The chain propagation reaction is explained with a model which is in most parts identical with the model proposed to describe the self sensitization effects of the diacetylene photopolymerization [16]. The similarity of the action spectra of photocurrent and chain propagation reaction in partly polymerized multilayers indicates that the optical excitation of the oligomer band-to-band transition leads to free charge carriers, which activate the chain end region and result in an addition reaction.

Two mechanisms are possible: firstly a transition from a nonreactive to a reactive chain end and secondly a charge carrier relaxation at the chain end with subsequent generation of vibronic states.

The only difference between the self sensitization and the sensitization with cyanine dyes is the origin of the photoelectron.

This model of the chain propagation reaction can explain the high yield of polymer which was found to be independent of the dye concentration and the large sensitization volume described in section 4.2.

However, is should be mentioned that there are still some unanswered questions concerning the electronic structures of the chain ends, which should enable charge carrier recombination and the generation of vibronic states.

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Fast Reaction Rates in IR-Photochemistry: $c-C_4F_8 \rightarrow 2C_2F_4$

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Absorptionsspektren, Infrarot / Photochemie / Reaktionskinetik / Vielphotonenanregung

Quantitative experimental results are reported for the photo-decomposition of octafluorocyclobutane under irradiation with intense, monochromatic light from a pulsed TEA-CO₂-laser in the range of the v_{21} fundamental near 963 cm⁻¹. The IR-photochemical rate coefficient is found to be

$$k(st) = 10^{6.3 \pm 0.3} (I/MW \text{ cm}^{-2}) \text{ s}^{-1}$$

for irradiation with P 8 at 954.6 cm⁻¹, close to the optimum frequency. It is shown that the intensity dependence is linear to a good approximation by comparing irradiation with intense self-mode-locked pulse trains and smooth single mode pulses of low peak intensity, generated by means of an intracavity absorber. Results on the frequency dependence and upon the influence of inert gas pressure in the IR-photochemistry of C_4F_8 are reported. The experimental results are found to compare well with theoretical predictions based on a Pauli equation treatment and simple models for the rate coefficient matrix.

1. Introduction

Many important chemical reactions are so fast that a direct, accurate, time resolved observation of reactant and product concentrations is difficult, if not impossible. Therefore methods have been developed, which allow for an indirect determination of fast reaction rates. As an example in photochemistry we may quote Weller's early observation of fast proton transfer reactions in electronically excited states, using

Ber. Bunsenges. Phys. Chem. 86, 504 - 509 (1982) - © Verlag Chemie GmbH, D-6940 Weinheim, 1982. 0005 - 9021/82/0606 - 0504 \$ 02.50/0 the method of fluorescence change, published just thirty years ago [1]. The quantitative determination of essentially diffusioncontrolled rates [2, 3] for these processes was even of a very general interest, since direct methods for measuring such rates in electronic ground states were only being developed then [4]. The method of fluorescence change falls among the competitive methods (rates are measured with respect to the fluorescence lifetime of the excited species). Another well-known example of the quantitative use of the competition between rate processes in photochemistry is, of course, the Stern-Volmer equation [5] and a more recent one the measurement of angular distributions in molecular beam photo-dissociation, where the molecular rotational period provides a "clock" (not always unambiguous) [6].

A different principle for indirectly measuring fast reaction rates relies upon the replacement of time as an independent variable by another, more easily accessible parameter. A simple textbook example are flow reactors, where distance replaces time [7].

A less obvious transformation has recently been shown to allow for quantitative, indirect rate constant measurements for fast reactions in IR-photochemistry, the youngest branch of photochemistry [8]. Samples are irradiated with pulses of a quantitatively defined fluence F (or radiation dose, intensity Iin the MW cm⁻² range, pulse duration $t_p < \mu$ s)

$$F=\int_0^{t_p}I(t)\,\mathrm{d}t.$$

One measures the reactant concentration c_R^* remaining after the irradiation. Under certain conditions it can be shown that the steady state rate coefficient k(st) for the fast IR-photochemical reaction is given by Eq. (1):

$$\lim_{F \to \infty} \left\{ -\frac{\mathrm{d} \ln \left[c_{\mathrm{R}}^{*}(F) / c_{\mathrm{R}}(0) \right]}{\mathrm{d} F} \right\} = k(\mathrm{st}) / I, \qquad (1)$$
$$= k_{I}(\mathrm{st}).$$

This equation is valid for constant intensity or if $k_I(st)$ is approximately constant over the intensity range of interest. This is often the case, giving in the limit a straight line Eq. (1). For a detailed discussion of the fundamental principles of the dynamics of IR-photochemistry, leading to Eq. (1), we refer to [9]. The method for determining rate coefficients in the range 10⁶ to 10⁹ s⁻¹, typically, has been illustrated with some data available from the literature [8]. Unfortunately, in almost all current experiments the fluence F is not sufficiently well defined and we therefore have developed quantitative experimental techniques for the evaluation of k(st) according to Eq. (1) [10, 11].

