches and bends in aromatic molecules is expected to be ultrafast and invisible in the experiment. Unfortunately, from the overall rate we measure, we cannot deduce specific relaxation pathways for the overtone region.

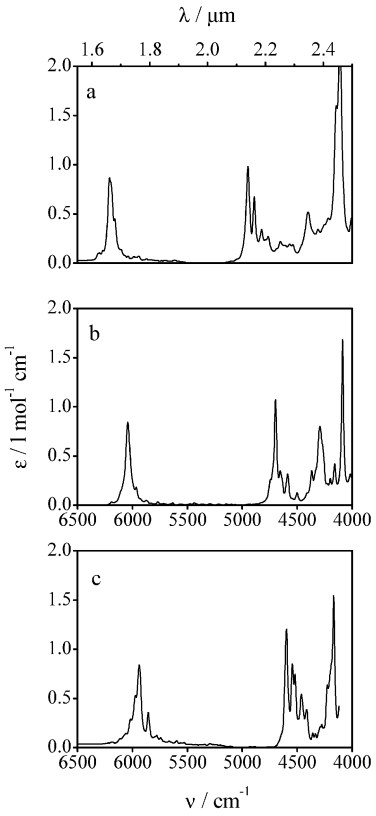


Figure 1. Near-IR absorption spectra of (a) benzonitrile, (b) *p*-difluorobenzene, and (c) pyrazine in $CF_2ClCFCl_2$.

The apparatus is the same as that used in similar, earlier experiments.[23−27] Briefly, we use laser pulses from a home-built regeneratively amplified Ti:Sapphire system pumping two optical parametric amplifiers (TOPAS, Light Conversion, and a home-built noncollinear optical parametric amplifier) with a pulse width of ∼50 fs and a bandwidth of ∼300 cm^{-1}.[23−25] The excitation and delayed probe pulses are focused (f = 200 mm) and overlapped with perpendicular polarization in a thin (500 μm) fused silica flow cell containing the liquid sample (1−2 molar solutions). A concentration dependence of the signals (in the range 0.5−3 mol/l) has not been observed. During the experiments, laser pulse intensities were properly attenuated to avoid multiphoton absorption or continuum generation or a local heating of the solvent which would add an offset to the absorption profiles. The relatively weak transient difference absorptions with signal amplitudes in the range 0.2−1 μOD (OD: optical density) were measured at 1 kHz with a noise level (after sufficient averaging) of about 5−10 μOD. The experimental time resolution is limited by the group velocity mismatch of the two laser pulses within the liquid sample to 400 fs.

III. IR- and UV-Spectroscopy and FC Active Modes

The molecules have been excited in the near-infrared and probed in the near-UV spectral range. The relevant spectra are given in Figures 1 and 2.

C−H stretch overtones and combination bands of benzonitrile were excited with pump pulses at 1661 and 2140 nm. In the two quanta region, the C−H stretch of substituted benzenes of

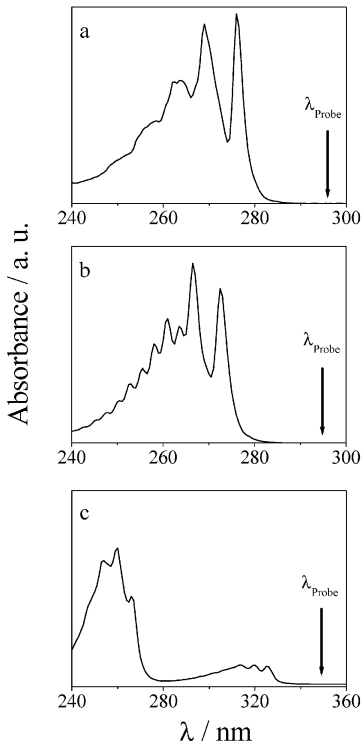


Figure 2. UV absorption spectra of (a) benzonitrile, (b) *p*-difluorobenzene, and (c) pyrazine in $CF_2ClCFCl_2$.

