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# Vibrational cooling after ultrafast photoisomerization of azobenzene measured by femtosecond infrared spectroscopy

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The vibrational cooling of azobenzene after photoisomerization is investigated by time resolved IR spectroscopy with femtosecond time resolution. Transient difference spectra were obtained in a frequency range where phenyl ring modes and the central N=N-stretching mode absorbs. The experimental data are discussed in terms of a simple theoretical model which was derived in order to account for the off-diagonal anharmonicity between the investigated high-frequency modes and the bath of the remaining low-frequency modes in a polyatomic molecule. It is shown that these off-diagonal anharmonic constants dominate the observed transient absorbance changes while the anharmonicity of the high-frequency modes themselves (diagonal anharmonicity) causes only minor effects. Based on the transient IR spectra, the energy flow in the azobenzene molecule can be described as follows: After an initial ultrafast intramolecular energy redistribution process, the decay of the related intramolecular temperature occurs via intermolecular energy transfer to the solvent on a time scale of ca. 20 ps. © 1997 American Institute of Physics. [S0021-9606(97)00502-3]

#### I. INTRODUCTION

The energy relaxation following a photochemical reaction of a molecule in solution is an interesting and not fully understood problem (for some review articles see Refs. 1-5). In an oversimplified picture, the process may be separated into two steps: (i) Intramolecular vibrational redistribution (IVR) which dissipates the energy from an initial, nonthermal energy distribution to a fully thermalized state where all vibrational modes are excited according to a thermal Boltzmann factor and an initial temperature of the molecule can be defined. (ii) Intermolecular energy transfer from the molecule to the solvent. The kinetics of both processes strongly depend on the mode density of both the molecule and the solvent and in particular on the spectral overlap between molecular and bath modes, and on the polarity of the system.<sup>5</sup> Especially in medium sized molecules, the time scales of both processes are not clear. The assumption that intramolecular vibrational redistribution is much faster than intermolecular energy transfer, i.e., the assumption that both processes are well separated, needs further experimental verification.

Most experiments published so far investigated large dye molecules and used the slope of the low energy edge of an electronic transition as an intrinsic molecular thermometer (see, for example, Ref. 3). In this way, it was possible to measure the energy flow from the molecule to the solvent. Another, more sophisticated estimate of the energy distribution can be given by modeling the temperature dependent absorption spectrum of the  $S_0-S_1$ -transition<sup>6,7</sup> where the Franck–Condon factors of the active modes are obtained from their resonance Raman intensities. Using this method, one can roughly estimate the energy distribution and/or the time dependent intramolecular temperature of the system. With the help of this kind of experiments it was proposed that IVR is not necessarily ultrafast (i.e., in the range of 10 ps), even in the case of rather big molecules like stilbene<sup>6</sup> or TINUVIN.<sup>7</sup> However, the interesting questions concerning the initial energy distribution and the detailed pathway to a thermal distribution is difficult to address with this kind of experiments since the vibronic structure of the electronic transition is usually not spectrally resolved in solution.

So far, only very few experiments with sufficiently high time resolution in connection with real mode selectivity have been published. Basically two experimental techniques are conceivable: (i) Time resolved (transient) Raman spectroscopy (see, for example, Refs. 1,8–14) and (ii) time resolved infrared spectroscopy (see, for example, Refs. 15–20). Transient anti-Stokes Raman spectroscopy is selective for vibrationally excited modes and therefore is favorable for measuring IVR. However, due to the small Raman cross section, Raman spectroscopy often fails for fluorescing molecules. In addition, subpicosecond time resolution simultaneously implies the loss of frequency resolution since frequency and time resolution are achieved during the same interaction between the short light pulse and the molecule.

With the recent technical progress in ultrafast IR spectroscopy with time resolution in the range of several hundred femtoseconds (see, for example, Refs. 19–25), transient IR experiments with subpicosecond time resolution have now become feasible. Due to the high repetition rate of modern Ti:sapphire systems, a sufficiently high signal-to-noise level can be obtained allowing to apply transient fs-IR experiments to a broad variety of different molecules. In addition, since frequency resolution can be incorporated after the measurement process (frequency selection in a spectrometer be-

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hind the sample), high frequency and high time resolution can be obtained simultaneously when carefully considering the coherent interaction between the ultrashort probing pulse and the sample.<sup>26,27</sup> The limiting factor now is the dephasing time  $T_2$  of the investigated vibrational mode. In other words, the sample itself finds the best compromise between frequency and time resolution.

While extensive theoretical work treated IVR process on one single electronic potential surface (for a review see, for example, Ref. 28), there are only few theoretical investigations that consider vibrational relaxation processes initiated by an ultrafast internal conversion process.<sup>29-31</sup> Multidimensional quantum mechanical simulations of a nonadiabatic cis-trans photoisomerisation process indicate that the energy redistribution of high-frequency modes coupled strongly to the electronic transition occurs on a time scale of several hundred femtoseconds<sup>30</sup> and therefore is too fast to be addressed with the present IR technology. Semiclassical simulations have shown, however, that the subsequent process of redistribution of these initially nonthermally excited vibrational modes into weakly coupled intra- and intermolecular modes occurs on a picosecond time scale<sup>31</sup> and should be observable experimentally. Consequently, transient femtosecond vibrational spectroscopy might give detailed information on modes coupled strongly to the internal conversion process. These technique might supplement the information obtained from stationary resonance Raman experiments which determine the dominant modes at the beginning of the reaction, i.e., during the electronic dephasing time (10–30 fs).

It is the aim of the present paper to study the ability of mode selective subpicosecond IR spectroscopy to measure the initial vibrational energy distribution, the subsequent intramolecular energy redistribution process, and the final intermolecular cooling process after photoisomerisation of cisazobenzene. This molecule was chosen for several reasons: (i) An electronically excited *cis*-azobenzene molecule reaches the electronic ground state after a very short time (<200 fs, see below), transferring most of the electronic energy into the vibrational degrees of freedom. (ii) The wavelength position of the lowest electronic transition of cisazobenzene fits well to the second harmonic of a Ti:sapphiresystem. (iii) Cis- and trans-azobenzene have spectrally separated electronic transitions. Therefore, the molecule may be reversibly switched from one configuration into the other by exciting it with light of the proper wavelength. Because of this properties, azobenzene was proposed as an ultrafast molecular switch or as an image storage device (see, for example, Ref. 32). In order to simulate the experimental data, a simple theoretical model is derived in the second part of the paper which is applied to describe the shape of a vibrational transition in a vibrationally excited molecule under distinct model assumptions. A direct comparison of the experimental data and the model will demonstrate the capability of the model description.

#### II. EXPERIMENT

### A. Background: Spectroscopic properties of azobenzene

First, the spectral properties of azobenzene shall be briefly summarized (for a review article, see for example Ref. 33).