In the present paper we report rate coefficients for the decomposition of octafluorocyclobutane:

$$c-C_4F_8 \xrightarrow{nh\nu} 2C_2F_4.$$
 (2)

For this reaction only one early, qualitative study was available, which indicated that the decomposition of C_4F_8 is a clean IRphotochemical process [12]. Reactant and product molecules are fairly well characterized with respect to both spectroscopy and thermochemistry and there is a close analogy to the ring opening of tetrafluorodithietane [10], which makes reaction (2) an attractive candidate for a more detailed investigation. We shall also report a new, sensitive technique which allows to check experimentally, whether $k_1(st)$ is independent of intensity.

2. Experimental

Octafluorocyclobutane and perfluoroethylene were obtained from Fluorochem Ltd. and Ventron (Karlsruhe). They were distilled and thoroughly outgassed by freeze-thaw cycles before use. The gaschromatograms did not show any important impurities and the IR-spectra corresponded to the published spectra [13-16]. The samples were irradiated at low gas pressures (typically <15 Pa) with and without N₂ as solvent (pressures between 150 and 3000 Pa). The sample cells were made of stainless steel and of glass (10 and 20 cm long) and were fitted with KCl windows. Reactant decay and product formation were followed by gaschromatography (Silicagel, l = 4 m, 150° C, FID) and mainly by quantitative IR-spectroscopy (Zeiss IMR 25). All our experiments indicated, that reaction (2) proceeds cleanly. The primary yield as a function of fluence is obtained using the Eqs. (3) and (4):

$$\ln (c_{\rm R}^n/c_{\rm R}^0) = n \ln (1-f), \tag{3}$$

$$P_{\rm app.} = f(V_{\rm c}/V_{\rm i}). \tag{4}$$

 c_R^n is the reactant concentration measured after irradiation with *n* laser pulses. These equations are illustrated in Fig. 1 for one typical example. The linearity of the experimental function is consistent with the absence of the interference of product formation with the primary reaction. Whereas *f* is the fraction dissociated per pulse in the entire cell (volume V_c), the apparent yield function P_{app} is arbitrarily normalized to the "irradiated volume" V_I . This is defined via an effective laser beam cross section, which is small compared to the cell diameter, constant over the cell length (parallel irradiation geometry with negligible absorption) but otherwise unimportant for the final evaluation (see below). The absence of any important thermal contribution to the reaction was shown by changing the reactant partial pressure and thus the absorbed energy by a factor of 6, maintaining the total pressure and the heat capacity by an excess of N₂. This has no effect upon the reaction yield, which proves the photochemical nature of the observed reaction [11].



Illustration of the experimental evaluation of P_{app} according to Eqs. (3) and (4) for irradiation of c-C₄F₈ (partial pressure P) with CO₂-laser pulses (number n)

Our TEA-CO₂-laser (Lumonics 103-2) is grating tuned to individual lines (measured with a grating monochromator) and fitted with unstable resonator optics providing a smooth and well defined, reproducible spatial fluence profile in the far field (25 to 30 m) as measured with a small diaphragm (see Ref. [11] for an example). The energy contained in a pulse is measured with pyroelectric detectors (Lumonics 50 D, 20 D) which were calibrated by comparison with other, calibrated detectors to an estimated absolute accuracy of about 10%. Further experimental details and checks that are carried out routinely in our experiments have been described in Ref. [11].