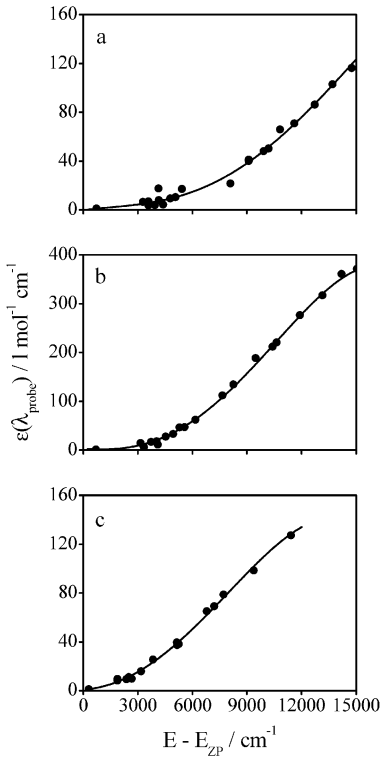


Figure 3. Energy dependence of the molar exctinction coefficient $\epsilon(\lambda_{probe})$ of (a) benzonitrile (λ_{probe} = 296 nm), (b) *p*-difluorobenzene (λ_{probe} = 294 nm), and (c) pyrazine (λ_{probe} = 348 nm) as measured in separate shock-tube experiments. The solid line is a polynomial expression to represent the data analytically (see Table 2). E_{ZP} is the zero-point energy of the molecules.

the pure overtones of the C−H stretch vibration ($2\nu_x$, x = 1, 2−5 for benzonitrile) dominate.[38−40] At lower excitation energy, combinations of C−H stretch vibrations ν_x (x = 1, 2−5) and C−C stretch vibrations ν_y (y = 7, 8−10) are excited. (Note, the numbering of modes of the substituted aromatic systems is made in such a way that the highest energy mode is assigned to mode 1 and with decreasing energy (frequency) the numbers of the other modes are increasing.) In the near-UV spectrum of benzonitrile, the (0, 0)-band of the $^1B_2 \leftarrow {}^1A_1$-transition is located at 274 nm.[41] The probe pulse of 296 nm is thus absorbed by molecules with significant vibrational energy in the FC modes of the electronic ground state. Fluorescence experiments[42] help us to identify the FC active modes (ν_{17}, ν_{18}, ν_{22}, and ν_{23}).

Experiments on *para*-difluorobenzene (pDFB) were carried out with near-IR pump pulses at 1655, 2130, and 2330 nm. As for benzonitrile, the spectral features around 1655 nm are dominated by the pure overtones of aromatic C−H stretch vibrations.[39] In the spectral region around 2130 nm, the symmetry allowed transitions to $1\nu_x1\nu_y$ (x = 1, 2−4, y = 5, 6, 7) occur. The complex structure at the excitation wavelength around 2330 nm we attribute to transitions from the ground state to $1\nu_x1\nu_y$ (x = 1, 2−4, y = 8, 9−13). In the condensed phase, the (0, 0)-band of the $S_1 \leftarrow S_0$ transition in pDFB is located at 274 nm.[43] ν_{11} and ν_{18} appear to be the FC active modes.[44] Progressions of these normal modes (and ν_{25}) are also visible in the fluorescence spectrum of pDFB at the wavelength of our UV-probe pulse (294 nm).[43]

Finally, pyrazine was excited in the two quanta C−H stretch overtone region at 1684 nm and in combination bands of the C−H and C−C stretch vibrations $1\nu_x\,1\nu_y$ (x = 1, 2−4, y = 5, 6−9) at 2210 nm. In the gas phase, the (0, 0)-band of the $S_1 \leftarrow S_0$ transition of pyrazine is located at 324 nm.[45] Fluorescence experiments[45,46] again suggest ν_{10}, ν_{18}, and ν_{22} to be the FC active modes at our probe wavelength (348 nm).

IV. Results

In this article, we investigate the effect of the chemical substitution on the intramolecular and intermolecular vibrational relaxation of aromatic molecules. The present experiments are an extension of our recent study on benzene, toluene, and α,α,α-trifluorotoluene.[27] All molecules were excited in the two quanta overtone region of the C−H stretch vibration (1660 nm) and in combination bands in the near-IR region (2100−2350 nm). The chemical substitution has only little impact on the characteristics of the UV absorption. In all of our model systems, the FC active modes for the electronic transitions were identified to be (mainly totally symmetric) vibrations of the aromatic ring. The observed effects on the rates and time scales of IVR and VET in a weakly interacting solvent are therefore directly related to the aromatic ring substitutions of the molecules.

The procedure to derive global rate coefficients for IVR and VET from our recorded absorption profiles is described in detail elsewhere.[23] Briefly, to simulate the experimental data we adopt a simple analytical model to fit the absorption profiles of the experiment. To obtain internal energy profiles, we convert the absorbance into internal energy using high-temperature absorption spectra. The temperature dependence of the molar extinction coefficients $\epsilon(\lambda_{PROBE})$ measured in separate shock-tube experiments has been used to determine the absorption coefficient as a function of internal energy. While Figure 3 displays $\epsilon(\lambda_{PROBE})$ as a function of internal energy, Table 1 contains the functional forms (polynomial expressions) for both the displayed energy dependence of $\epsilon_\lambda(E)$ and the temperature dependence of $\epsilon_\lambda(T)$ at the probe wavelength λ_{probe} for all molecules under investigation.