*Electronic spectra.* The two lowest electronic transitions of *trans*-azobenzene are the  $\pi - \pi^*$  transition centered at 320 nm and the  $n - \pi^*$  transition centered at 440 nm. While the  $\pi - \pi^*$  transition is strong ( $\epsilon = 21\ 000\ M^{-1}\ cm^{-1}$ ) the  $n - \pi^*$  transition is formally symmetry forbidden ( $\epsilon = 405\ M^{-1}\ cm^{-1}$ ). The corresponding transitions of *cis*-azobenzene are found at 260 nm ( $\pi - \pi^*$ ,  $\epsilon = 10\ 000\ M^{-1}\ cm^{-1}$ ) and at 440 nm ( $n - \pi^*$ ,  $\epsilon = 1250\ M^{-1}\ cm^{-1}$ ).

Photoreaction. Cis-azobenzene isomerizes into the trans-configuration with a quantum yield of  $\approx 40\%$  when exciting the  $\pi - \pi^*$  transition and with a quantum yield of  $\approx$ 55%, when exciting the  $n-\pi^*$  transition, respectively. The quantum yield depends slightly on the polarity of the solvent.<sup>33,34</sup> One open question is whether the isomerisation pathway is through rotation or inversion.33,35,36 Extended femtosecond VIS-pump-near-UV-probe experiments (pump: 435 nm, probe 350–435 nm, cross correlation time 250 fs) have been performed which will be described in detail elsewhere.<sup>37</sup> The basic results of these experiments are as follows: Around delay zero, a strong induced excited state absorption occurs which decays with a time constant on the order <200 fs. Afterward, absorption changes are observed on a time scale of 10 ps which may be related to a vibrational cooling process of the initially hot (or vibrationally excited) cis- and trans-azobenzene. Thus, the transition from the electronically excited state to the ground state is completed after several hundred femtoseconds yielding a mixture of vibrationally excited cis- and the trans-azobenzene in the electronic ground state. Since we treat here only delay times after the electronic decay, the stationary vibrational absorption spectra of both species can be used as a starting point for the discussion of the IR spectra of the vibrationally excited molecules.

Vibrational spectra. Stationary mid-IR-absorption spectra of *trans*- and *cis*-azobenzene are shown in Fig. 1(a) and (b) (dissolved in DMSO- $d_6$ , the contribution of the solvent is small in the investigated spectral range and has been subtracted). The time resolved experiments presented in this paper were performed between 1400 and 1550 cm<sup>-1</sup> where the strongest IR transitions of azobenzene are found. Five IR-active vibrational transitions are observed in this spectral range in which a trustworthy assignment can be given:<sup>38,39</sup> In cis-azobenzene, the N=N-stretch mode is observed at 1512  $cm^{-1}$  ( $\nu_{N=N}$ ) while the corresponding transition in *trans*azobenzene is IR forbidden due to its inversion symmetry. In a Raman spectrum, the N=N-stretch mode of transazobenzene shows up at 1440 cm<sup>-1</sup>. In addition, two inplane phenyl ring modes are observed at 1454 cm<sup>-1</sup> ( $\nu_{19b}$ ) and 1484 cm<sup>-1</sup> ( $\nu_{19a}$ ) in the *trans*-configuration and at 1446  $\mathrm{cm}^{-1}(\nu_{19b})$  and 1480  $\mathrm{cm}^{-1}(\nu_{19a})$  in the *cis*-configuration, respectively. These modes are assigned to the antisymmetric



FIG. 1. Absolute mid-IR-absorption spectrum of (a) *trans*-azobenzene and of (b) *cis*-azobenzene in DMSO- $d_6$ . The small contribution of the solvent in this spectral range is subtracted. For a assignment of the absorption lines, see text.

linear combination of a fundamental ring mode of both benzene rings,<sup>40</sup> namely the  $\nu_{19}$  mode (1482 cm<sup>-1</sup>, Wilson numbering used throughout the paper) which is twofold degenerate in benzene and which splits into two transitions due to the perturbed symmetry in azobenzene. The  $\nu_{19b}$ -mode shifts significantly from 1446 cm<sup>-1</sup> to 1454 cm<sup>-1</sup> when switching from the *cis*- to the *trans*-configuration allowing one to estimate the proportions of the *cis*- to *trans*-configuration in a mixture.

#### B. Materials and methods

A standard excite and probe scheme was used. Excitation was performed by femtosecond pulses (pulse duration:  $\tau$ =150 fs FWHM; center wavelength:  $\lambda$ =408 nm) generated by frequency doubling the output of a 1 kHz Ti:sapphireregenerative amplifier. The generation of the IR-probing pulses and the detection scheme was described in detail in Refs. 22 and 23. Briefly, the absorbance changes of the sample were recorded by tunable probing pulses generated by difference frequency mixing between the output of the regenerative Ti:sapphire amplifier and the output of a tunable traveling wave dye laser in an AgGaS2 crystal. Pulses with a pulse duration of  $\approx 300$  fs and a spectral bandwidth of  $\approx 60$  $cm^{-1}$  were obtained. The probing pulses were dispersed in a grating spectrometer (spectral resolution:  $5 \text{ cm}^{-1}$ ) after passing the sample. A 10-element MCT-detector array was used to cover the complete spectral bandwidth of the probing pulses simultaneously. The time resolved spectra shown below are a superposition of several 10-point spectra which overlap by several elements. The noise of two different points of one single 10-element spectrum is strongly correlated, yielding time resolved difference spectra with a relative accuracy which is better than the absolute accuracy of one single data point. A signal to noise level sufficient to detect absorbance changes as small as  $\Delta A = 5 \times 10^{-5}$  was achieved.

Trans-azobenzene (Sigma) was dissolved in deuterated DMSO (99 atom % deuterium) at a concentration of 50 mM. No concentration dependent changes in the electronic and in the vibrational spectra were observed even at much higher concentrations of up to 200 mM. Therefore, we can exclude disturbing effects by aggregation at a concentration of 50 mM. The solvent is transparent in the investigated spectral range between 1400 and 1550 cm<sup>-1</sup>. The sample was held in a CaF<sub>2</sub> cuvette (path length:  $\approx$ 50  $\mu$ m) which was rotated in order to exchange the sample between two successive laser shots. In addition, the cuvette holder was translated perpendicular to the beam axis. In total, a ring with  $\approx 20$  mm in diameter and  $\approx 3$  mm broad was sampled by the excitation pulses. In the fs experiment, the  $cis \rightarrow trans$  isomerization of azobenzene was investigated by exciting the  $n-\pi^*$  transition of *cis*-azobenzene. In order to regenerate the sample during the measurement, the sample was illuminated by a filtered broadband cw-light source which selectively excited the  $\pi - \pi^*$  transition of *trans*-azobenzene and thus shifted the cis-trans-photostationary equilibrium strongly to the cisconfiguration. This was done by a filtered Hg(Xe) lamp (Oriel, Stanford, with glas filters UG11, WG305, Schott, Mainz, combined transmission range: 300 nm-380 nm) transmitted through a fused silica fiber bundle (diameter: 3 mm) which was used to illuminate the same ring of the sample as the excitation light (total power of the cw light at the sample:  $\approx 100$  mW). The photostationary equilibrium was essentially unchanged when the femtosecond excitation pulses at 408 nm illuminated the sample (which switched the molecules from the *cis*- to the *trans*-configuration) since the average power of the Hg(Xe) lamp was much higher than the average power of the pumping light. A steady-state IR experiment was used to measure the photostationary cis-transdistribution. By using two well separated IR transitions at 1454 cm<sup>-1</sup> (*trans*) and at 1446 cm<sup>-1</sup> (*cis*) as marker modes (see Fig. 1), one could estimate that more than 70% of the molecules are in the cis-configuration under these illumination conditions. Taking into account that the cross section of the  $n-\pi^*$  transition of *cis*-azobenzene is three times larger than that of trans-azobenzene, one concludes that more than 90% of the excited molecules started from the *cis*-state while a small fraction of below 10% started from in the trans-state.