If the intensity were constant during irradiation, rate coefficients could always be determined according to Eq. (1). A rectangular pulse shape with constant intensity was produced only very recently using electro optical crystal switching [18]. In general, intensity depends upon time during the irradiation pulse. It is then important to check for the absence of intrinsic nonlinear intensity dependencies [8, 9, 17]. This can be done qualitatively by measuring the reactant decay using pulses of the same fluence but different maximum intensity. If there is no effect upon the reaction yield, one has $k(st)/I = k_I(st) \neq f(I)$ in the considered range, which is a condition for the evaluation of k(st), if I is not constant. The maximum intensity can be changed by using pulses with and without "N2-tail" [19]. This method in our case allows for changes of the relevant peak intensity by about 30 to 40% at a given total fluence [10, 11]. A more sensitive method would be to compare the irradiation with our ordinary, very intense self mode-locked pulses [11] with the irradiation from a single longitudinal mode laser, which has a smooth intensity profile with a much lower peak intensity [20]. Single mode pulses have been produced for IR-photochemistry by using an additional intracavity CW-laser section [18, 20]. A simpler technique using an intracavity selective absorber has been suggested in a different context by Nurmikko, Temple and Schwarz [21]. We have successfully adopted this method, which requires only the introduction of an intracavity evacuable absorption cell. A typical result with multiand single longitudinal mode operation on the P 20 line at 944 cm⁻¹ is shown in Fig. 2. The multimode pulse (with no absorber) consists of one main train of pulses, separated by the roundtrip time of the laser cavity (about 18 ns), as shown previously [11]. In contrast, with about 40 Pa of SF_6 in the intracavity absorption cell (the pressure conditions must be carefully optimized) one obtains stable single longitudinal mode operation with a smooth intensity profile. The pulse energy is reduced by about 30%. At a given fluence, the apparent peak intensity is about a factor of 1.5 higher for the multimode pulse, as measured with a limited time resolution (the rise time of the photon drag detector - 100 MHz oscilloscope combination is about 3 to 4 ns). This un-



Signal from a fast photon drag detector irradiated with CO_2 -laser pulses. In the upper part one has multilongitudinal mode operation with self mode locking, in the lower part one has single mode operation achieved by an intracavity absorber (here SF_6 , see also text)

derestimates the intensity ratio. The theoretical maximum value of the intensity ratio is about a factor of 50, the real intensity ratio being probably closer to the latter figure. In the multimode pulse in general several pulse trains overlap in a fashion which is not exactly reproducible. This would prevent us from giving an exact number for the intensity ratio, even if a higher time resolution is achieved [22]. In any case, the present technique provides a more sensitive test on non-linearities than our previous use of short and long pulses. The pulses in the upper part of Fig. 2 can be produced with and without N₂-tail.

3. Results

3.1. The Frequency Dependence of the Reaction Yield

Fig. 3 shows the absorbance of C_4F_8 in the range near 960 cm⁻¹, which has been attributed to a ring deformation (v_{21} , e_u vibration) [15]. Superimposed are the apparent yields P_{app} for 13 laser lines in this range at a nominal fluence (maximum in the fluence distribution) $F_0 = 2.5 \text{ J cm}^{-2}$. Note that $P_{app} > 1$ is perfectly permissible in the present definition. To the blue the yield spectrum matches approximately the absorbance spectrum, whereas to the red the yield spectrum is broader. Although we were not able to cover the frequency range between P8 and R8, the maximum in the yield spectrum is probably broad and close to P8. The shape of the yield spectrum is, of course, dependent upon the choice of F_0 . Fig. 3 is shown in order to provide a qualitative survey. A more significant function is the frequency dependence of the steady-state rate coefficient.



Absorbance of c-C₄F₈ (full line) and apparent yield for reaction under single frequency irradiation, P_{app} (points), with a nominal fluence $F_0 = 2.5 \text{ J cm}^{-2}$, see also text

3.2. The Rate Coefficient for off Resonance Excitation

Although fluence is a well controlled, reproducible, and smooth function under our experimental conditions, it is not uniform over the cell diameter [11]. The simple Eq. (1) is thus not directly applicable. The steady state rate coefficient $k_I(st)$ can in practice be obtained by a nonlinear least squares fit [11, 24] using either of two functional forms:

$$P_{\rm app} = \sum_{i} \frac{\delta Qi}{Q_{\rm B}} \left[1 - g \left(c_i F_{\rm max} \right) \right]$$
⁽⁵⁾

$$g(x) = \exp\left\{\frac{1}{2}k_{f}(st)\,\varphi\left[2\sqrt{\pi} + \sum_{n=0}^{\infty}\frac{(-1)^{n}}{n!\,(n-1/2)}\left(\frac{\varphi}{F}\right)^{2n-1}\right]\right\} \quad (6a)$$

or else

$$g(x) = \sum_{K=1}^{N} \phi_{K}^{\star} \exp(\kappa_{K} x) h(x - F_{m}).$$
(6b)