In the simplest version, the analytical model consists of two consecutive first-order processes for the intra- and intermolecular

TABLE 1: Analytic Expressions for the Representation of the Temperature and Energy Dependence of the Absorption Coefficient $\epsilon(\lambda_{Probe})$ of Benzonitrile ($\lambda_{Probe} = 296$ nm), *p*-difluorobenzene ($\lambda_{Probe} = 294$ nm), and Pyrazine ($\lambda_{Probe} = 348$ nm) between 300 K and 1500 K[a]

Benzonitrile

$$\log(\epsilon(296\text{ nm})/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}) = -0.75 + 2.37\cdot10^{-3}\cdot T/\text{K} + 6.54\cdot10^{-7}\cdot T^2/\text{K}^2 - 6.09\cdot10^{-10}\cdot\text{T}^3/\text{K}^3$$

$$\epsilon(296\text{ nm})/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1} = -0.292 + 1.99\cdot10^{-3}\cdot\delta E - 4.17\cdot10^{-7}\cdot\delta E^2 + 1.03\cdot10^{-10}\cdot\delta E^3 - 3.16\cdot10^{-15}\cdot\delta E^4$$

$$\delta E = (E - E_{ZP})\text{ cm} = (E - 21054\text{ cm}^{-1})\text{ cm}$$

p-Difluorobenzene

$$\log(\epsilon(294\text{ nm})/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}) = -1.59 + 5.95\cdot10^{-3}\cdot T/\text{K} - 2.13\cdot10^{-6}\cdot T^2/\text{K}^2$$

$$\epsilon(294\text{ nm})/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1} = 2.91 - 2.25\cdot10^{-3}\cdot\delta E + 6.68\cdot10^{-7}\cdot\delta E^2 + 2.99\cdot10^{-10}\cdot\delta E^3 - 1.51\cdot10^{-14}\cdot\delta E^4$$

$$\delta E = (E - E_{ZP})\text{ cm} = (E - 17959\text{ cm}^{-1})\text{ cm}$$

Pyrazine

$$\log(\epsilon(348\text{ nm})/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}) = 3.28 - 1420\text{ K}/T + 14510^{-7}\text{ K}^2/T^2$$

$$\epsilon(348\text{ nm})/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1} = 0.753 - 1.2\cdot10^{-3}\cdot\delta E + 1.21\cdot10^{-6}\cdot\delta E^2 + 2.52\cdot10^{-11}\cdot\delta E^3 - 4.73\cdot10^{-15}\cdot\delta E^4$$

$$\delta E = (E - E_{ZP})\text{ cm} = (E - 16308\text{ cm}^{-1})\text{ cm}$$

[a] E_{ZP} is the zero-point energy of the molecules.

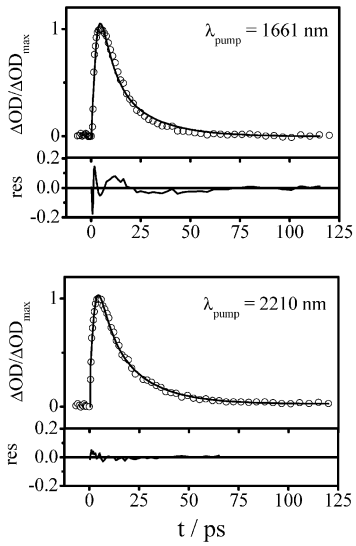


Figure 4. Normalized transient absorption time profiles for benzonitrile (o) in $CF_2ClCFCl_2$ at different excitation wavelengths λ_{pump}. Also shown is a fit using the model described in the text (—). Residuals (res) are displayed to show the quality of the fits. λ_{probe} is 296 nm in this case.

