

# Forschung, Wissenschaft

## Photochemistry with Infrared Radiation\*

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### Abstract

The irradiation of polyatomic molecules with intense infrared radiation from pulsed laser light sources can induce photochemical reactions, which require the absorption of many (10 to 50) quanta. The experimental principles are outlined and the primary processes due to vibrational excitation in the electronic ground state are discussed. A method for determining quantitative rate parameters is presented and illustrated with some recent experimental results for  $\text{CF}_3\text{I}$ - and  $\text{C}_2\text{F}_4\text{S}_2$ -IR photolysis. Simple theoretical correlations for absolute rate coefficients provide an understanding of the most important molecular parameters determining the rate of an IR-photochemical reaction. The relationship of IR-photochemical and thermal, collisional reactions is analyzed. Qualitative experimental effects and quantitative rates in IR-photochemistry can be rationalized with somewhat different success using various theoretical descriptions for the primary processes. A brief summary of the current status of experiments and theories concludes the article.

### 1. Photochemistry after Vibrational Excitation

Every chemist is familiar with the concepts of traditional molecular photochemistry, which proceeds after one— or two photon excitation of electronic states, usually with visible or ultraviolet light. This is an efficient process even with ordinary light sources, such as sunlight, since the collisional quenching of electronic excitation is often unimportant. In IR-photochemistry, on the other hand, the rotational and vibrational energy of polyatomic molecules is very easily removed by collision. Furthermore, more than ten quanta of vibrational fundamental absorption in the IR are often necessary for overcoming the threshold energies for ordinary chemical reactions. Thus *vibrational photochemistry* of polyatomic molecules in the electronic ground state has become possible only recently, using efficient multiphoton pumping with high power, pulsed, monochromatic infrared lasers [1,2]. Potential applications have emerged soon [3], much of the interest centering around laser isotope separation [4–7] (for a recent list of separated isotopes from H to U see ref. [8]). Another already practical application is the creation of large amounts of unstable species in situ on short time scales ( $< 10^{-7}$  s) by IR-laser flash photolysis, which can be used for chemical reactions [9], energy transfer [10, 11] and spectroscopic studies of free radicals, for example [11–13].

Apart from the applications, the most exciting fundamental questions currently center around the mechanisms of collisionless IR-multiphoton excitation and the subsequent reactive processes, which are still not completely understood [14]. These questions will be the major concern of the present article. After a short introduction into the experimental aspects of the laser-sources, we shall discuss the theoretical and computational approaches, some spectroscopic and mechanistic evidence, and the information that can be gained by quantitative kinetic experiments in IR-photochemistry. Finally, a brief comparison with thermal reactions will be made, including also some comments on IR-photochemistry under collisional conditions.

### 2. The Radiation Sources

IR-photochemistry in the gas phase has been reported under a variety of experimental conditions ranging from beam [15] to bulk at atmospheric pressure, although most experiments are carried out at low pressures ( $< \text{k Pa}$ ) in bulk [11–17]. The most important characteristic obviously is the nature of the light source. Fig. 1 shows a scheme for the most commonly used source, the  $\text{CO}_2$ -laser. This laser provides operation on rotational lines of two vibrational transitions with the asymmetric stretching fun-

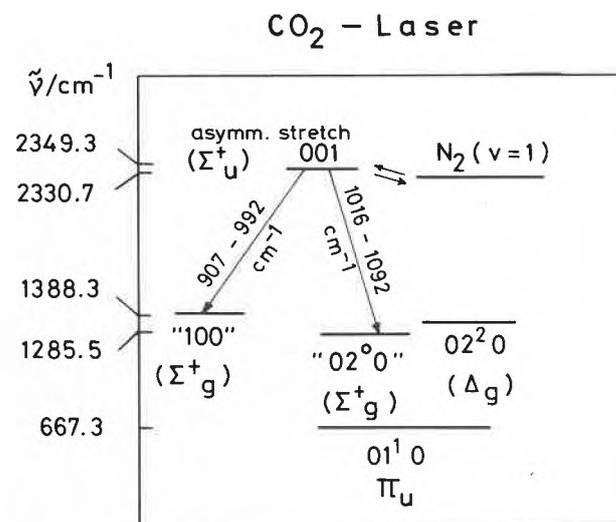


Fig. 1: Level scheme for transitions in the  $\text{CO}_2$ -Laser.

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damental as upper state and the Fermi-doublet of the symmetric stretching fundamental and the  $\Sigma_g^+$  component of the bending overtone as lower states. Using a grating in the laser cavity one has a practical line tunability from about 907 to 992  $\text{cm}^{-1}$  and from 1016 to 1092  $\text{cm}^{-1}$ , respectively, with a distance of a few  $\text{cm}^{-1}$  between the lines. The frequency range can be extended using  $^{13}\text{CO}_2$ . The spectral purity is ordinarily better than 0.1  $\text{cm}^{-1}$ , but is rarely measured accurately. The  $\text{CO}_2$ -laser is the only IR-laser found also in nature, so far (in the Mars atmosphere [18]).

Typical pulsed, atmospheric  $\text{CO}_2$ -lasers used in IR-photochemistry give lasing action during a few hundred ns, extending to a  $\mu\text{s}$  or more if nitrogen is added to the lasing gas mixture, due to a near-resonant energy transfer from vibrationally excited  $\text{N}_2$  to  $\text{CO}_2$  (see Fig. 1). The time dependent intensity  $I(t)$  may have a variety of shapes, depending upon the optical set-up. Single transverse and longitudinal mode operation provides a smooth intensity profile [13] as shown in Fig. 2a. Single transverse mode, multi-longitudinal mode operation using unstable resonator optics gives a train of short (ns), intense pulses, due to self-modelocking as shown in Fig. 2b (such pulses are used in our laboratory [16]).

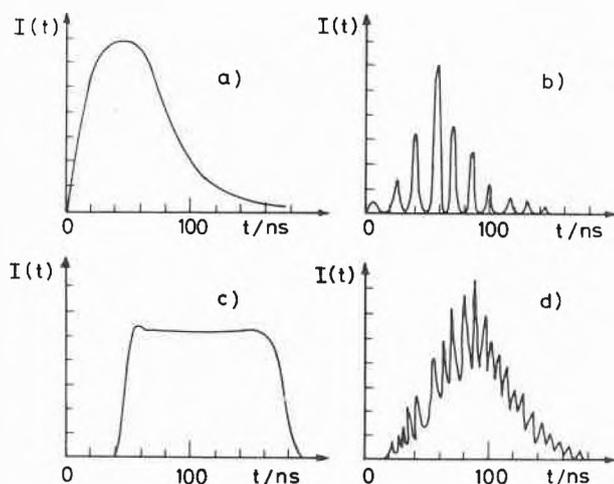


Fig. 2: Time dependent intensity for various  $\text{CO}_2$ -Laser pulses (idealized, see text).

Recently it has become possible to create nearly rectangular pulses (Fig. 2c), using electro-optical crystal switching [19]. Only under these conditions is intensity a well defined experimental variable, but these ideal pulses so far suffer from low intensity. Most current work uses multi-longitudinal multi-transverse mode operation giving irregular intensity profiles (Fig. 2d) [12]. Typical peak intensities can range from 1 MW to 10 GW  $\text{cm}^{-2}$ . Whereas the pulses in Fig. 2a, c, are, in principle, exactly reproducible, the time dependence shown for the conditions of Fig. 2b, d is not. However, the total energy contained in one laser pulse is reproducible in all cases within a few percent.