Two effects disturb the time resolved results around the experimental delay zero position: (i) The coherent perturbed free induction (PFID) decay effect<sup>26,27</sup> which is of importance when the inhomogeneous dephasing time of a vibrational transition is longer than the pulse duration of the probing pulses. However, it should be kept in mind that the PFID effect contributes only at negative delay times and during the overlap of excitation and probing pulse but not at larger positive delay times.<sup>26</sup> (ii) Due to the short wavelength and the high energy of the excitation pulses, an optical Kerr effect originating mainly from the cuvette windows was observed which causes a transient frequency shift of the probing pulses around delay zero.<sup>41</sup> The Kerr effect mimics absor-



FIG. 2. (a) Transient difference spectra after photoisomerisation of *cis*azobenzene measured 1 ps (open circles), 10 ps (gray squares), and 70 ps (filled triangles) after electronic excitation. (b) 70 ps difference spectrum (triangles) compared with a difference spectrum obtained in a FTIR spectrometer under steady-state illumination by light at  $\lambda$ =300–380 nm.

bance changes which are about three times larger than the absorbance changes caused by the photoisomerisation of azobenzene. All experiments presented below are done with the polarization of the probe perpendicular to that of the pump since this considerably reduces this effect. Both effects (i.e., the PFID effect and the Kerr effect) overlap around delay zero. As a consequence, the experimental data were analyzed for delay times >0.7 ps only, when both disturbing effects have vanished.

#### C. Results

Figure 2 shows the experimental results obtained between 1420 and 1540 cm<sup>-1</sup>. In Fig. 2(b), a time resolved difference spectrum measured 70 ps after electronic excitation (triangles) is compared with a stationary difference spectrum (solid line). The stationary spectrum was obtained in a FTIR spectrometer by switching trans-azobenzene into the *cis*-configuration with the filtered Hg(Xe) lamp ( $\lambda$ =300–380 nm). In order to fit the 70 ps spectrum to the stationary spectrum, the stationary spectrum was inverted (since the cis-trans-transition is observed in the time resolved experiment) and linearly scaled. In addition, a small baseline correction (+0.05 mOD) is necessary to match the 70 ps and the stationary spectrum. The corrected baseline is depicted in Figs. 2(a) and 2(b). The baseline shift is also observed for later delay times up to 300 ps.] A perfect agreement between the transient 70 ps spectrum and the stationary difference spectrum is obtained demonstrating the precision of the time resolved experiments and indicating that both the photoreaction and the cooling process are completed after 70 ps as expected from the UV experiments.<sup>37</sup> The base line shift may be explained by a temperature dependent broadening of neighboring solvent bands (observed at 1050 cm<sup>-1</sup> and at 2100 cm<sup>-1</sup>) which are orders of magnitudes stronger ( $A \approx 2$  OD) than the transient azobenzene absorption lines ( $\Delta A \approx 0.1 \text{ mOD}$ ). A similar baseline shift is also observed in a static absorption spectrum of pure DMSO upon heating. In any case, the baseline shift is a small broadband effect and we discuss here only the narrow band features originating from the sample molecules.

In detail, the following spectral features are observed in the 70 ps spectrum: The N—N-stretching mode (1512 cm<sup>-1</sup>) which is IR active only in the *cis*-configuration bleaches upon switching from the *cis*- into the *trans*-configuration. In addition, both phenyl ring modes  $\nu_{19b}$  and  $\nu_{19a}$  are frequency shifted when photoisomerizing from the *cis*-state (1446 cm<sup>-1</sup> and 1480 cm<sup>-1</sup>) to the *trans*-state (1454 cm<sup>-1</sup> and 1484 cm<sup>-1</sup>).

More interesting are the transient difference spectra at earlier delay times: In Fig. 2(a), time resolved difference spectra measured 1 ps (open circles) and 10 ps (gray squares) after electronic excitation are shown together with the 70 ps spectrum (triangles). The transient difference spectra are a superposition of negative and positive contributions. While the negative contributions are due to bleaching *cis*azobenzene bands (and eventually due to a stimulated emission of a vibrationally excited state, see discussion), the positive contributions are due to transient photoproducts. Both contributions will be discussed separately:

(i) In all transient difference spectra, three negative absorption lines are found close to the spectral positions of *cis*-azobenzene bands (1446 cm<sup>-1</sup>, 1481 cm<sup>-1</sup>, and 1515 cm<sup>-1</sup>). The spectral positions of these negative bands do not change with time, as expected for bands of the disappearing *cis*-azobenzene molecules. However, the amount of the bleach changes with time. For two bands (1481 cm<sup>-1</sup> and 1515 cm<sup>-1</sup>), a partial refill of the initial bleach can be recognized, while the third band (1446 cm<sup>-1</sup>) shows a further absorption decrease between 1 ps and 70 ps.

(ii) Two *trans*-azobenzene bands are clearly observed in the late (70 ps) spectrum ( $\nu_{19b}$ , 1454 cm<sup>-1</sup> and  $\nu_{19a}$ , 1484 cm<sup>-1</sup>). However, these bands are absent in the earlier difference spectra. Instead of them, three pronounced new bands peaked at 1431 cm<sup>-1</sup>, 1466 cm<sup>-1</sup>, and 1491 cm<sup>-1</sup> are observed. They exhibit large bandwidths in the order of 10–20 cm<sup>-1</sup>. These new bands (which will be called "hot-bands" throughout the paper) are most pronounced in the 1 ps spectrum and start to decay in the 10 ps spectrum. In combination with a decay of intensity of these bands, a shift to higher frequencies can be recognized in particular for the band at 1466 cm<sup>-1</sup> between 1 ps and 10 ps.

Kinetic absorption data are shown in Fig. 3 for several selected frequency positions (marked by arrows in Fig. 2):

In Fig. 3(a), a measurement close to the peak position of an absorption line of the reactant *cis*-azobenzene ( $\nu_{19a}$ , 1481 cm<sup>-1</sup>) is shown. Immediately after electronic excitation, a strong bleach of this band due to the disappearance of *cis*azobenzene is observed. At later delay times, the bleach recovers [see also the transient difference spectra in Fig. 2(a)]. However, two temporal phases may be identified for this



FIG. 3. The temporal evolution of the absorption changes at three selected spectral positions [marked by arrows in Fig. 2(a)]: (a)  $1481 \text{ cm}^{-1}$ : refill of the bleach of a cold *cis*-azobenzene absorption line; (b)  $1456 \text{ cm}^{-1}$ : formation of a cold *trans*-azobenzene absorption line; (c)  $1466 \text{ cm}^{-1}$ : decrease of a hot-band of both *cis*- and *trans*-azobenzene.

process: While between 1 ps and 10 ps, a small additional absorption decrease is observed, the refill of the bleach proceeds only between 10 ps and 70 ps.