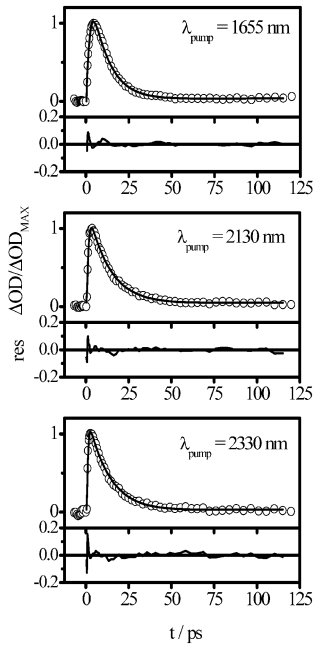


Figure 5. Normalized transient absorption time profiles for *p*-difluorobenzene (o) in $CF_2ClCFCl_2$ at different excitation wavelengths λ_{pump}. Also shown is a fit using the model described in the text (—). Residuals (res) are displayed to show the quality of the fits. λ_{probe} is 294 nm in this case.

energy transfer. To describe the IVR, we assume that the initially local energy, E_{loc}, is redistributed among the background states of the molecule via a first-order process with the rate coefficient τ_{IVR}^{-1}. The sum of the energies of the background states we term "redistributed" energy E_{red}. The subsequent VET occurs via coupling of background states to the surrounding liquid on a longer time scale with a time constant τ_{VET}. This ansatz yields the analytical expression

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

where τ_{IVR} and τ_{VET} are adjustable parameters, but E_0, which is the initial excitation energy, is not. It is determined by the photon energy $E_0 = h\nu_{pump}$ of the IR pump pulse. The transient signal we observe in the experiment can now be calculated from eq 2

$$\Delta\text{OD}(t) \propto \epsilon(E_{red}(t)) - \epsilon(E_{roomtemp}) \quad (2)$$

using the expressions of Table 1. The absorption profiles and simulations for benzonitrile are shown in Figure 4. The derived rate coefficients are nearly identical for excitation in the C−H stretch overtone region ($\lambda_{PUMP} = 1661$ nm) and for excitation in C−H stretch and C−C stretch combination bands ($\lambda_{PUMP} = 2130$ nm). *p*-Difluorobenzene (pDFB) has the same structure and the same number of degrees of freedom as benzene. Experimental traces together with the simulations are given in Figure 5. The extracted time constants (Table 2) show—contrary to the experiments on benzonitrile—a significant energy (or mode) dependence. While the change in the VET rates is less pronounced, the effect on the IVR rates is stronger, that is, they differ significantly by a factor of 2. The simple two-step model described above allowed us to simulate all data in ref 27 as well as our present traces for benzonitrile and pDFB with high accuracy. The extracted rate constants are summarized in Table 2. For comparison, the rate constants reported in ref 27 are also given.

The expression for the two-step process fits the experimental traces for benzonitrile and pDFB well because they are characterized by a fast but not instantaneous rise and a complete decay of the absorption. The simple model above implies that intermolecular vibrational energy transfer proceeds intramolecular vibrational energy redistribution which is modeled as a

TABLE 2: 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
	Benzonitrile	
$\lambda_{pump} = 1661$ nm	1.7 ± 0.5	19 ± 4
$\lambda_{pump} = 2140$ nm	1.9 ± 0.5	19 ± 3
	p-Difluorobenzene	
$\lambda_{pump} = 1655$ nm	1.7 ± 0.5	24 ± 5
$\lambda_{pump} = 2130$ nm	0.8 ± 0.2	30 ± 3
$\lambda_{pump} = 2330$ nm	0.6 ± 0.2	30 ± 3
	Pyrazine	
$\lambda_{pump} = 1684$ nm	$0.2^a/5.2 \pm 0.5$	26 ± 3
$\lambda_{pump} = 2210$ nm	$0.2^a/5.1 \pm 0.5$	28 ± 3
	Benzene	
$\lambda_{pump} = 1664$ nm	2.2 ± 0.5	70 ± 5
$\lambda_{pump} = 2139$ nm	1.8 ± 0.5	69 ± 5
	Toluene	
$\lambda_{pump} = 1668$ nm	2.9 ± 0.5	13 ± 2
$\lambda_{pump} = 2165$ nm	2.0 ± 0.5	18 ± 2
$\lambda_{pump} = 2340$ nm	2.3 ± 0.5	17 ± 2
	α,α,α-Trifluorotoluene	
$\lambda_{pump} = 1664$ nm	1.2 ± 0.3	20 ± 3
$\lambda_{pump} = 2130$ nm	1.1 ± 0.3	21 ± 3

[a] $\tau_{instIVR}$ as explained in the text, $A_{inst} = 0.6$ for $\lambda_{Pump} = 1684$ nm, and 0.9 for $\lambda_{Pump} = 2210$ nm, respectively.