In order to define the spatial properties of the radiation one uses the fluence  $F$  (or the "radiation dose" [3]):

$$F(x, y, z, t) = \int_0^t I(t') dt' \quad (1)$$

The upper integration limit is usually taken such as to include the total energy in one pulse. It turns out that under certain conditions *fluence* (not intensity) is the most important independent variable in IR-photochemistry (see section 4). In order to obtain well defined conditions for quantitative work,  $F$  should be a smooth and well defined function of the coordinates  $x$  and  $y$  (parallel beam, no  $z$ -dependence), as shown schematically for the far field of an unstable resonator in Fig. 3 (see ref. [16] for actual measurements). Unfortunately, most current work uses multimode optics with irregular spatial fluence profiles and large fluctuations on a small scale ("hot spots") although with low resolution the shape may appear to be smooth and even approximately rectangular, if many transverse modes contribute.

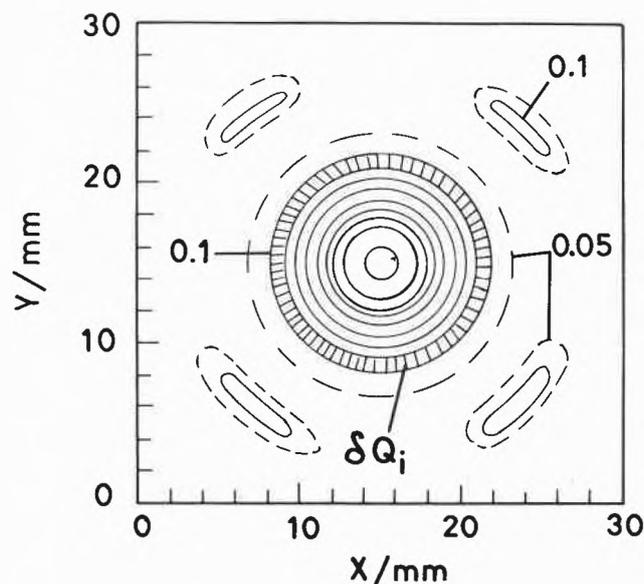


Fig. 3: Fluence distribution in a  $\text{CO}_2$ -laser beam with unstable resonator optics [16]. The full lines indicate schematically lines of equal fluence, normalized to the maximum in the center and separated by 0.1 units (dashed lines: 0.05 units).

Line tunable  $\text{CO}_2$ -lasers with pulse energies up to 70 J are now commercially available and fairly simple tools (we use a Lumonics TEA 103-2, with a maximum output of 15 J/pulse in our work). They are probably the most convenient light sources at present. There have also been reports with continuously tunable, very high pressure  $\text{CO}_2$ -lasers [20] with picosecond [22] and CW-laser excitation [23] and with HF (DF) lasers [21], covering a range from 3800 to 2400  $\text{cm}^{-1}$ . There are many further candidates for IR-laser sources in other spectral ranges.

### 3. Primary Processes in IR-Photochemistry

The number of observed IR-photochemical reactions exceeds already 100. Although this may seem to be a

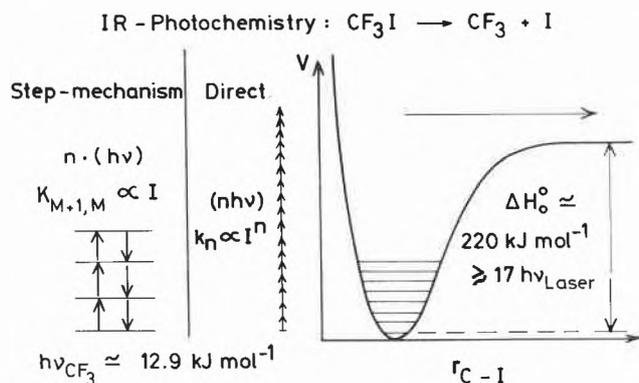


Fig. 4: Scheme for  $\text{CF}_3\text{I}$  IR-laser photolysis (see text).

small number to the chemist, there is good indication that IR-photochemistry is a general phenomenon: All polyatomic molecules ( $\geq 4$  to 5 atoms) can presumably be brought to reaction if irradiated with light of appropriate frequency and sufficient intensity. The energetic situation is illustrated in Fig. 4 for the IR-photolysis



The absorption of more than 17 quanta is required for the C-I bond fission to occur. The frequency which leads to efficient multiphoton excitation corresponds to the  $\text{CF}_3$  symmetric stretching mode ( $A_1$ ), naively speaking "at the other end of the molecule". Two mechanisms, also shown in Fig. 4, are currently popular in discussions of the multiphoton excitation: a direct  $n$ -photon transition, giving a nonlinear  $I^n$  dependence, and a stepwise process, giving an intensity proportional rate (and combinations of these two). A more detailed theoretical treatment shows that the situation is in fact more complicated [14, 24].

The time dependent Schrödinger equation for molecules moving under the influence of a strong, classical (many photons per mode!) field of frequency  $\omega$  can be written in the basis of molecular eigenstates or spectroscopic states (amplitude vector  $\mathbf{b}$  in basis  $\varphi_k$ ):

$$i \dot{\mathbf{b}} = \{ \mathbf{W} + \mathbf{V} \cos \omega t \} \mathbf{b} \quad (2)$$

The point denotes derivation with respect to time.  $\mathbf{W}$  is the diagonal matrix of eigenstate frequencies ( $W_{kk} = 2\pi E_k/h$ ), including possibly an imaginary part.  $\mathbf{V}$  is the coupling matrix with matrix elements in the dipole approximation being proportional to the transition moment times the square root of the radiation intensity [24]. The solution of this equation is formally given by the time evolution matrix  $\mathbf{U}(t)$ :

$$\mathbf{b}(t) = \mathbf{U}(t) \mathbf{b}(0) \quad (3)$$

In practice,  $\mathbf{U}(t)$  can be computed by series expansion and numerical, stepwise procedures (for example the Magnus expansion) or in a closed, exponential form by

using the quasidegenerate approximation [24]. In the absence of collisions this solves the dynamical problem quite generally, for example also for the time dependent density matrix  $\mathbf{P}$  (Liouville-von Neumann equation in the basis  $\varphi_k$ ):

$$\mathbf{P}(t) = \mathbf{U}(t) \mathbf{P}(0) \mathbf{U}^\dagger(t) \quad (4)$$

$P_{kk} = \langle b_k b_k^* \rangle$  is the population of the quantum state  $\varphi_k$  at time  $t$ . For any time dependent observable  $\mathbf{Q}$  one has the Heisenberg equation of motion in the basis  $\varphi_k$ :

$$\dot{\mathbf{Q}}(t) = \mathbf{U}^\dagger(t) \mathbf{Q}(0) \mathbf{U}(t) \quad (5)$$

These equations have been solved for a number of model problems (quantum mechanical trajectories involving of the order of a hundred states) [24–26]. For real molecules difficulties arise because the spectroscopy is not sufficiently well known (molecular energies  $E_k$  and transition moments for all states), and because the order of the matrices is much larger than one could ever hope to treat (the number of effectively coupled rovibrational states easily exceeds  $10^{20}$  below the reaction threshold). One could simplify the problem either by using a separable approximation (say, uncoupled harmonic oscillators) or, more realistically, by using statistical approximations. The situation that has emerged from analytical considerations and from numerical solutions of Eq. (4), subject to experimental test, ultimately, is that a statistical-mechanical master equation for coarse grained level populations  $p_k$  describes the situation often quite well, if