In Fig. 3(b), data measured at the peak position of an absorption band of the photoproduct *trans*-azobenzene ( $\nu_{19b}$ , 1456 cm<sup>-1</sup>) are presented showing the formation of this band. Again, two temporal phases may be found: Starting from a small instantaneous absorption increase, a small absorption decrease between 1 ps and 10 ps is observed followed by a subsequent absorption increase which is finished after ca. 70 ps.

In Fig. 3(c), data at the peak position of the strongest positive absorption line of the 1 ps difference spectrum are presented (1466 cm<sup>-1</sup>). At this frequency, neither cold *cis*-nor the cold *trans*-azobenzene absorbs. A relatively large instantaneous absorption rise is observed here which vanishes in about 70 ps. For this curve, a monotone decay is obtained which, however, cannot be fit satisfactorily by using one single exponential function. The best biexponential fit yields 1 ps and 20 ps as decay time constants (solid line). At 1471 cm<sup>-1</sup>, only 5 cm<sup>-1</sup> at higher frequencies and still within the hot-band, a biphasic behavior is evident again (data not shown): Here, the absorption increase stays almost constant between 1 and 10 ps, but most of the decrease of the signal is observed between 10 ps and 70 ps [see also Fig. 2(a)].

The solid curves shown in Fig. 3 were obtained by fitting

the data with a sum of two exponential functions. However, it shall be noted that these fit curves should be understood only as a smoothed representation of the experimental data since the values obtained from the fit algorithm certainly are unphysical, in particular for the data shown in Fig. 3(a) and (b). The fit algorithm yields two almost identical time constants (4 ps and 6 ps) with unphysical large fit amplitudes with opposite signs, indicating that modeling the experimental data with the help of exponential functions is not adequate. An explanation of this phenomenon will be given in the next section.

#### **III. THEORY**

As long as the vibrational spectrum of a molecule is described in the harmonic approximation, no absorption changes are expected in a transient vibrational spectrum when exciting a vibrational mode from the ground state to a vibrationally excited state. This is a consequence of the properties of the quantum mechanical harmonic oscillator: (i) The energy spectrum is equidistant, i.e., the frequency of the ground state transition  $n=0 \rightarrow n=1$  and that of a higher transition  $n\rightarrow n+1$  are identical. (ii) The absorption cross section  $A(n\rightarrow n+1)$  of a vibrationally excited mode increases linearly with (n+1).<sup>40</sup> However, on the other side, stimulated emission gives rise to a negative contribution  $-A(n\rightarrow n-1)$  which increases linearly with n, i.e., the sum of both contributions is independent on n and does not change with the level of excitation.

The anharmonicity of the molecule gives rise to anharmonic frequency shifts and consequently is responsible for detectable difference bands. Therefore, the anharmonicity is essential to understand the IR spectrum of a vibrationally excited molecule. Therefore, the formalism of the anharmonic constants shall be briefly reviewed in the following (for more details, see, for example, Refs. 42–46): The energy states of a molecule (without degenerate modes<sup>47</sup>) including the anharmonic corrections can be expressed as<sup>42,46</sup>

$$E/\hbar = \sum_{i} \omega_{i}(n_{i}+1/2) + \sum_{i \leq j} x_{ij}(n_{i}+1/2)(n_{j}+1/2).$$
(1)

 $\omega_i$  is the harmonic frequency of the *i*th mode,  $n_i$  the level of excitation of this mode, and  $x_{ij}$  are the anharmonic constants which can be expressed in terms of the cubic and quartic force constant in a normal coordinate basis. Equation (1) describes the system in the harmonic approximation (i.e., in the formalism of eigenfrequencies and eigenmodes), while the anharmonicity is treated by perturbation theory. One can derive the transition frequency of a selected mode *k* coupled to the bath of the remaining modes  $i \neq k$ :

$$\nu(n_k \to n_k + 1) = \nu_k + 2x_{kk}n_k + \sum_{i \neq k} x_{ik}n_i, \qquad (2a)$$

where the first term

ı

$$\nu_k = \omega_k + 2x_{kk} + \sum_{i \neq k} x_{ik}/2 \tag{2b}$$

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is the anharmonic correction of the  $n_k=0 \rightarrow n_k=1$  transition in the vibrational ground state, i.e., in the cold molecule. The second (diagonal) term of Eq. (2a) describes the anharmonic shifts of an excited vibrational mode k, and the third term describes the frequency shifts due to the off-diagonal anharmonicity between the selected mode k and the remaining bath modes.

In the following, an expression describing the shape of an absorption line  $A_k(\omega)$  of one selected vibrational mode k is derived. In a first step, the off-diagonal constants terms in Eq. (2a) are neglected. The cross section for absorption and stimulated emission are modeled in the harmonic approximation (see above). According to the "Golden Rule," one obtains:

$$A_{k}(\omega) \propto \sum_{n_{k}=0}^{\infty} (\alpha(n_{k}) - \alpha(n_{k}+1))(n_{k}+1)$$
$$\times \delta(\omega - \nu_{k} - 2x_{kk}n_{k}).$$
(3a)

 $\alpha(n_k)$  is a given population distribution of the mode k with normalization  $\sum_{n_k} \alpha(n_k) = 1$ .  $\delta$  is the delta function which later will be replaced by a line shape function with finite bandwidth. The first term  $+ \alpha(n_k)$  in Eq. (3a) describes the absorption between the states  $n_k \rightarrow n_k + 1$  (depending linearly on  $n_k + 1$ ), while the second term  $-\alpha(n_k + 1)$  is responsible for the stimulated emission between the states  $n_k + 1 \rightarrow n_k$ (again depending linearly on  $n_k + 1$ ).

When taking into account vibrational excitation of the bath modes, the energy spectrum  $A_k(\omega)$  is further shifted according to the off-diagonal constants in Eq. (2a):

$$A_{k}(\omega) \propto \sum_{n_{k}} \left[ (\alpha(n_{k}) - \alpha(n_{k} + 1))(n_{k} + 1) \right] \times \sum_{\substack{n_{1}, \dots, n_{j}, \dots, n_{m} \\ j \neq k}} \left[ \left( \prod_{i \neq k} \alpha(n_{i}) \right) \right] \times \delta \left( \omega - \nu_{k} - 2x_{kk}n_{k} - \sum_{i \neq k} x_{ik}n_{i} \right) \right].$$
(3b)

*m* is the number of vibrational modes and the  $\alpha(n_i)$  the population distribution functions for all bath modes  $i \neq k$ , again with normalization  $\sum_{n_i} \alpha(n_i) = 1$ . This expression models the absorption band by taking into account all possible transition frequencies of Eq. (2a) and weighting each individual line by its probability  $\prod_{i \neq k} \alpha(n_i)$ .