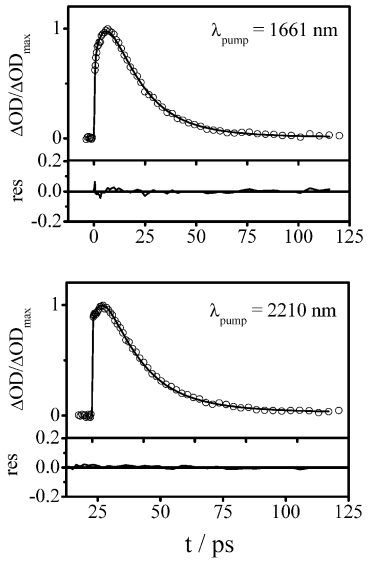


Figure 6. Normalized transient absorption time profiles for pyrazine (o) in $CF_2ClCFCl_2$ at different excitation wavelengths λ_{pump}. Also shown is a fit using the model described in the text (—). Residuals (res) are displayed to show the quality of the fits. λ_{probe} is 348 nm in this case.

one-step process. The latter is certainly a crude simplification of IVR but it provides a quantitative measure for the rate-determining step in a relaxation cascade in which the initial (primary) steps are probably invisible. Also, we rely on the fact that the initially excited nonstationary "state" has vanishing FC factors for the electronic transition. If one of the assumptions breaks down, the traces will look differently and data processing has to be modified. The traces obtained for pyrazine show slightly different features and the expression for the two-step process was inadequate to fit the data. For pyrazine, the absorption increases within the experimental time resolution to 60% ($\lambda_{PUMP} = 1684$ nm) and 90% ($\lambda_{PUMP} = 2210$ nm) of the maximum signal amplitude, respectively (see Figure 6). The maximum absorption is in turn reached at a time delay of approximately 6 ps. To account for the instantaneous rise in the traces, we used a biexponential ansatz for the IVR process, introducing a new rate coefficient $\tau_{instIVR}$ (for a fast instantaneous process) which is determined (and fixed) by our experimental time resolution. Defining $\tau_{instIVR} \equiv 200$ fs, the only new parameter in this refined model is the relative amplitude, A_{inst}, of the IVR rates coefficients ($A_{inst} = 0.6$ for $\lambda_{PUMP} = 1684$ nm and 0.9 for $\lambda_{PUMP} = 2210$ nm)

$$E_{red}(t) = E_0\left[A_{inst} \cdot \left(\frac{1/\tau_{instIVR}}{1/\tau_{instIVR} - 1/\tau_{VET}}\right) \times (\exp(-t/\tau_{VET}) - \exp(-t/\tau_{instIVR})) + (1 - A_{inst}) \times \left(\frac{1/\tau_{IVR}}{1/\tau_{IVR} - 1/\tau_{VET}}\right)(\exp(-t/\tau_{VET}) - \exp(-t/\tau_{IVR}))\right] \quad (3)$$

Equations 3 and 2 were used to fit the absorption profiles of pyrazine displayed in Figure 6, and we derived rate coefficients for IVR and VET, each of them being quite similar for both excitation wavelength (see Table 1).

V. Discussion

A. IVR of Aromatic Molecules. We recently studied the effect of chemical substitution on the energy transfer in aliphatic molecules.[23−26,36] Our results led to the conclusion that IVR in solution is still governed by specific low-order resonances[25] and not correlated with the total density of states of the molecules. In aromatic molecules, however, the mechanisms that govern the overall IVR relaxation process after overtone excitation appeared to be more subtle and, again, IVR was found to be not yet statistical.[27] The results from our previous study could 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.[27]

In the present article, we have investigated benzonitrile, pyrazine, and pDFB in weakly interacting solvents. All investigated aromatic molecules together constitute a nice group of molecules with systematic chemical substitutions at the aromatic ring and at (what we will call) the side chain which enable us to systematically study the impact of chemical substitution on the IVR of aromatic molecules in solution. At first glance, the variations of IVR rates upon chemical modification of the aromatic ring or the side chain are difficult to judge and appear erratic. The wavelength or mode dependence is rather small in general; however, the exception appears to be pDFB. The (small) enhancement of the overall relaxation rate for the excitation of combination modes of the aromatic molecules as opposed to the dynamics for pure overtone excitation may be attributed to an enhanced number of (low-order) coupling possibilities of the excited combination modes to background states as opposed to pure (zeroth order) overtones. We recently found the opposite trend for CH_2I_2. In that case, the relaxation of the pure overtone was faster than that of a combination tone at somewhat lower energy which was attributed to the larger anharmonicity of pure overtones compared to combination tones or, alternatively, to a larger number of (zeroth order) coupling partners at the higher energy.