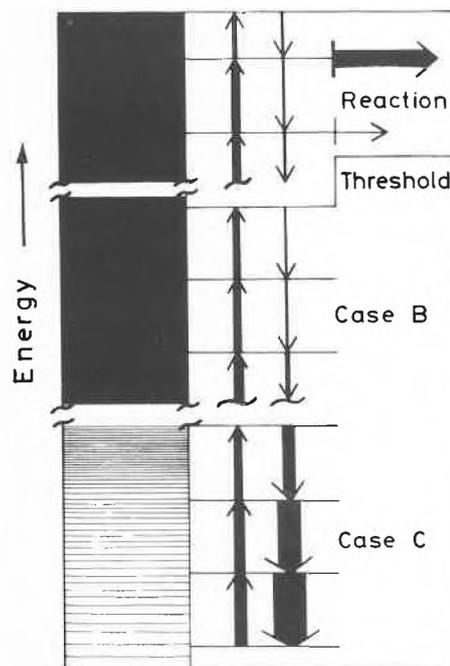


Fig. 5: Stepwise excitation in IR-photochemistry. The widths of the lines indicate semiquantitatively the transition rates (from ref. [26]).

many states at each level of excitation contribute appreciably:

$$\dot{\mathbf{p}} = \mathbf{K} \mathbf{p} \quad (6)$$

The level population is the sum of state populations in an energy band centered at multiples of the laser quantum  $\hbar\omega$ . Disregarding further complications due to angular momentum etc. [24, 27], Eq. (6) is easily solved, since the number of relevant levels is much less than 100, typically (see fig. 4 and the examples in section 5). Since it turns out that only adjacent levels are coupled by appreciable matrix elements  $K_{MN}$ , the primary process of multiphoton excitation can be understood as a series of stepwise "one-photon" transitions, as indicated schematically in Fig. 5 for a typical condition. Several limiting cases (A, B, C, D) depending upon spectroscopic conditions can be derived for the  $K_{MN}$ . In order to avoid the misunderstanding that stepwise transitions are necessarily associated with intensity proportional rate coefficients, we summarize the intensity dependencies and qualitative ratios of up and down transitions in table 1, together with qualitative considerations concerning typical validity ranges. Quantitative expressions and a method for combining the quantum mechanical equations for the first excitation steps in small molecules and the master equations for the higher excitation steps have been given in refs. [14, 24]. For complex spectral absorption structures in highly excited molecules more complicated intermediate cases and combinations can arise. The seemingly small nonlinearity in case C can lead to a large nonlinearity in the effective reaction rate [25]. Above the reaction threshold there is competition between optical pumping and reaction as indicated in Fig. 5. The specific reaction rate increases rapidly with the level of excitation, according to the statistical theory of unimolecular reactions [8]. It can be quite low for large polyatomic molecules. Therefore, with intense optical pumping, one can have multiphoton excitation well above the reaction threshold. Noting that the first steps can always be treated using Eqs. (2)–(5), the statistical mechanical treatment of the primary processes in IR-photochemistry briefly discussed here would allow for quantitative calculations and

detailed predictions, if enough were known about the high and low resolution IR-spectra of highly excited molecules. Unfortunately, the spectroscopic questions are largely unsolved. Still, one can use the mechanistic concepts summarized in table 1 and Fig. 5 for qualitative predictions and explanations of experimental effects and also for some quantitative estimates, if one introduces in addition simple model assumptions. In this context one should also compare with other theoretical approaches. We mention here the most popular ones:

a) *Rate equations with Einstein coefficients.* One might assume phenomenologically that a rate equation of the form of Eq. (6) applies with rate constants equal to *Einstein* coefficients for absorption and stimulated emission [28, 29]. The rate coefficients can then also be written in terms of an intensity independent spectroscopic cross section  $\sigma$  at the laser frequency:

$$K_{M+1, M} = \sigma_M \cdot I/h\nu \quad (7a)$$

$$K_{M+1, M}/K_{M, M+1} = \rho_{M+1}/\rho_M \quad (7b)$$

Such a treatment would be qualitatively similar to case B in table 1 and is often used. It would be valid for incoherent, white light [27], which is, however, not applicable.

b) *Classical trajectory calculations.* Instead of the quantum mechanical equations of motion one may solve the classical equations of motion for conjugate coordinates  $q_i$  and momenta  $p_i$  of the atoms in the molecule:

$$\frac{\partial H}{\partial p_i} = \dot{q}_i \quad (8a)$$

$$\frac{\partial H}{\partial q_i} = -\dot{p}_i \quad (8b)$$

The hamiltonian function includes the potential energy from a hypersurface calculated using the *Born-Oppenheimer* approximation and it also includes the interaction with the classical electromagnetic field [30, 31]. The difficulties arise from the limited validity of classical mechanics [32] and from the fact that Eq. (8) can be accurately solved only for short times (ps-range), whereas experimental times are in the ns to  $\mu$ s range.

Table 1: Statistical-mechanical limiting cases for coherent optical pumping

	Case A	Case B	Case C	Case D
effective absorption: $K_{M+1, M}$	$\propto I$	$\propto I$	$\propto I$	$\propto \sqrt{I}$
stimulated emission: $K_{M, M+1}$	0	$\propto I$	$\propto \sqrt{I}$	$\propto \sqrt{I}$
detailed balance: $(K_{M+1, M}/K_{M, M+1})^a$	( $\infty$ )	$> 1$	$< 1$	$= 1$
typical applicability	first one-photon step into region of high $\rho$	high I high $\rho$ large $\Gamma^b$	low I low $\rho$	ultrahigh I high $\rho$ small $\Gamma^b$

a) assuming that the density  $\rho$  of effectively coupled states increases with energy (typically  $\rho(E) \propto E^{s-1}$ ,  $1 < s < \text{number of internal degrees of freedom}$ ).

b) Width of absorption structure.

c) *The two-ladder, three-regions model.* In this model one assumes that the first few photons are absorbed just in one separable vibrational mode (ladder one) in a high order ( $n = 3$  to  $7$ ) multiphoton process with an  $I^n$  intensity dependence (region one, low energies) [33,34]. At higher levels of excitation (region two) one assumes rapid intramolecular transfer of vibrational energy from ladder one to ladder two, which consists of a dense "quasi-continuum" of states provided by the other vibrational modes. The optical pumping in this second ladder is assumed to be stepwise, incoherent. In region three at high energies one has finally the possibility of reaction. The difficulties of this model are that a high order multiphoton process by means of direct dipole coupling ( $n = \text{odd resonances}$ ) or by means of the *Goeppert-Mayer* mechanism ( $n = \text{even resonances}$ ) [35] is too inefficient to explain the experimental dissociation rates [High order resonances are, of course, automatically included in Eq. (2)].

There exist furthermore conceptual difficulties related to the separable approximation at low energies and to the assumed "intramolecular vibrational energy transfer".

d) *Reduced density matrix for the pumped mode and the pumping-dumping model.* In this treatment one again assumes approximate separability of one optically active vibrational mode (the "system") from the other degrees of freedom ("the bath"). The interaction of the "system" with the radiation field and with the bath is described by *Bloch*-type equations for the reduced density matrix of the "system" [36]. One has optical "pumping" of the system and "dumping" of the energy into the bath. In estimating the usefulness of such an approach one should not be too impressed by the fairly detailed mathematical elaborations available now., which are largely borrowed from the theory of magnetic resonance in the condensed phase. The approach does not cope well with fairly discrete, perturbed spectra, as they arise in case C, and with situations where the absorption from several vibrational modes (several "systems"?) interferes, a common situation in the IR-spectra of polyatomic molecules.