Equation (3b) models the line shape in a static picture, i.e., it describes a cw-absorption spectrum of the sample. It will be seen later that the shape of the absorption line changes on a time scale of several picoseconds due to the cooling process. A dynamic picture considering the polarization of the vibrational transition would be required (in analogy to Refs. 26 and 27) when faster processes would be investigated. However, for the time scales discussed here, the static description should be a reasonable approximation. Finally, it shall be noted that an alternative description based on the so-called exchange theory modeling the temperature dependent shape of an absorption line was reported in Refs. 48–50.

When the frequencies  $\nu_k$  and the anharmonic constants  $x_{ik}$  are all known, the shape of a vibrational transition can be evaluated for given population distributions of the observed mode k ( $\alpha(n_k)$ ) and the bath modes  $i \neq k$  ( $\alpha(n_i)$ ). While the  $\nu_k$  are measurable and can be computed with reasonable precision, the determination of the anharmonic constants still is a real challenge, from an experimental as well as from a theoretical point of view. They are, at least in principle, measurable when a complete set of overtone and combination bands is known. However, in a molecule as large as azobenzene, this will be an impossible task since the assignment of the enormous number of very weak combination modes certainly would fail. In order to calculate the anharmonic constants  $x_{ik}$ , it is necessary to derive the Taylor expansion of the ground state potential surface to fourth order with high precision.<sup>42–45</sup> Consequently, no anharmonic constants have been determined for azobenzene. Therefore, a different approach has to be adopted here: In a first step, the effects of the anharmonicity are analyzed by using realistic anharmonic constants of a large molecule. A complete set of anharmonic constants exists for benzene,<sup>44</sup> which was calculated on an ab initio MP2 level. Since two of the experimentally observed vibrational modes are the phenyl ring modes of azobenzene, it is justified to use the anharmonic constants of benzene for an first order estimate of the anharmonic effects in azobenzene. In a second step, a direct comparison between the model calculation and the experimental data will be discussed using estimated anharmonic constants.

#### A. Model calculations

In the following, two simulations of the transient IR spectrum will be discussed assuming two limiting cases: (i) ultrafast IVR and (ii) slow (compared to our time resolution) IVR. The calculations address the question whether ultrafast vibrational spectroscopy is able to distinguish between IVR (i.e., thermalization within the molecule itself) and the intermolecular energy relaxation (i.e., the energy transfer from the molecule to the solvent).

#### 1. Ultrafast IVR

In the first limiting case, it is assumed that the excess energy is redistributed over the molecule in a very short time (<1 ps) while intermolecular energy transfer, i.e., cooling, is considerably slower. In this case, the molecule may be viewed initially as an isolated system and an internal temperature of the molecule can be determined after the IVR process. At later delay times, intermolecular energy transfer between the solute and the solvent leads to a decrease of the temperature of the molecule. An upper limit of the initial temperature can be estimated: When taking into account a thermal Bolzmann distribution, the initial temperature of the molecule is determined according to

$$E_{\rm ph} = \sum_{i} \frac{\hbar \omega_i}{1 - \exp(-\hbar \omega_i / kT)} - E(T_0). \tag{4}$$



FIG. 4. Simulated shape of the  $\nu_{19}$  mode of benzene at different temperatures according to the anharmonic constants reported in Ref. 44. Frequency shift is plotted relative to the frequency of  $\nu_{19}$  in the cold molecule (0 K). (a) Absorption spectrum A(T); (b) difference spectrum  $\Delta A(T) = A(T) - A(300 \text{ K})$ .

 $E_{\rm ph}$  is the energy of the exciting photon,  $E(T_0)$  the energy content of the molecule at room temperature, and *i* numbers all vibrational modes of the molecule with frequency  $\omega_i$ . Assuming a thermal Bolzmann distribution for the population distribution functions  $\alpha(n_k)$  for a selected mode k and  $\alpha(n_i)$  for the intramolecular bath modes, a temperature dependent shape of the absorption line of this mode k can be calculated. This was done for the  $v_{19}$  mode of benzene using the harmonic frequencies and anharmonic constants reported in Ref. 44. The  $\nu_{19}$  mode was selected since this mode is directly related to the investigated vibrational modes in azobenzene. In order to account for a limited spectral resolution (for example, due to a homogeneous or inhomogeneous broadening of the transition or due to the limited experimental resolution), the calculated curves are subsequently convoluted with a Gaussian line shape function with a FWHM of 2 cm<sup>-1</sup>. The results are shown in Fig. 4 starting at room temperature (300 K) and continuing with several higher temperatures up to 1150 K. The latter value corresponds to the situation where the total photon energy is dissipated over all vibrational modes of azobenzene (frequencies as reported in Ref. 39; two normal modes reported with negative frequencies in Ref. 39 are set to  $+10 \text{ cm}^{-1}$ ). In Fig. 4(a), the absolute absorption spectra A(T) are shown while in Fig. 4(b), the difference signals  $\Delta A(T) = A(T) - A(300 \text{ K})$ are plotted. The spectra in Fig. 4(a) correspond to the observation during the formation and cooling of an absorption line of a photoproduct (i.e., a species which is not present prior to excitation), while the plots of Fig. 4(b) correspond to the transient IR-difference spectra for the vibrational mode of the reactant. Both sets of spectra are presented (although essentially carrying the same information) since they are directly related to the situation in the experiment where absorption lines of trans-azobenzene (formation of a photoproduct) and cis-azobenzene (vibrational cooling of the reactant) are involved. At 300 K, only a minor frequency shift ( $\approx -0.05$  cm<sup>-1</sup>) compared to the zero-temperature position (origin of the x axis) is observed. However, at 400 K a larger frequency shift in the order of -0.15 cm<sup>-1</sup> is found which increases considerably at higher temperatures and reaches a value of  $-5 \text{ cm}^{-1}$  at 1150 K. In addition, a strong asymmetric broadening of the band is observed for higher temperatures. Since almost all of the anharmonic constants  $x_{i,19}$  are negative, the peak position of the line is shifted to smaller frequencies. It is important to note that the main contribution to the anharmonic effects is due to the offdiagonal anharmonic constants  $x_{ik}$ ,  $i \neq k$ , in particular to those to the low-frequency modes, and not due to the diagonal term  $2x_{kk}$ . This becomes evident when one considers (i) that even at the highest temperature used in this simulation, the excitation probability of the  $\nu_{19}$  mode is only  $\approx 15\%$ , (ii) that the diagonal harmonic constant  $(2x_{19,19} = -1.8 \text{ cm}^{-1})$  is comparably small, and (iii) that the sum of the off-diagonal elements of all low-frequency modes (which are excited considerably at this temperature and therefore, are responsible for the anharmonic effect) is much larger than the diagonal term (a value of  $\sum x_{i,19} = -21 \text{ cm}^{-1}$  is obtained when taking into account all modes with frequencies smaller than that of  $\nu_{19}$ ). The monotone behavior of the frequency shift and line broadening with temperature allows an interesting application of this phenomenon: The measurements of the absorption spectra can be used as a molecular thermometer for the intrinsic temperature of the solute molecule (see also below).