The δQ_i are the surface elements, for which the actual fluence is $c_i F_{\text{max}}$ and Q_B is the nominal beam cross section ($V_I = Q_B x$ length of cell). The set of constants $\delta Q_i/Q_B$ and c_i has to be determined once for a given optical alignment of the laser beam. F_{max} is the maximum fluence in the center of the laser beam and is usually taken to be equal to the nominal fluence F by definition in our work. The g(x) are theoretical functions for the remaining reactant concentration. Eq. (6a) results from the activation equation and contains two parameters, $k_I(st)$ and φ [23]. Eq. (6b) results from the general solution of the Pauli equation for coherent optical excitation [8]. With truncation at N = 2 it contains 4 parameters with $\kappa_1 = -k_I(st)$ being retained as the only significant one. F_m in Eq. (6b) is introduced in order to avoid artifacts arising from truncation, using the step function h(x > 0) = 1, h(x < 0) = 0. These two quite different mathematical functions both provide the same physical parameter, $k_I(st)$. Any differences in the results may be used to check for the dependence of the results upon the fit function used. The method of evaluation has been tested with theoretical model calculations and with experimental results. It was found to be reliable. Details have been discussed elsewhere [10, 11].

Fig. 4a shows the apparent yield function P_{app} for irradiation with the P 20 line at 944.2 cm⁻¹, considerably to the red of the absorbance maximum in Fig. 3. The open circles are for single mode irradiation (low intensity). The points are for multimode irradiation (high intensity). There is no significant effect. This indicates the absence of any intrinsic nonlinearity for the considered intensity range. The same result is obtained on other lines also when comparing "short" and "long" pulses (with N₂-tail). The full line in Fig. 4a is from a fit using



a) Apparent reaction yield P_{app} in the nominal irradiated volume as a function of fluence under irradiation with the P 20 line of the CO₂-laser. The points are for multimode irradiation (see Fig. 2a) the open circles for single mode operation (see Fig. 2b). The line is from a least squares fit using Eqs. (5) and (6b) with two terms.

a least squares fit using Eqs. (5) and (6b) with two terms.
b) True yield function - ln F^(a) as a function of true fluence calculated from the fits to the experimental results in a). The full line (2) is from the two exponential term fit (Eq. (6b)), the dashed line from the activation Eq. (6a).

Eq. (5) with Eq. (6b). From the parameters obtained in the fit one can calculate the true yield function $-\ln F_R$, which applies for irradiation with uniform fluence. The star in parentheses indicates that a precise distinction between F_R and $F_R^* = c_R^*/c_R(0)$ cannot be made, due to collisional quenching after the pulse, not important for the evaluation of k(st) [11]. The true yield function is shown in Fig. 4b, which also shows the similarity of the results obtained by using either Eq. (6a) for

the fit (a.e.) or Eq. (6b) with two exponentials (2). The difference at large values of $-\ln F_R$ is not experimentally significant, since these values correspond to essentially complete decomposition of C_4F_8 . The rate coefficients obtained are

$$k(st) = 1.6 \cdot 10^{6} (I/MW \text{ cm}^{-2}) \text{ s}^{-1}$$

from Eq. (6a) and

$$k(st) = 1.27 \cdot 10^{6} (I/MW \text{ cm}^{-2}) \text{ s}^{-1}$$

from Eq. (6b). The latter value is presumably somewhat better, but at least uncertain to within the differences shown by the different fits.

3.3. The Rate Coefficient for Near Resonance Excitation and the Influence of Inert Gas Pressure

Fig. 5 shows yield functions evaluated as discussed in section 3.2 but for irradiation with the P 8 line near 954.6 cm⁻¹. Results are presented for total gas pressures of 13, 200, and 2600 Pa ($p_{C_4F_8} \le 13$ Pa, with N₂ being added). As expected the yields decrease due to collisional quenching. However, the parameters $k_I^a(st)$ evaluated for the various pressures by the above procedure are relatively insensitive to the inert gas pressure. This point has been established in more detail by calculations and by experiments in Ref. [11]. In the present case the apparent k_I^* (st) decreases slightly with pressure from 1.89 to 1.79 to $1.15 \cdot 10^6 (I/MW \text{ cm}^{-2}) \text{ s}^{-1}$. This insensitivity allows one to perform approximate rate coefficient determinations with a reactant diluted in inert gas solvent. This provides to some extent better controlled conditions with respect to the absence of thermal heating and possible wall effects. We stress again [11] that in this kind of experiment approximate values for the collisionless k(st) are obtained under highly collisional conditions. The evaluation of the collisional k(st) for the particular pressure would require fluence variation at constant intensity by changing the laser pulse length. By approximate numerical