The analogy to magnetic resonance and nonlinear optics might be helpful for large polyatomic molecules, if two conditions are satisfied: (i) A fairly isolated optically active mode exists. (ii) The coupling with the field is strong compared to the intramolecular coupling with the bath. These couplings can energetically be associated with power broadening and with the vibrational absorption bandwidth in the low resolution spectrum, respectively. In a lifetime picture they are associated with the time between radiative transitions in the pumped mode and with the rate of radiationless transitions out of the pumped mode, the various quantities being qualitatively related through the uncertainty principle. Little is known about homogeneous intramolecular vibrational bandwidths in large polyatomic molecules in the gas phase, although this problem can be attacked by conventional spectroscopic methods [37, 38]. Fig. 6 shows an IR-spec-

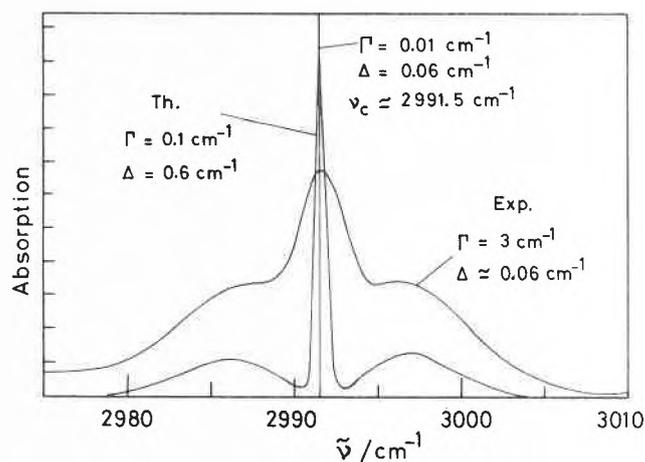


Fig. 6: Spectrum of the C-H fundamental in  $(\text{CF}_3)_3\text{CH}$ . The sharp line indicates the expected width of the Q-branch of a single vibrational line at the experimental resolution  $\Delta = 0.06 \text{ cm}^{-1}$ , linewidth  $\Gamma = 0.01 \text{ cm}^{-1}$  (collisional). Also shown is a theoretical spectrum at intermediate resolution with P, Q, R structure. The experimental spectrum was taken with the kind help of J. Gast at Bruker, March 1980. It can be fitted by associating with each rotational line a "vibrational width"  $\Gamma = 3 \text{ cm}^{-1}$  (see text and ref. [37], also Diplomarbeit H. R. Dübal, Göttingen 1980).

trum of an ideal model system: a parallel transition of an isolated C-H stretching vibration in the heavy symmetric top  $(\text{CF}_3)_3\text{C-H}$  [37]. In such a molecule one would expect to see an extremely sharp Q-branch, well separated from P and R-branch absorption. The experimental spectrum has, however, a broad structure, which can be fitted by attributing a Lorentzian of vibrational "width"  $\Gamma = 3 \text{ cm}^{-1}$  to each rotational line. If homogeneous, such a width would correspond to a lifetime of 2ps of a local C-H stretching excitation of the system. The "width" arises from many unresolved but still discrete vibrational lines (the density of vibrational states corresponds to more than  $10^7$  states in a  $\text{cm}^{-1}$  interval in the relevant energy range). Optical pumping occurs only on a ns timescale in IR-photochemistry (power broadening width  $\ll \Gamma$ ), which would make the system-bath relaxation picture less useful. Intramolecular vibrational relaxation would then not be a relevant primary process on the time scale of IR-photochemistry.

Some of the experimental width may correspond to inhomogeneous structure. A complete discussion cannot be given here, but temperature dependent studies indicate for the example of  $(\text{CF}_3)_3\text{C-H}$  [37] that the homogeneous width is an appreciable fraction of  $3 \text{ cm}^{-1}$ . Unambiguous interpretations are possible if the vibrational fine structure can be resolved, as in the case of  $\text{CF}_3\text{H}$ , where one arrives at similar conclusions concerning the strengths of couplings [38], but where the system-bath picture would be obviously inappropriate anyway. A resolution of the fine structure for  $(\text{CF}_3)_3\text{C-H}$  will be a formidable task. Another test for the homogeneous structure would be possible by means of hole burning

somewhat similar to experiments in matrix [39], although we stress the differences in the gas and in the condensed phase.

*e) The two ensembles model.* It has been suggested [40] that the pumped molecules can be divided into two ensembles: One being reactive and pumped according to Eq. (7), one nonreactive and not pumped at all. The fraction in each set is made intensity dependent through a somewhat vague concept of power broadening or through multiphoton resonances. It is obvious that the different molecules in a thermal ensemble may react generally (but not always!) at different rates in IR-photochemistry [27]. The separation into just two ensembles has been helpful in rationalizing some collisional effects, but it is not quite realistic and has not been useful for predictive purposes.

#### 4. Quantitative Kinetic Concepts and Experimental Rate Constants

Which parameters characterize best the rate of an IR-photochemical reaction? In answering such a question one has also to account for the experimental boundary conditions in order to obtain *molecular* parameters and not parameters of the experimental arrangement or of the laser used. In analogy to ordinary chemical reactions one

$$k(F, I, t) = - \frac{d \ln [c(F, I, t)/c(0)]}{dt} \quad (9)$$

can define a rate coefficient  $k(F, I, t)$  as in Eq. (9),  $c$  is the reactant concentration remaining after irradiation with intensity  $I$  during a time  $t$  and with fluence  $F$  (concentration  $c[0]$  before irradiation). Considering first irradiation under ideal conditions with constant  $I$ , one can write the remaining dependence upon time from the solution of Eq. (6) [26, 27]:

$$F_R^{(*)} = c^{(*)}(t)/c(0) = \sum_K \Phi_K^{(*)} \exp(\lambda_K t) \quad (10a)$$

$$k^{(*)}(t) = - \left[ \sum_K \Phi_K^{(*)} \lambda_K \exp(\lambda_K t) \right] \left[ \sum_K \Phi_K^{(*)} \exp(\lambda_K t) \right]^{-1} \quad (10b)$$

Eq. (10) is valid for starred and unstarred quantities. The starred quantities  $F_R^*$ ,  $k^*(t)$  include the reaction of molecules above threshold after the end of irradiation (cf. Fig. 5). The parameters  $\lambda_K$  (always negative) and  $\Phi_K^{(*)}$  depend upon the intensity but not upon time or fluence. The long time limit of Eq. (10) provides the steady state rate coefficient:

$$\lim_{t \rightarrow \infty} \left( - \frac{d \ln F_R^{(*)}}{dt} \right) = k(st) = k^*(st) = - \lambda_1 \quad (11)$$

The steady state rate coefficient is formally identical to the ordinary rate constant in thermal reactions, which proceed usually at steady state. Eq. (11) is the basis for evaluating  $k(st)$  from experiments without time resolved

concentration measurements, just by changing the irradiation time (or fluence, see below) [41].

In IR-photochemistry it is necessary to include several terms in the expansion, Eq. (10), in order to describe the initial phase of the reaction: One has a pronounced delay or incubation phenomenon. Another, approximate description with just two parameters is possible using the activation equation [42]:

$$k(t) = k(st) \exp[-(\Theta/t)^2] \quad (12)$$

This equation illustrates nicely, how the steady state rate coefficient is approached with time, delayed by an activation time  $\Theta$ , characterizing the time, which is about necessary to activate the molecules from their initial low temperature distribution to high levels of excitation (see Fig. 5).