If one considers benzonitrile, toluene, and trifluorotoluene on one hand and benzene, pDFB, and pyrazine on the other hand, molecules are grouped together in which chemical substitution is at the side chain ("methyl group") as opposed to substitution directly at the aromatic ring. The time dependence of the traces for excitation in the pure C−H overtone region is

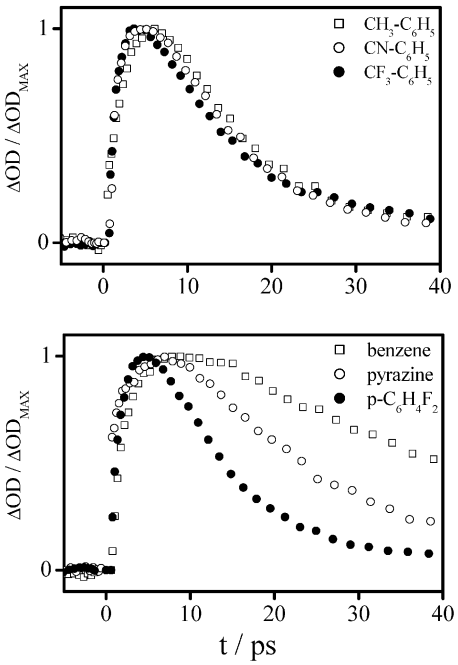


Figure 7. Comparison of the normalized transient absorption time profiles of different aromatic model systems (separated in two groups) excited in C−H stretch overtones ($\lambda_{pump} = 1660$ nm).

displayed in Figure 7. The trend for the fluorination of a methyl group in comparison with benzene has already been discussed in ref 27. Upon comparing benzonitrile with the latter systems, it becomes obvious that the methyl group does not play a very special role for IVR in solution as one may have concluded from gas-phase studies. In fact, the overall IVR rate constant of benzonitrile is just between that of the two "toluenes". If we compare benzene with the toluenes and with benzonitrile, we conclude that a methyl rotor is not more efficient for accelerating IVR than a CN group at the aromatic ring. If the IVR rates of benzene are compared with pDFB, it is obvious that substitution directly at the aromatic ring is also able to accelerate IVR, as is a fluorinated methyl group in trifluoro-toluene. The relaxation in these molecules appears to be governed by specific accidental couplings. Since the rates are not correlated with the number of lowest-order resonances in the molecule, we conclude that also the very high number of somewhat higher-order resonances may play a decisive role. Because of the "size" of the molecules, it is very difficult to map out such relaxation pathways.

Pyrazine in this group appears to be special. As was shown in the previous section, the increase of absorption which we attribute to IVR in the molecule could only be fitted with two exponentials being correlated with an instantaneous rise and a slower increase of absorption. The physical picture behind the model above is that in the case of pyrazine we likely probe FC active combination modes in (different) earlier and later tiers (coupled differently to the initially excited C−H overtone), and the measured absorption signal is probably a superposition of at least two contributions.

Although we have found characteristic variations in the IVR rates for systematic variations in chemical substitution, we notice that the overall variations for all molecules investigated are only moderate. In fact, the variations of the IVR time scales (see Table 2) are all within a factor of 5. As opposed to aliphatic systems, the time scales for IVR in aromatic molecules are shorter in general. After we have identified the surprisingly small variations in the global IVR relaxation coefficients of aromatic molecules, we want to address the question why the observed relaxation rates do not vary dramatically and why they may not be expected to do so. From work on isolated molecules in the gas phase, in particular, from a series of experiments by Nesbitt et al. and Lehmann and co-workers who investigated a variety of molecules in the gas phase containing an acetylenic group,[47,48] it is known that IVR lifetimes correlated with the C−H chromophore can be remarkably insensitive to the nature of the substitution group.

For the present case of substituted aromatic molecules, we excite preferentially zeroth order C−H stretch modes of the aromatic ring[27] and probe characteristic FC active modes of the ring "chromophore". Therefore, we may consider the aromatic ring as the pumped and probed chromophore which is chemically modified. Obviously, IVR rates correlated with the IVR of zeroth order C−H stretches of the aromatic ring are also 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 and thus overall relaxation pathways significantly.

B. VET of Aromatic Molecules. Unfortunately, there are no data on the VET in solution for the present set of molecules in the lower excitation energy range. As discussed in ref 27, only the VET time constants for benzene can be compared with those from a recent IR−Raman experiment of Dlott and coworkers[12] and are in good agreement with our results if a small or negligible energy dependence of the VET is assumed.