Model calculations simulating a kinetic experiment at several distinct frequency positions (marked by arrows in Fig. 4) are shown in Fig. 5, again for both situations of Fig. 4 [Fig. 5(a): A(T(t)), Fig. 5(b):  $\Delta A(T(t)) = A(T(t))$ -A(300 K)]. In the modeling it was assumed that the temperature T(t) decreases exponentially from 1150 K to 300 K with a time constant of 20 ps (see dotted line).<sup>51</sup> Interestingly, the absorption response does not behave exponentially. The deviation from an exponential behavior is most evident at a frequency position of  $-2 \text{ cm}^{-1}$ , i.e., at the lowfrequency tail of the absorption line of the cold molecules: Here, two phases are observed, starting with an initial absorption rise followed by a subsequent absorption decrease. This response is a consequence of the interplay between the temperature dependent band broadening and the frequency shift.

The previous model calculations were obtained by using one special mode of benzene. However, there are arguments that the presented features and conclusions are general: The anharmonic frequency shifts and broadening effects are accumulated effects depending not so much on the actual anharmonic constants  $x_{ik}$  of each specific bath mode but rather on the average of all constants (weighted with its contribution according to the Bolzmann factor of each individual mode). Even when using one fixed value x for all anharmonic constant  $x_{ik}$ , very similar results are obtained besides



FIG. 5. Simulation of a kinetic experiment at several selected frequency positions (marked by arrows in Fig. 4). Solid lines: Absorption changes (left axis); dotted line: underlying temperature dependence (right axis) which was assumed to be exponential. (a) Absorption spectrum A(T); (b) difference spectrum  $\Delta A(T) = A(T) - A(300 \text{ K})$ .

a smaller broadening effect. In this simple case, the frequency shift depends linearly on this fixed value.

In the next step, the results of a model calculation adopted directly to the time resolved difference spectra of azobenzene are presented (see Fig. 6 and Fig. 7). The following model assumptions were used:

The spectra were calculated for a fully thermalized energy distribution. Consequently, an intramolecular temperature can be assigned to each spectrum (960 K: open circles; 720 K: gray squares; 320 K: filled triangles). These temperatures are obtained at a delay time of 1 ps, 10 ps, and 70 ps if a time constant of 20 ps for the decay of the intramolecular temperature from 1000 K to 300 K is assumed. In this sense, the model spectra of Fig. 6 may be directly compared with the experimental data shown in Fig. 2(a). The initial temperature 1000 K is taken somewhat smaller than the maximal value of 1150 K calculated from Eq. (4), since a fraction of the excitation energy probably is transferred to the solvent immediately during the initial large amplitude motion of the molecule.

The frequencies, intensities, and bandwidths of both the *cis*- and the *trans*-modes in the cold molecule were obtained from a multi-Gaussian fit of the absolute spectra in Fig. 1.

The method of calculation is identical to that used in Fig. 4 summing up all investigated vibrational modes. The difference spectra are a superposition of three contributions

$$\Delta A_{\text{tot}}(T) = \eta A_{trans}(T) + (1 - \eta) A_{cis}(T) - A_{cis}(300 \text{ K}).$$
(5)

 $\eta$ =0.5 is the isomerization quantum yield,  $A_{trans}(T)$  is the contribution from the hot *trans*-azobenzene molecules,



FIG. 6. (a) Model calculation simulating the transient spectra of azobenzene assuming a thermal energy distribution and an exponential decrease of temperature from 1000 K to 300 K with a time constant of 20 ps. Open circles: 960 K (corresponds to 1 ps); gray squares: 720 K (corresponds to 10 ps); filled triangles: 320 K (corresponds to 70 ps). This plot may be directly compared to the experimental data of Fig. 2. (b) Simulation of the temporal evolution at 1456 cm<sup>-1</sup> [see arrow in (a)]. This plot may be directly compared to the experimental data of Fig. 3(b).

 $A_{cis}(T)$  the contribution from the hot *cis*-azobenzene molecules, and  $A_{cis}(300 \text{ K})$  the bleaching ground state contribution.

The frequencies of all coupled bath modes were used as reported in Ref. 39.

As mentioned before, no anharmonic constants are known for azobenzene. Consequently, in a simplified model they are assumed to be equal for all investigated high-frequency modes  $x_{ik} = x_i$ . In addition, a linear dependence of the anharmonic constant  $x_i$  on the frequency of bath mode *i* is assumed, in approximate agreement with the numbers reported for benzene in Ref. 44:

$$x_{ik} = x_i = x \cdot \omega_i \,. \tag{6}$$

Consequently, only one model parameter x remains which is estimated from a separate FTIR experiment measuring the absolute spectrum of *trans*-azobenzene (solved in DMSO) in a heated cuvette: The absorption spectra recorded between 300 K and 400 K yielded a relative frequency shift of  $\approx -1$ cm<sup>-1</sup> for both phenyl ring modes. x is adjusted to reproduce this frequency shift. A value of  $x = 0.9 \times 10^{-3}$  is obtained in good agreement with the corresponding averaged value of



FIG. 7. Simulated shape of the  $\nu_{19}$  mode of benzene for non-thermal energy distributions for this mode (broken line, dotted line, broken-dotted line, for details see text) compared with the fully thermalized 800 K spectrum of Fig. 4 (solid line). (a) Assumed population density of mode  $\nu_{19}$ ; (b) resulting absorption spectrum A(T); (c) resulting difference spectrum  $\Delta A(T) = A(T) - A(300 \text{ K})$ .

 $1.3 \times 10^{-3}$  for the  $\nu_{19}$  mode of benzene. This procedure might be viewed as a first calibration of the intramolecular thermometer.

Qualitatively, the model spectra [Fig. 6(a)] and the experimentally obtained transient difference spectra (Fig. 2) are in excellent agreement. All observed spectral features, i.e., the refill of the bleached ground state *cis*-bands, the late rise of the product state bands, the decay, and the blue shift of the hot-bands, are well reproduced by the model. Also, the non-exponential, biphasic time dependence is well reproduced: The simulation of a kinetic experiment in Fig. 6(b) at the peak of the  $\nu_{19a}$  mode of *trans*-azobenzene [arrow in Fig. 6(a)] may be directly compared with the experimental data of Fig. 3(b). In this case, the biphasic behavior is caused by the contribution of two different modes: The initial absorption decrease is due to the early narrowing of the  $\nu_{19a}$  mode, while the subsequent absorption rise is due to the formation of the cold  $\nu_{19b}$  mode.

This analysis shows that the presented model is able to qualitatively describe the experimental data. However, due to the lack of more detailed model parameters (i.e., a complete set of reliable anharmonic constants) we did not attempt to fit the model function to the experimental data. In particular, the experimentally observed band broadening is larger than predicted by the model, most probably due to the simplifying assumption for the anharmonic constants.

### 2. Slow IVR and selective excitation of a distinct vibrational mode

It was shown in the previous section that in the case of a fully thermalized molecule, the off-diagonal anharmonic constants dominate the anharmonic effects. On the other hand, assuming a selective, highly nonthermal excitation of one selected mode, the diagonal anharmonic terms  $x_{kk}$  may also become important. Three limiting cases shall be discussed in the following. Again the  $v_{19}$  mode of the benzene molecule will be treated where realistic anharmonic constants are known.<sup>44</sup> Shown in Fig. 7(a) are different distribution functions  $a(n_k)$  of the  $v_{19}$  mode, Fig. 7(b) presents the corresponding absorption spectra A; and Fig. 7(c) the resulting difference spectra  $\Delta A = A - A(300 \text{ K})$ .