The *time* dependence during irradiation with constant intensity has to be supplemented by the *intensity* dependence of the rate coefficient at steady state (no more time dependence). This may be written formally (with  $n$  not being strictly a constant) as:

$$k(st) = cI^n \quad (13)$$

One can thus define three régimes of IR-photochemistry: (i) nonlinear with  $n > 1$  being a strong function of  $I$ . This applies in case C, at low intensities, typically. With  $M$  steps satisfying case C (table 1) one finds, indeed, approximately [25]

$$k(st) = cI^{(M+1)/2} \quad (14)$$

A nonlinear law would also apply with a rate determining, coherent  $n$ -photon process. (ii) Linear with  $n \approx 1$ , defining an intensity independent coefficient  $k_I(st)$ , typically valid at intermediate intensities:

$$k_I(st) = k(st)/I \quad (14)$$

(iii) Nonlinear with  $n < 1$ , at very high intensities, possibly.

In the linear régime of IR-photochemistry, fluence is the relevant experimental irradiation parameter. This is seen by rewriting Eq. (6) approximately with an intensity independent matrix  $K_I$  [27]:

$$\dot{p} \approx K_I \cdot I(t) p \quad (15a)$$

$$p(t) = \exp \left[ K_I \int_0^t I(t') dt' \right] p(0) \quad (15b)$$

In Eq. (15b) the fluence  $F$  from Eq. (1) emerges as the independent variable. Deviations from this fluence scaling arise from some steps obeying case C or case D instead of case B with  $K_{M,N} \propto I$ , from the fact that the diagonal of  $K$  contains the specific rate constants  $k_M$ , which are not proportional to  $I$ , and from collisions. In practically all current experiments intensity is not quantitatively controlled, whereas fluence is (at best). For the evaluation of experiments we shall therefore now restrict our attention

to situations with fluence scaling and refer to refs. 24 to 27 for a more detailed general treatment.

Even if fluence scaling applies, one has to take into account the spatial variations in  $F$  (Fig. 3). This can be done by defining an *apparent* experimental product yield in an arbitrary, apparent irradiated volume  $V_I$ :

$$P_{app} = f \cdot (V_c/V_I) \quad (16a)$$

$$c_m = c_0 (1 - f)^m \quad (16b)$$

The  $c_m$  are the bulk reactant concentrations remaining after irradiation with  $m$  laser pulses in the cell volume  $V_c$  ( $f$  = fraction decomposed). The volume  $V_I$  is, for instance, defined by the cross section  $Q_B$  at which the parallel, unfocussed beam has  $1/e$  of its maximum fluence  $F_{max}$ . One can fit now the measured points  $P_{app}$  with a theoretical yield function  $g(x)$ :

$$P_{app} = \sum_i \frac{\delta Q_i}{Q_B} [1 - g(c_i F_{max})] \quad (17)$$

The  $\delta Q_i$  in the sum, indicated in Fig. 3, must be chosen to be sufficiently small that the actual fluence in this surface element can be taken to be constant, equal to  $c_i F_{max}$ . The set of constants  $\delta Q_i/Q_B$  and  $c_i$  has to be determined experimentally once for a given optical set-up. For  $g(F)$  we can take the expansion in Eq. (10) with a few terms, or alternatively the fluence scaled result from the two parameter Eq. (12) [42]:

$$g(F) = F_R^* = \exp \left\{ \frac{1}{2} k_I(st) \varphi \left[ 2\sqrt{\pi} + \sum_{n=0}^{\infty} \frac{(-1)^n}{n! (n-1/2)} \left( \frac{\varphi}{F} \right)^{2n-1} \right] \right\} \quad (18)$$

The final result of the experiment would then be  $k_I(st)$  and the activation fluence  $\varphi$ , only  $k_I(st)$  being taken as physically significant [16]. The same parameter  $k_I(st)$  is also obtained if the quite different Eq. (10) is used in the evaluation.

Fig. 7 illustrates with a model calculation how this procedure works in the IR-photolysis of  $CF_3I$ . The experimental results reported in ref. 16 are very similar, indeed, but would not allow us to compare with the "exact" values (here the exact computational result). The line is a least squares fit to the "experimentally" scattered points  $P_{app}$  (crosses) using two terms of Eq. (10). It approximates also the "exact" apparent yield in Fig. 7a (points). In Fig. 7b one finds that the two term expansion (dashed line) again approximates well the real fluence dependence of  $-\ln F_R^*$ , including the initial curvature. The result in Fig. 7b would be obtained for irradiation with uniform fluence  $F$  and is the physically significant result. The final slope  $k_I(st)$  is even well approximated with a one term, steady state approximation in Eq. (10), giving the straight line 1(st). The reaction is delayed, as required by the multi-step mechanism, since otherwise one would have a straight line through the origin from an ordinary exponential decay law. A quantitative evaluation of data

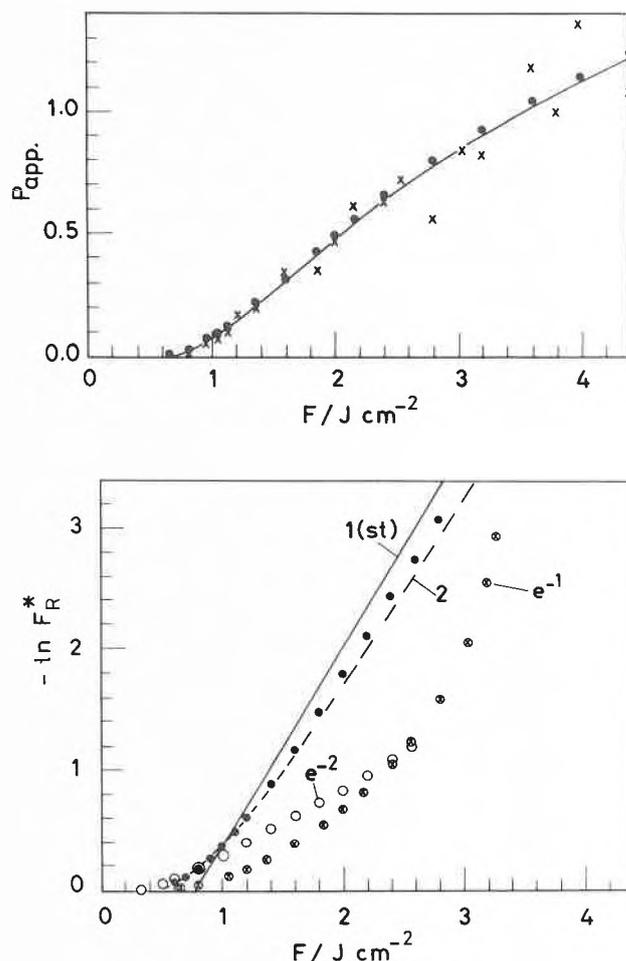


Fig. 7: Theoretical simulation of the procedure for obtaining  $k(st)$  for  $CF_3I$ -photolysis (see ref. [16] for a detailed discussion and experimental results).

a) Apparent yield, points are exact, crosses with scatter added from a random number table. Line is a nonlinear least squares fit to the crosses.

b) True yield function in terms of  $-\ln F_R^*$  (see text for detailed explanation).

providing absolute rate coefficients has only recently been carried out [16, 17]. That it is necessary is shown by two often used approximations, taking  $P_{app} \approx 1 - g(F)$  i. e. *one* term of the sum in Eq. (17). The formally constant fluence  $F$  and the corresponding  $V_I$  are calculated either by dividing the total pulse energy by the beam cross section defined by the  $e^{-1}$  criterion (line at which  $F_{real} = e^{-1} F_{max}$  giving a nominal fluence  $F = F_{max}$  for a Gaussian) or by the corresponding  $e^{-2}$  criterion (giving  $F = F_{max}/2$  for a Gaussian). Neither of these assumptions gives a quite adequate description. The situation is more favourable with irradiation from multimode lasers and flatter fluence profiles, but then "hot" and "cold" areas may arise in the fine structure, preventing quantitative evaluation.