Since the rate of intermolecular energy transfer is anticipated to depend significantly on the number of low-frequency modes in the molecule, we had expected that the chemical substitutions would introduce significantly different numbers of low-frequency modes such that the VET should be sufficiently different for the systems under investigation. If we inspect Table 2, we do not find a simple correlation of the VET rates with the molecules' number of low-frequency modes for the majority of the molecules that have been investigated here and in a previous study.[27]

Although the trends of the VET rates of different aromatic molecules on chemical substitution are difficult to rationalize in terms of pair potentials or the frequency dependent friction $\xi(\omega)$ for the systems under investigation,[23] a surprising but very interesting correlation is obvious. It is seen best in Figure 7. If we again consider the two groups of molecules (benzene, pyrazine, pDFB on the one and benzonitrile, toluene, and trifluoro-toluene on the other hand), it is striking that VET appears to be affected only if the substitution is directly at the aromatic ring and it is not for substitutions at the side chain. This may indicate that the side chain is merely a spectator in the VET of the molecule, which appears to be dominated by the low-frequency ring modes. It looks as if only chemical substitution directly at the ring changes these ring modes and in turn accelerates VET of the molecule. This observation may be important for an understanding of dynamic aspects and efficiencies of single collisions in solution.

VI. Conclusions

In conclusion, we employed near-infrared and near-ultraviolet fs laser absorption spectroscopy for the direct time-resolved measurement of IVR and VET of benzonitrile, *p*-

difluorobenzene, and pyrazine in solution. In the present study, we have continued to study the effect of chemical substitution on the rates of IVR and VET of aromatic molecules. Although we have found characteristic variations in the global IVR rates in systematic chemical substitution, we noticed that the overall variations for all molecules investigated are all within a factor of 5 only. At the same time, the IVR rates we measure are not (yet) statistical. Obviously, overall IVR rates we measure that are correlated with the IVR of zeroth order C−H stretch overtones of the aromatic ring are quite insensitive to chemical substitution. These findings are comprehensible because we likely 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 and thus overall relaxation pathways significantly. At the same time, we did not find a simple correlation of the VET rates with the molecules' number of low-frequency modes. Instead, VET appears to be correlated with the site of substitution, that is, substitution directly at the ring or at the carbon side chain.

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 the reviewers for helpful 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 gratefully acknowledged.