- a) Apparent yield for irradiation with P 8 (954.5 cm⁻¹) and various total pressures (indicated in Torr by the numbers) at fixed partial pressure of c-C₄F₈. The lines are from least squares fits using Eq. (5) with Eq. (6b) and two exponential terms to the respective experimental points.
- b) True yield function $-\ln F_R^{(*)}$ as a function of fluence calculated from the parameters obtained in the fits to the experimental results in a) (see also text)

simulations one can also evaluate the yields under collisional conditions in terms of a competition between optical pumping and collisional quenching rates in IR-photochemistry [25, 26, 28].

Table 2						
Rate coefficients and molecular parameters for two ring opening reactions ^a)						

4. Comparison of the Experimental Rate Coefficients with Theoretical Estimates and with Other Reactions

The experimental rate coefficients for various irradiation frequencies and pressure conditions are summarized in Table 1. Although neither a continuous variation of the laser frequency nor collision free conditions can be achieved in the current bulk experiments, the weak frequency and pressure dependence in agreement with general theoretical expectation shows that the rate coefficient for optimum pumping in the frequency range of this vibrational band is, with a rough estimate for the error limits:

$$k(st) = 10^{6.3 \pm 0.3} (I/MW \text{ cm}^{-2}) \text{ s}^{-1}$$

That is, with irradiation of a constant intensity of, say, 30 MW cm^{-2} which corresponds to the maximum intensity of the single mode laser pulse at a fluence of 2 J cm^{-2} , one predicts the steady state limit for the rate coefficient obtained in a time resolved experiment:

 $k(st) = 6 \cdot 10^7 s^{-1}$.

The rate coefficient should be approximately proportional to the intensity in the range 10 MW cm⁻² to 100 MW cm⁻², at least. From Table 1 one sees also that there is no meaningful correlation between the frequency dependent rate coefficient and the absorption cross section at that frequency.

Table 1 Summary of rate coefficients

Laser line	ṽ∕cm ^ 1	$\sigma/10^{-19}$ cm ²	p _{N2} /Pa	$lg\left\{\frac{k(st)/s^{-1}}{I/MW \text{ cm}^{-2}}\right\}$	
P 20	944.2	1.2	200.0	6.1	
P 10	952.9	18.0	-	6.2	
P 8	954.6	25.0	-	6.3	
P 8	954.6	25.0	200.0	6.3	
P 8	954.6	25.0	2600.0	6.1	
R 8	96 7.7	22.0	-	6.1	

A good theoretical correlation and prediction of rate coefficients with optimum pumping is, however, possible using as major input the molecular frequencies, the integrated band strengths of the pumped vibration and the threshold energy for the reaction [23]. Table 2 summarizes experimental and theoretical results for the two somewhat comparable ring opening reactions which we have investigated recently. It seems that in both cases the fundamental at 960 $\rm cm^{-1}$ is a fairly similar kind of ring deformation. The integrated band strengths are proportional to the square of the vibrational transition moment. They have been determined quantitatively, as always in our work [10, 28]. The threshold energies for the reactions, $E_{\rm T}$, are estimated from thermal studies [27, 29]. With these input parameters the simple model of Ref. [8] allows for a low estimate of the rate coefficient with optimum pumping into any well separated band without further adjustable parameters. The model for the rate coefficient matrix is necessarily approximate [8]. The

				$lg\left\{\frac{k(st)/s^{-1}}{I/MW \text{ cm}^{-2}}\right\}$	
Reaction	ṽ/cm ^{−1}	$G/10^{-20} \mathrm{cm}^2$	<i>E</i> _T /cm ⁻¹	Exp.	Th.)
$c-C_4F_8 \rightarrow 2 C_2F_4$	963.0	7.6 ± 2.0	25500.0	6.3	5.8
$c - C_2 F_4 S_2 \rightarrow 2 C F_2 S$	965.5	1.52 ± 0.4	16000.0	5.9	5.3
	1080.0	11.5 ± 3.0	16000.0	6.5	6.1

^a) For pumping with a laser frequency close to the optimum.

b) This is a low estimate, but for the optimum frequency.

theoretical values in Table 2 are, however, from otherwise exact solutions of the Pauli equation [30] for optical excitation and chemical reaction. The theoretical foundations for the use of the Pauli equation in IR-photochemistry have been established [9]. Appropriate algorithms for the solution of the Pauli equation have been formulated [8]. Thus, these calculations are now routinely performed in our work, not needing any further discussion here.