The values of  $k_I(st)$  derived by the above quantitative method are a useful measure of the rate of an IR-photochemical reaction and they do not depend sensitively upon laser properties ( $I(t)$ ), provided that one can show

that the linear régime applies (for instance using pulses of different duration with the same fluence). The method works even, if substantial amounts of inert gas are present [16]. Before summarizing some experimental results, one may ask, how the rate coefficients depend upon molecular properties [26,42]. A general expression including the most important parameters is given in Eq. (19):

$$k(\text{st}) = F [I^a, G, s, g, \nu, \nu_1, E_T, E_Z, f(\nu', \nu'', \Delta\nu), T] \quad (19)$$

The intensity dependence may be nonlinear. The integrated band strength of the pumped vibration is

$$G = \int_{\text{band}} \sigma(\nu) d \ln \nu \quad (20)$$

Further parameters are the number of effectively coupled internal degrees of freedom,  $s$  (and their frequencies), the order of a molecular symmetry group,  $g$ , the frequency of the pumped vibration  $\nu_1$  and the laser frequency  $\nu$ , the threshold energy  $E_T$ , the total molecular zero point energy  $E_Z$  and finally the absorption bandshape  $f(\nu', \nu'', \Delta\nu)$  as a function of initial energy  $h\nu''$ , final energy  $h\nu' = h\nu'' + h\nu$ , and bandwidth  $\Delta\nu$ . There is furthermore a secondary influence of the initial temperature  $T$  [27, 46]. It is obvious that of all parameters the bandshape is the least well known, particularly so at high levels of excitation [37]. This current lack of spectroscopic knowledge prevents an accurate a priori prediction of rate coefficients. Nevertheless, one can try simple parametrizations and arrives at the following expression for the *linear régime* of IR-photochemistry [42] (see also [43]):

$$k(\text{st}) = xIG \Delta\nu^{-1} s^a \nu_1^b (E_T + E_Z)^{-c} \quad (21)$$

This expression should give a *low estimate* for  $k(\text{st})$  with optimum pumping into the strongest (or any well separated) vibrational band, if one sets  $\Delta\nu \approx \nu_1$ ,  $b < 2$ ,  $0 < a < 1$ , and  $2 < c < 3$ , with a constant  $x$  (unam-

biguous values for the parameters are obtained from a solution of Eq. (6) [27]). The spirit of this expression, which has first been given in terms of a few rules, is to provide a priori, without fits to experiments, some general phenomenology of the rates in IR-photochemistry. Comparison with experiment should help to show, to what extent detailed spectroscopic features contained in  $f(\nu', \nu'', \Delta\nu)$  are in fact important or whether they are partly averaged out by the complex multistep excitation process.

Table 2 summarizes the pertinent data on some IR-photochemical reactions, including also some results from the literature, where, however, accurate fluence control was not possible and therefore the  $k(\text{st})$  must be considered as preliminary (see also [44]). For the reaction



the pumping of two different vibrational bands has been possible, providing a direct check upon the influence of  $G$  [17].  $\text{SF}_6$  decomposition is the only case, where the theoretical *low estimate* is higher than the experimental result, which, however, must be considered with caution, in spite of the many investigations available for this reaction. A classical trajectory calculation for  $\text{SF}_6$  also predicts a larger rate coefficient [31]. Concerning the general order of magnitude agreement between the theoretical estimate and experiment it must be noted that many simple models (harmonic oscillator model, direct multiphoton model, constant coupling model [45] etc.) would predict rates by orders of magnitude different from experiment. In fact, apart from the classical trajectory calculation [31], none of the other approaches discussed in section 3 has been used, so far, for any a priori prediction of rates. It seems, that the crude Eq. (21) is not unreasonable, although much remains to be done in the comparison of quantitative experimental and theoretical data. Also the treatment of the nonlinear régime is more complicated [25,26].

Table 2: Rate constants for IR-Photochemistry (near optimum frequency  $\bar{\nu}$ )

Reaction	$\bar{\nu}/\text{cm}^{-1}$	HS	$E_T/\text{cm}^{-1}$	HS	Ref.	
$\text{CF}_3\text{I} \rightarrow \text{CF}_3 + \text{I}$	1075	9.0	18 700.	6.2	(5.61) <sup>b)</sup>	[16]
$\text{C}_2\text{F}_4\text{S}_2 \rightarrow 2\text{CF}_2\text{S}$	1076	11.5	16 000.	6.5	(6.13) <sup>b)</sup>	[17]
$\text{C}_2\text{F}_4\text{S}_2 \rightarrow 2\text{CF}_2\text{S}$	955	1.52	16 000.	5.9	(5.26) <sup>b)</sup>	[17]
approximate values: $\text{SF}_6 \rightarrow \text{SF}_5 + \text{F}$	(944)	20.7	31 500.	ca. 5.3	(5.6) <sup>b)</sup>	[11, 15, 27, 46]
		classical trajectories:		5.6		[31]
$\text{CF}_2\text{HCl} \rightarrow \text{CF}_2 + \text{HCl}$	1090	7.2	19 600	ca. 5.6	(5.3) <sup>b)</sup>	[44]
$\text{UO}_2(\text{HFACAC})_2 \cdot \text{THF}$ $\rightarrow$ (elim. of THF)	956	—	(12 000?)	ca. 7.2	(—)	[23]

a) The unit implies that for  $\text{CF}_3\text{I}$  at  $100 \text{ MWcm}^{-2}$  (typical) one has  $k(\text{st}) = 1.6 \cdot 10^8 \text{ s}^{-1}$ , for example.

b) Low estimate from Eq. (21).

### 5. Thermal Reactions, IR-Photochemistry, and Collisional Effects

Both in thermal reactions and in IR-photochemistry the primary activation step involves vibrational and rotational excitation in the electronic ground state, quite in contrast to UV-VIS-photochemistry, involving excited states. This has some simple general consequences, of which we may quote a few examples. Product and product state distributions in thermal and IR-photochemical reactions reflect the dominant contribution from the electronic ground state. For instance  $\text{CF}_3\text{I}$  thermolysis and IR-photolysis give mainly ground state I ( $^2P_{3/2}$ ) atoms (no  $^2P_{1/2}$  atoms have been detected, so far, although they are expected in small amounts). In contrast to this, UV-photolysis of  $\text{CF}_3\text{I}$  is known to yield a large excess of excited I ( $^2P_{1/2}$ ), the basis for the iodine atom laser. Another, fairly general consequence, which, has not been subjected to systematic experimental test, concerns the electronic symmetry correlation rules for chemical reactions. To the extent that the *Woodward-Hoffmann* rules are applicable at all [47], one common set of predictions is obtained for both thermal and IR-Photochemical reactions, whereas the ordinary UV-VIS photochemistry obviously is different. While these examples stress the similarity between IR-photochemistry and thermal reactions, an important but obvious difference is due to the highly selective monochromatic IR-pumping. We discuss here some further, less obvious points.

a) *The dependence of rate constants upon threshold energy and temperature.* Consider the temperature dependence of the thermal rate constants of a unimolecular reaction in the high pressure limit:

$$k_{\infty}(T) = A(T) \exp(-E_A/RT) \quad (22)$$

The phenomenological Arrhenius law [48] may be supplemented by the transition state expression [49], which gives a useful, possibly predictive relationship to molecular parameters contained in the partition functions  $Q$  and threshold energies  $E_T$  (compare Eqs. [19] and [21]):

$$k_{\infty}(T) = \frac{kT}{h} \frac{Q^{\ddagger}(T)}{Q(T)} \exp(-E_T/RT) \quad (23)$$