References and Notes

(1) Assmann, J.; Kling, M.; Abel, B. *Angew. Chem., Int. Ed.* **2003**, *42*, 2226.
(2) Owrutsky, J. C.; Raftery, D.; Hochstrasser, R. M. *Annu. Rev. Phys. Chem.* **1994**, *45*, 519.
(3) Stratt, R. M.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 12981.
(4) Kaeb, G.; Schroeder, C.; Schwarzer, D. *Phys. Chem. Chem. Phys.* **2002**, *4*, 271−278.
(5) Bakker, H. J.; Planken, P. C. M.; Langendijk, A. *Nature* **1990**, *347*, 745.
(6) Seifert, G.; Patzlaff, T.; Graener, H. *J. Chin. Chem. Soc.* **2000**, 667.
(7) Seifert, G.; Zurl, R.; Patzlaff, T.; Graener, H. *J. Chem. Phys.* **2000**, *112*, 6349.
(8) van den Broek, M. A. F. H.; Bakker, H. J. *Chem. Phys.* **2000**, *253*, 157.
(9) Bakker, H. J.; Planken, P. C. M.; Kuipers, L.; Langendijk, A. *J. Chem. Phys.* **1990**, *94*, 1730.
(10) Bonn, M.; Brugmans, M. J. P.; Bakker, H. J. *Chem. Phys. Lett.* **1996**, *249*, 81.
(11) Iwaki, L. K.; Dlott, D. D. *Chem. Phys. Lett.* **2000**, *321*, 419.
(12) Iwaki, L. K.; Deak, J. C.; Rhea, S. T.; Dlott, D. D. *Chem. Phys. Lett.* **1999**, *303*, 176.
(13) Iwaki, L. K.; Dlott, D. D. *J. Phys. Chem. A* **2000**, *104*, 9101.
(14) Deak, J. C.; Iwaki, L. K.; Dlott, D. D. *J. Phys. Chem. A* **1998**, *102*, 8193.
(15) Deak, J. C.; Iwaki, L. K.; Dlott, D. D. *Chem. Phys. Lett.* **1998**, *293*, 405.
(16) Deak, J.; Iwaki, L. K.; Dlott, D. D. *Phys. Chem. A* **1999**, *103*, 971.
(17) Hong, X. Y.; Chen, S.; Dlott, D. D. *J. Phys. Chem.* **1995**, *99*, 9102.
(18) Chen, S.; Hong, X. Y.; Hill, J. R.; Dlott, D. D. *J. Phys. Chem.* **1995**, *99*, 4525.
(19) Lauberau, A.; Kaiser, W. *Rev. Mod. Phys.* **1978**, *50*, 607.
(20) Emmerling, F.; Lettenberg, M.; Lauberau, A. *J. Phys. Chem.* **1996**, *100*, 19251.
(21) Bingemann, D.; King, A.; Crim, F. F. *J. Chem. Phys.* **2000**, *113*, 5018.
(22) Cheatum, C. M.; Heckscher, M. M.; Bingemann, D.; Crim, F. F. *J. Chem. Phys.* **2001**, *115*, 7086.
(23) Charvat, A.; Assmann, J.; Abel, B.; Schwarzer, D. *J. Phys. Chem. A* **2001**, *105*, 5071.
(24) Charvat, A.; Assmann, J.; Abel, B.; Schwarzer, D.; Henning, K.; Luther, K.; Troe, J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2230.
(25) Assmann, J.; Charvat, A.; Schwarzer, D.; Kappel, C.; Luther, K.; Abel, B. *J. Phys. Chem. A* **2002**, *106*, 5197.
(26) Assmann, J.; Charvat, A.; von Benten, R.; Abel, B. In *Ultrafast Phenomena*; Miller, R. D., Murnane, M. M., Scherer, N. F., Weiner, A. M., Eds.; Springer Series in Chemical Physics; Springer: New York, 2003; p 490.
(27) Assmann, J.; von Benten, R.; Charvat, A.; Abel, B. *J. Phys. Chem. A* **2003**, *107*, 1904.
(28) Hartl, I.; Zinth, W. *J. Phys. Chem. A* **2000**, *104*, 4218.
(29) Laenen, R.; Rauscher, C. *Chem. Phys. Lett.* **1997**, *274*, 63.
(30) Laenen, R.; Simeonidis, K. *Chem. Phys. Lett.* **1999**, *299*, 589.
(31) Lauberau, A.; Kehl, G.; Kaiser, W. *Opt. Commun.* **1974**, *11*, 74.
(32) Woutersen, S.; Emmerichs, U.; Bakker, H. J. *Science* **1997**, *278*, 658.
(33) Nienhuis, H.-K.; Woutersen, S.; Santen, R. A.; Bakker, H. J. *J. Chem. Phys.* **1999**, *111*, 1494.
(34) Elles, C. G.; Bingemann, D.; Heckscher, M. M.; Crim, F. F. *J. Chem. Phys.* **2003**, *118*, 5587.
(35) Heckscher, M. M.; Sheps, L.; Bingemann, D.; Crim, F. F. *J. Chem. Phys.* **2002**, *117*, 8917.
(36) Assmann, J. Time-resolved investigations of vibrational energy transfer of organic molecules in liquids. Ph.D. Thesis, University of Göttingen, 2002, p 200.
(37) Sekiguchi, K.; Shimojima, A.; Kajimoto, O. *Chem. Phys. Lett.* **2002**, *356*, 84.
(38) Gough, K. M.; Henry, B. R. *J. Phys. Chem.* **1983**, *84*, 3433.
(39) Gough, K. M.; Henry, B. R. *J. Am. Chem. Soc.* **1984**, *106*, 2781.
(40) Rospenk, M.; Leroux, N.; Zeegers-Huyskens, T. *J. Mol. Spectrosc.* **1997**, *183*, 245.
(41) Brand, J. C. D.; Knight, P. D. *J. Mol. Spectrosc.* **1970**, *36*, 328.
(42) Bass, A. M. *J. Chem. Phys.* **1950**, *18*, 1403.
(43) Childs, A. F.; Dunn, T. M.; Francis, A. H. *J. Mol. Spectrosc.* **1983**, *102*, 56.
(44) Coveleskie, R. A.; Parmenter, C. S. *J. Mol. Spectrosc.* **1981**, *86*, 86.
(45) McDonald, D. B.; Rice, S. A. *J. Chem. Phys.* **1980**, *74*, 4893.
(46) Udagawa, Y.; Ito, M.; Suzuka, I. *Chem. Phys.* **1980**, *46*, 237.
(47) Lehmann, K. K.; Scoles, G.; Pate, B. H. *Annu. Rev. Phys. Chem.* **1994**, *45*, 241.
(48) Nesbitt, D. J.; Field, R. F. *J. Phys. Chem.* **1996**, *100*, 12735.