Some comments may be useful, however, concerning the properties of a molecule which is fairly large and heavy, containing many low frequency vibrations, such as c-C₄F₈. The average vibrational, thermal energy of this molecule is about 1700 cm⁻¹ (20.4 kJ mol⁻¹) at 300 K. The vibrational ground state has only a population of 0.003. The density of vibrational states at 1700 cm⁻¹ is about 50 states in a cm⁻¹ interval. The maximum of the vibrational energy distribution at 300 K is near 1300 cm⁻¹ with a full width half maximum of about 2000 cm⁻¹ for the distribution. The essentials of these properties must be included in the initial state for the solution of the master equation. The lifetimes of molecules excited just above the threshold energy for reaction $E_{\rm T}$ are of the order of several days, as estimated from the statistical theory of unimolecular reactions. Therefore the maximum of the steady state distribution at typical laser intensities is more than ten CO₂-laser quanta above the threshold energy. Much reaction occurs after the irradiation and then also considerable collisional quenching occurs even at low pressures. In principle, the calculated amount of collisional quenching after the laser pulse depends strongly upon the activated complex model used. As already discussed, this has little effect upon the rate coefficient evaluation. This is borne out by theoretical calculations and by our experimental results.

Another secondary effect occurs due to the theoretical possibility of a "turnover" [17]. This implies that the time (or fluence) dependent rate coefficient does not uniformely approach its steady state value but that it has a maximum at intermediate times:

$$k(t) = -\frac{d \ln [c_{\mathbf{R}}(t)/c_{\mathbf{R}}(0)]}{dt}$$
$$1 \ge k(st)/k_{\max}^*(t_{\mathbf{m}}) \ge a.$$

Our calculations indicate that for the present example $a \le 0.62$. The best fits to the experimental results do not indicate a turnover, but the effect is probably within experimental scatter. This may tend to produce sometimes experimental values for k(st) that are somewhat higher than the correct ones. This is certainly a small effect in the present case.

When comparing experimental and theoretical values in Table 2 and also in other cases [9-11] one finds that the theoretical low estimates are indeed low, consistently by about a factor of 3 to 4. This is an excellent success of the theory, noting that other theoretical approaches have not been able to provide any kind of quantitatively reliable a priori predictions and correlations in this field, which is still full of puzzles. One may wonder why the simple model for the rate coefficient matrix should work so well, in the absence of any detailed spectroscopic knowledge about the highly excited molecules. The answer to this is partly, that details are averaged out over the many excitation steps. Furthermore, the simple model predicts accurately only a theoretically convenient, if important guantity: the steady state rate coefficient for optimum pumping in the linear régime. Nonlinear effects and the detailed frequency dependence of the rate coefficients are not so easily predicted from a simple model although the general theory provides for them, if only sufficient spectroscopic input is available [9]. Future experimental work should be directed also towards quantitative measurements of k(st) in the nonlinear régime, which is possible by using the pulse shaping techniques of Ashfold, Atkins and Hancock [18].

Another point is that the few reactions studied quantitatively, so far, have all a fairly similar, fast rate, in the upper range of expected rates. This has experimental reasons. It is difficult to find molecules showing a much faster IR-photochemical reaction, since this would require a combination of much larger integrated band strengths with low threshold energies for molecules giving a clean reaction. For technical reasons it is also difficult to obtain quantitative results for molecules which react much more slowly. Experimental work in these directions is in progress, in order to provide a larger range of meaningful rate parameters and a more stringent test for theory.

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Rotational and Vibrational Relaxation in the Degenerate Vibrations v_{24} and v_{21} of Cyclohexane in the Liquid State

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Flüssigkeiten / Ramanspektren / Rotation

Correlation functions $\phi(t)$ and correlation times were obtained by Fourier transformation of the degenerate fundamental bands v_{24} and v_{21} of liquid cyclohexane. Reorientational correlation functions were calculated based on the Kubo line shape theory in order to extract the contribution of vibrational relaxation. Dephasing caused by short range interactions is a possible mechanism for vibrational relaxation at least for v_{21} .

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