In both equations the strong, exponential dependence of  $k$  upon the threshold energy and upon the temperature  $T$  is visible ( $E_T/E_A \approx 1$  for  $E_T/RT \gg 1$ ). In contrast to this the rate constant in IR-photochemistry depends upon the threshold energy only weakly, with a negative power of 2 to 3 [see Eq. (21)], temperature being absent from the simple rate expression (the dependence upon *initial* temperature in Eq. [19] is a secondary effect). One may ask, at which temperatures in thermal reactions one has rate constants which are comparable to the IR-photochemical ones [50]. Let us take a typical value for  $\text{CF}_3\text{I}$  at 100  $\text{MW cm}^{-2}$  from table 2, giving  $k = 1.6 \cdot 10^8 \text{ s}^{-1}$ . A transition state model for  $\text{CF}_3\text{I}$  decomposition discussed in [42] (but including rotation) gives for the range 1500 K <  $T$  < 1900 K (high pressure limit):

$$k_{\infty}(T) = 1.4 \cdot 10^{15} \exp(-207.8 \text{ kJ mol}^{-1}/RT)$$

hence, a comparable rate constant at about 1560 K (excluding rotations one has a somewhat higher  $T$ ). However, this figure is quite misleading, because the high pressure limit will not be obtainable at this temperature, in practice. At low pressures of a weak collider (Ar) in the kPa-range one estimates  $k(T) = 4 \cdot 10^7 \text{ s}^{-1}$  at  $T > 16000 \text{ K}$  (see below, pressure proportional and somewhat hypothetical because other processes become important at such high  $T$ ). Qualitatively speaking, the IR-photochemical rate and the thermal rate at low pressures and high temperatures are kinetically determined, whereas the hypothetical rate at high pressures, Eq. (23), is thermodynamically controlled. Unfortunately, there are some quite misleading discussions of the role of temperature in the literature of IR-photochemistry.

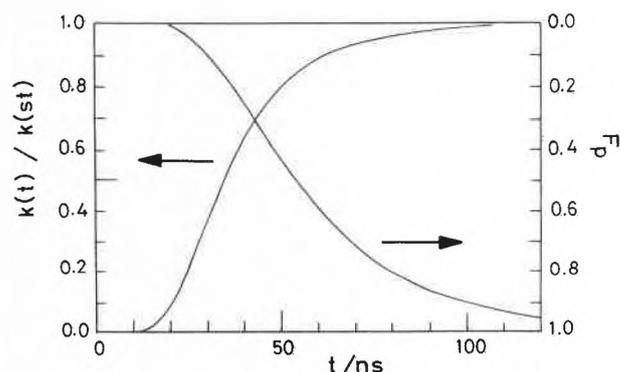


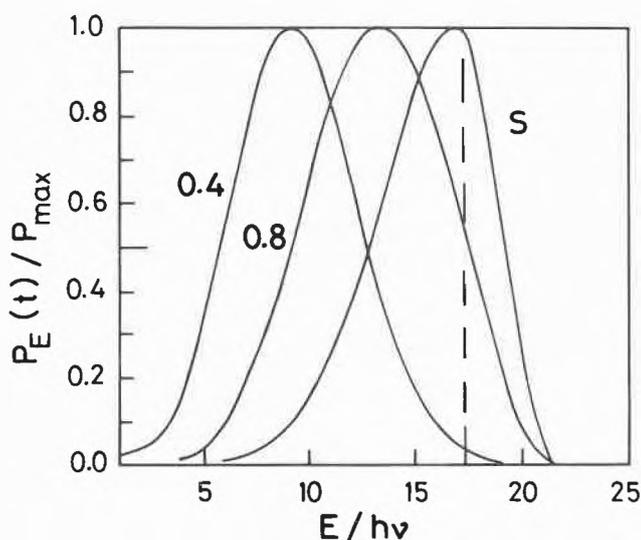
Fig. 8: Time dependence of the rate constant for  $\text{CF}_3\text{I}$ -thermolysis at 16200 K and low pressures of a weak collider gas (calculated, see text and ref. 26 for similar results on IR-photolysis,  $F_p = 1 - F_R$  is the product formation).

b) *The dependence of rate constants upon time.* We have discussed in section 4 the pronounced dependence of the rate coefficient in IR-photochemistry upon time. Thermal reactions, on the other hand, proceed ordinarily with a rate "constant", at steady state. However, at high temperatures and low pressures the time dependence is important also for the rate coefficient in thermal reactions. This is shown for a low pressure, weak collider, stepladder model of thermal  $\text{CF}_3\text{I}$ -decomposition at  $T > 16000 \text{ K}$ . There is a pronounced delay before the reaction starts, similar to the IR-photochemical reactions [26]. In fact, IR-photochemistry sometimes can be considered as an extreme thermal reaction ( $T \rightarrow \infty$ ), with strict stepladder activation, since the limiting distribution law is "Boltzmann without  $\exp(-E/kT)$ " [24]. In thermal reactions such extreme conditions are not usually realized, but some investigations of incubation phenomena exist (see the review [51] and the theory of Dove and Troe [52]).

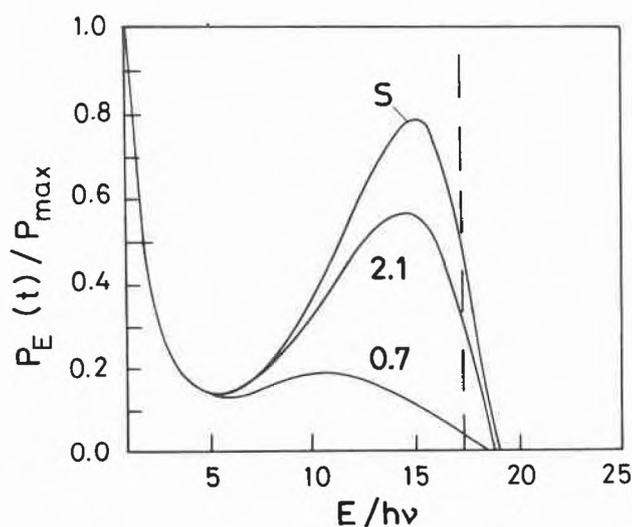
c) *Level populations.* A more detailed observable than the rate coefficient is the level population, i.e. the relative number of molecules at the different excitation steps in

IR-photochemistry. No quantitative measurement and few semi-quantitative attempts are available [53]. However, approximate theoretical calculations can help the understanding of the nature of molecular distribution functions. Fig. 9 summarizes the results of such calculations for a simple model of  $\text{CF}_3\text{I}$  decomposition, disregarding rotation (the same model is used for IR-photochemistry and the thermal reaction, for consistency). Fig. 9a shows the fluence dependent populations in the linear régime of IR-photochemistry. The steady state distribution (S) above threshold will depend slightly upon intensity. Fig. 9b shows the populations for a

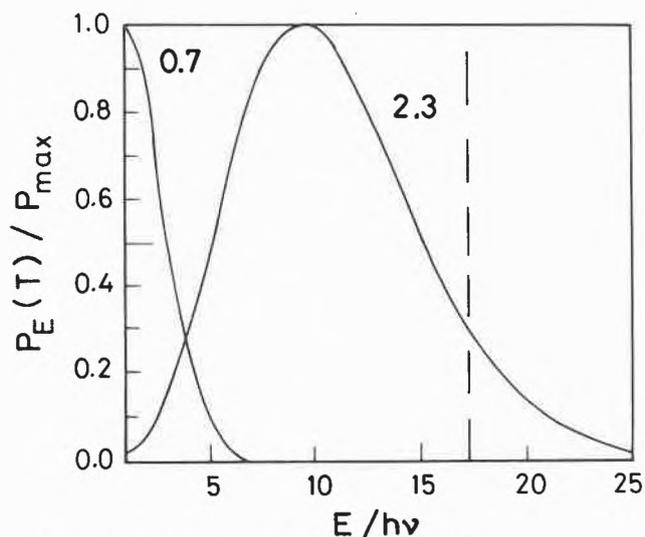
Fig. 9: Level populations in IR-photochemistry and in thermal reactions of  $\text{CF}_3\text{I}$  (model). All distributions are individually normalized to their maximum values. The energy scale is in multiples of a  $\text{CO}_2$ -laser quantum. The dashed line indicates the threshold energy  $E_T$