In a first unrealistic limiting case only the  $v_{19}$  mode is highly excited, while the remaining bath modes are vibrationally cold, i.e., in the ground state. Figure 7(b) and (c) (broken line) shows the absorption changes for a Gaussian population distribution  $a(n_k)$  centered around the  $n_k=3$ level with a width of  $\Delta n_k=2$  [see Fig. 7(a), broken line]. The most pronounced feature is a negative signal around  $\Delta \omega = 0$  which is a consequence of the population inversion giving rise to stimulated emission.

As a second model distribution, a much more realistic situation is discussed: It is assumed that a selected mode is excited according to a nonthermal one quantum excitation [Gaussian function centered at  $n_k=1$ , width  $\Delta n_k=1$ ; see Fig. 7(a) dotted line] and that this mode is coupled to the bath of the remaining modes which are thermally excited according to a Boltzmann distribution (a temperature of 800 K is used as an example). The result is shown in Fig. 7(b) and (c) as dotted lines. Again, a negative signal due to the  $1\rightarrow 0$ -population inversion can be seen [Fig. 7(b)] which now is less pronounced. In particular in the case of the situation shown in Fig. 7(c), it will be difficult to resolve the stimulated emission signal experimentally since the bleaching cold molecule contribution also gives rise to an additional strong negative signal.

A more moderate nonequilibrated population distribution without population inversion, i.e., which does not give rise to stimulated emission, is obtained when assuming that the  $\nu_{19}$  mode has a higher temperature (1600 K) than the bath modes (800 K). However, this situation (Fig. 7, brokendotted line) yields a spectrum very similar to a pure thermal distribution where the  $\nu_{19}$  mode as well as the bath modes both have the same temperature of 800 K (Fig. 7, solid line). An experimental distinction between both situations requires very accurate experimental data and a good knowledge of the anharmonic constants.

A direct comparison of the slow IVR model situation with the experimental results (as it was done before in Sec. III A 1) is not possible since there are too many unknown model parameters, i.e., the population distributions  $\alpha(n_i)$  of both the observed high-frequency modes and the anharmonically coupled low-frequency bath modes. Yet, one important conclusion is possible: As seen from Fig. 7, a stimulated emission signal would be a clear indication for a strong nonthermal energy distribution which, however, is not observed experimentally for azobenzene. Thus, at least a strong deviation from a thermal energy distribution can be excluded for the observed vibrational modes, although the absence of a stimulated emission signal cannot show that the molecule is fully thermalized.

#### **IV. CONCLUSION**

As seen in Fig. 6, the results on azobenzene can be explained without contradiction under the assumptions of a thermal population distribution of the molecule in the investigated time range of >1 ps. There is no experimental evidence for a stimulated emission signal which would be indicative of a highly nonthermal energy distribution. Thus, a strong deviation from a thermal distribution of these vibrational modes seems to be very unlikely in terms of the present model. On the other hand, the model involving ultrafast IVR explains the observed hot-bands with the help of the anharmonic constants  $x_{ii}$  between the investigated vibrational modes and the bath of the remaining modes very well. Consequently, one basically observes the cooling of the whole molecule due to the energy transfer from the molecule to the solvent and not a mode selective de-excitation of the investigated modes. The time scale of the cooling via intermolecular energy transfer (ca. 20 ps) is in a reasonable range<sup>3,4</sup> and compares well with the results of the transient UV experiments in Ref. 37. The anharmonic frequency shifts and broadening effects are a consequence of the intramolecular temperature and can be regarded as a intramolecular thermometer which can be calibrated precisely with the help of model calculations and also with steady-state experiments.

A clear distinction between thermal and a moderate nonthermal energy distribution presently is not possible. In other words, the concept of an intramolecular temperature eventually is a rough approximation. However, since this approximation readily can explain the experimental results as shown in Sec. III A 1, this approach seems to be justified.

During the electronic excitation process, the Franck– Condon active modes are excited, which may be observed by transient Raman experiments. On the other hand, the transient IR experiments performed here investigates the "bath" modes which may have a different equilibration time than the hot Franck–Condon modes.

The attempt to explain anharmonic frequency shifts only with the diagonal anharmonic constants  $x_{kk}$  which are obtained when measuring the frequency of the overtone (as it was done, for example, in Refs. 13, 16, 17, and 19) does not explain the investigated experimental situation. Such a treatment will give reasonable results only in the special situation where the sum of the off-diagonal elements is smaller than the diagonal element, i.e., (i) for very small molecules, (ii) for a special mode with extremely large diagonal anharmonic constant term, or (iii) when energy flows selectively into only one or very few modes. Without a clear stimulated emission signal, an unambiguous assignment of an anharmonic frequency shift to a nonthermal selective excitation of one vibrational mode will be difficult. It is interesting to note that not necessarily very particular and strongly coupled modes like the central bending and torsional modes of azobenzene or stilbene (see, for example, Ref. 13) are responsible for strong anharmonic effects. Also a great number of only weakly coupled modes may give rise to considerable effects, as shown here in the case of the rather rigid benzene molecule. This is seen from the fact that the averaged value of the anharmonic constants of the  $v_{19}$  mode of benzene  $(1.3 \times 10^{-3})$  is of the same order (even slightly larger) than the estimated corresponding value necessary to reproduce the experimental results in azobenzene  $(0.9 \times 10^{-3})$ .

In conclusion, we have demonstrated here the concept of a new intermolecular thermometer. The experimental data obtained by transient IR spectroscopy combined with model calculations give valuable qualitative insights into the effects which can be expected when investigating the excitation of vibrational modes initiated by a photoreaction. Future investigations going beyond this qualitative approach require several improvements: (i) A higher time resolution on the order of ca. 100 fs; (ii) smaller systems which can be modeled theoretically with higher accuracy; (iii) selected vibrational modes which, on the one side, have a large diagonal anharmonic constant and on the other side, are strongly coupled to the internal conversion process; and (iv) an extension of the frequency range into the  $<1000 \text{ cm}^{-1}$  regime in order to address for example torsional modes (found in this spectral range) which might be expected to be strongly coupled modes.

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- <sup>1</sup>A. Lauberreau and W. Kaiser, Rev. Mod. Phys. **50**, 607 (1978).
- <sup>2</sup>D. W. Oxtoby, Annu. Rev. Phys. Chem. **32**, 77 (1981).
- <sup>3</sup>A. Seilmeier and W. Kaiser, in *Ultrashort Laser Pulses*, edited by W. Kaiser (Springer-Verlag, New York, 1988), p. 279.
- <sup>4</sup>T. Elsaesser and W. Kaiser, Annu. Rev. Chem. Phys. 42, 83 (1991).
- <sup>5</sup>J. C. Owrutsky, D. Raftery, and R. M. Hochstrasser, Annu. Rev. Phys. Chem. **45**, 519 (1994).
- <sup>6</sup>R. Sension, S. Repinec, A. Szarka, and R. M. Hochstrasser, J. Chem. Phys. **98**, 6291 (1993).
- <sup>7</sup>K. Lenz, M. Pfeiffer, A. Lau, and T. Elsaesser, Chem. Phys. Lett. **229**, 340 (1994).
- <sup>8</sup>W. Zinth, C. Kolmeder, B. Benna, A. Irgens-Defregger, S. F. Fischer, and W. Kaiser, J. Chem. Phys. **78**, 3916 (1983).
- <sup>9</sup>S. J. Doig, P. J. Reid, and R. A. Mathies, J. Phys. Chem. **95**, 6372 (1991).
   <sup>10</sup>W. L. Weaver, L. A. Hutson, K. Iwata, and T. L. Gustafson, J. Phys. Chem. **96**, 8956 (1992).
- <sup>11</sup>K. Iwata and H. Hamaguchi, Chem. Phys. Lett. 196, 462 (1992).
- <sup>12</sup>J. Qian, S. L. Schultz, R. G. Bradburn, and J. M. Jean, J. Phys. Chem. 97, 10638 (1993).
- <sup>13</sup>D. L. Phillips, J. M. Rodier, and A. B. Myers, Chem. Phys. 175, 1 (1993).

- <sup>14</sup>M. Hofmann and H. Graener, Chem. Phys. **206**, 129 (1996).
- <sup>15</sup> J. C. Owrutsky, Y. R. Kim, M. Li, M. J. Sarisky, and R. M. Hochstrasser, Chem. Phys. Lett. **184**, 368 (1991).
- <sup>16</sup>P. O. Stoutland, R. B. Dyer, and W. H. Woodruff, Science 257, 1913 (1992).
- <sup>17</sup> S. K. Doorn, R. B. Dyer, P. O. Stoutland, and W. H. Woodruff, J. Am. Chem. Soc. **115**, 6398 (1993).
- <sup>18</sup>D. Raftrey, E. Gooding, A. Romanovsky, and R. M. Hochstrasser, J. Chem. Phys. **101**, 8572 (1994).
- <sup>19</sup>T. Lian, S. E. Bromberg, H. Yang, M. Asplund, R. G. Bergmann, and C. B. Harris, in *Ultrafast Phenomena X*, OSA Technical Digest Series, Vol. 8, Paper FE-27 (Optical Society of America, Washington, DC, 1996).
- <sup>20</sup> J. Owrutsky and A. Baonavskiu, in *Ultrafast Phenomena X*, OSA Technical Digest Series, Vol. 8, Paper PDP-4 (Optical Society of America, Washington, DC, 1996).
- <sup>21</sup>P. A. Anfinrud, C. H. Han, T. Lian, and R. M. Hochstrasser, J. Phys. Chem. **95**, 574 (1991).
- <sup>22</sup>P. Hamm, C. Lauterwasser, and W. Zinth, Opt. Lett. 18, 1943 (1993).
- <sup>23</sup>P. Hamm, S. Wiemann, M. Zurek, and W. Zinth, Opt. Lett. **19**, 1642 (1994).
- <sup>24</sup> T. P. Dougherty and E. J. Heilweil, Opt. Lett. **19**, 129 (1994).
- <sup>25</sup>F. Seifert, V. Petrov, and M. Woerner, Opt. Lett. 19, 2009 (1994).
- <sup>26</sup>P. Hamm, Chem. Phys. **200**, 415 (1995).
- <sup>27</sup> K. Wynne and R. M. Hochstrasser, Chem. Phys. **193**, 211 (1995).
- <sup>28</sup>T. Uzer and W. H. Miller, Phys. Rep. **199**, 73 (1991).
- <sup>29</sup>R. Schneider, W. Domcke, and H. Köppel, J. Chem. Phys. **92**, 1045 (1990).
- <sup>30</sup>L. Seidner and W. Domcke, Chem. Phys. **186**, 24 (1994).
- <sup>31</sup>G. Stock, J. Chem. Phys. **103**, 10 015 (1995).
- <sup>32</sup>T. Ikeda and O. Tsutsumi, Science **268**, 1873 (1995).
- <sup>33</sup> H. Rau, in *Photochromism: Molecules and Systems*, edited by H. Durr and H. Bouas-Lauran (Elsevier, Amsterdam, 1990), p. 165.
- <sup>34</sup>N. Siampiringue, G. Guyot, S. Monti, and P. Bortolus, J. Photochem. 37, 185 (1987).
- <sup>35</sup>R. Cimiraglia and H. J. Hofman, Chem. Phys. Lett. 217, 430 (1994).

- <sup>36</sup>N. Biswas and S. Umupathy, Chem. Phys. Lett. **236**, 24 (1995).
- <sup>37</sup>J. Wachtveitl, T. Nägele, B. Puell, W. Zinth, M. Krüger, S. Rudolph-Böhner, D. Oesterhelt, and L. Morode, Photochem. Photobiol. (in press); T. Nägele, W. Gable, W. Zinth, and J. Wachtveitl (in preparation).
- <sup>38</sup> R. Kübler, W. Lüttke, and S. Weckherlin, Z. Elektrochem. **64**, 650 (1960).
   <sup>39</sup> D. R. Armstrong, J. Clarkson, and W. E. Smith, J. Phys. Chem. **99**, 17 825 (1995), and references therein.
- <sup>40</sup>E. B. Wilson, J. C. Decius, and P. C. Cross, in *Molecular Vibrations* (Dover, New York, 1955).
- <sup>41</sup>T. Lian, Y. Kholodenko, B. Locke, and R. M. Hochstrasser, J. Phys. Chem. 99, 7272 (1995).
- <sup>42</sup>H. H. Nielsen, Rev. Mod. Phys. 23, 90 (1951).
- <sup>43</sup>J. Pliva, J. Mol. Spect. **139**, 278 (1990).
- <sup>44</sup> P. E. Maslen, N. C. Handy, R. D. Amos, and D. Jayatilaka, J. Chem. Phys. 97, 4233 (1992).
- <sup>45</sup>A. Willettsm and N. C. Handy, Chem. Phys. Lett. 235, 286 (1995).
- <sup>46</sup>G. Herzberg, in *Molecular Spectra and Molecular Structure*. II. Infrared and Raman Spectra of Polyatomic Molecules (Van Nostrand Reinhold, New York, 1945).
- <sup>47</sup> In a more general form, Eq. (1) contains additional terms taking into account the degeneracy and the vibrational angular momumentum quantum numbers of the vibrational modes. Since azobenzene has no degenerate modes these terms can be omitted.
- <sup>48</sup>R. M. Shelby, C. B. Harris, and P. A. Cornelius, J. Chem. Phys. **70**, 34 (1979).
- <sup>49</sup>C. B. Harris, H. Auweter, and S. M. George, Phys. Rev. Lett. 44, 737 (1980).
- <sup>50</sup>C. B. Harris, R. M. Shelby, and P. A. Cornelius, Phys. Rev. Lett. **38**, 1415 (1977).
- <sup>51</sup>The description of the time dependence of the temperature by an exponential function is a simple model assumption which may not be justified in realistic cases. However, it is used as a reasonable assumption in the present case where it will be shown that the transient absorption changes may have a time response completely different from the time dependence of the temperature.