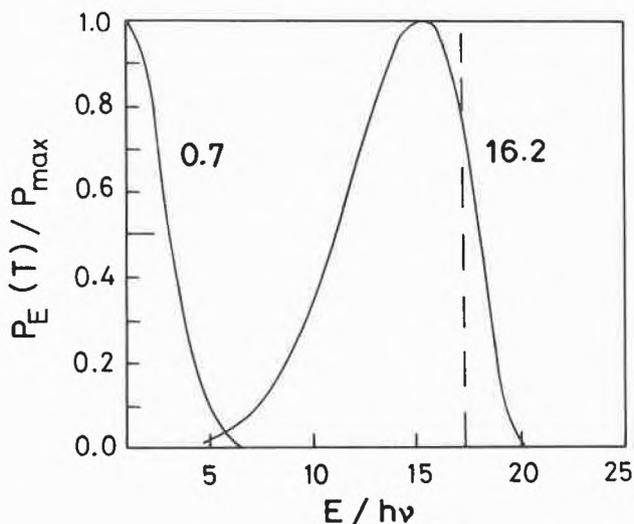
a) Distribution after irradiation with 0.4 and 0.8  $\text{Jcm}^{-2}$  and at steady state (S), linear régime (high intensity, case B)



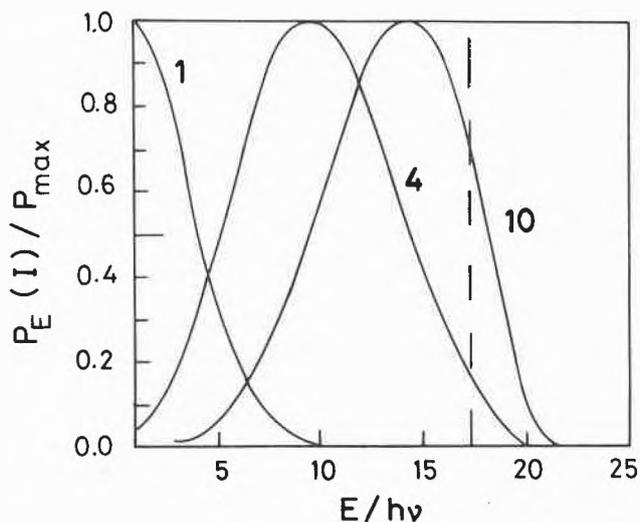
b) Nonlinear régime, 0.7 and 2.1  $\text{Jcm}^{-2}$  (low intensity, case C)



c) Boltzmann distributions at 700 and 2300 K



d) Steady state distributions under low pressure heating with a weak collider (700 and 16200 K)



e) Steady state distributions under collisional conditions with IR-laser pumping of different relative intensity as indicated by the numbers

nonlinear situation (case C and case B, see Fig. 5). One obtains bimodal distributions which quickly reach steady state at low levels of excitation, but more slowly at high excitation (larger  $F$  needed compared to 9a). The steady state distribution at low energies is strongly intensity dependent [26]. The thermal Boltzmann distributions (high pressure limit) in Fig. 9c are visibly different from either IR-photochemical distribution. Fig. 9d shows low pressure limit thermal distributions, which are Boltzmann at 700 K, but completely kinetically determined and far from Boltzmann at 16200 K. Fig. 9e finally shows steady state level populations under conditions where IR-laser pumping and collisions with a cold inert bath gas compete.

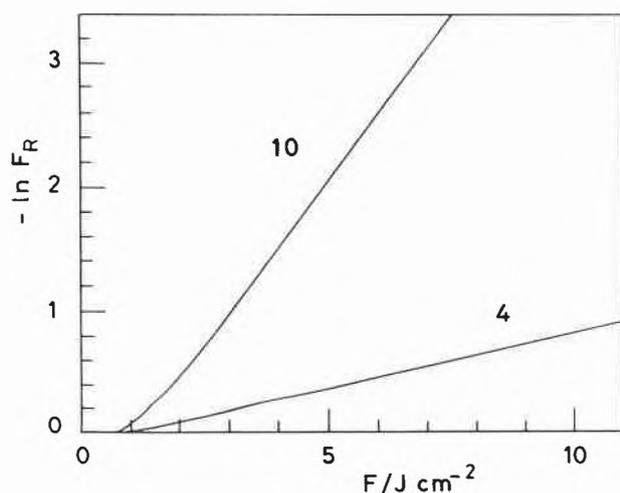


Fig. 10: Yield function in terms of  $-\ln F_R$  as a function of fluence under collisional conditions (kPa range of an excess of inert gas at 300 K) with two different laser intensities (indicated in relative units by the numbers).

d) *Rate constants for IR-photochemistry with collisional cooling.* If collisions with an excess of cold inert gas compete effectively with IR-laser pumping, fluence scaling does not apply. Two experimental situations can arise. (i) Fluence is changed parallel with intensity (constant pulse duration). Then an evaluation as discussed in section 4 gives apparent limiting slopes  $-\ln F_R/dF$ , close to the *collisionless* value of  $k_I(st)$  [16]. (ii) Fluence is changed at constant intensity through pulse duration [19]. In this case one obtains from the evaluation directly the steady state rate coefficient for the collisional case, as illustrated with a model calculation in Fig. 10. The linearity compared to Fig. 7b indicates the early approach to steady state under collisional conditions. The rate coefficient changes considerably with fairly small changes in inert gas pressure. There are no quantitative experiments of this kind available, yet, but some aspects of both collisional enhancement in the nonlinear régime [54, 26] and collisional quenching have been discussed [16, 55–57].

## 6. Experimental Effects and Theoretical Models

We have put more stress than is usual in this field upon a quantitative understanding of the primary processes in IR-photochemistry. We conclude by summarizing in table 3 our current understanding, using various theoretical approaches for predicting experimental effects qualitatively and quantitatively. The table is largely self-explanatory. The theories a) to d) are as labeled in section 3, e) is omitted from the discussion as are all purely descriptive models. The theory u) is the unified master equation including nonlinearity and combination with the Schrödinger equation. The major experimental facts in IR-photochemistry are mentioned in table 3.

Table 3: Experimental effects and theoretical models

Theory (Section 3)	Effect	Isotope sep.	Qualitative intensity dep. $k \propto I^n$			Branching ratios	Static fields	Quantitative $k(st)$
			$n = 1$	$n < 1$	$n > 1$			
a)		+	+	(-)*	-	(+)	-	-
b)		+	+	?	?	(+)	?	(+)
c)		+	+	-	+	?	-	-
d)		+	+	-	+	?	-	-
u)		+	+	+	+	+	+	+
Experiment available?		+	+	?	+	+	+	

a) is the Einstein coefficient rate equation model

b) classical trajectory calculations

c) two-ladder, three-regions model

d) pumping dumping model

u) unified master equation

see section 3 for detailed explanations

\*) small effect from intensity fall-off [24]

a) *Isotope separation.* This is predicted by all theories. Some however, predict in addition to the linear mechanism, which corresponds just to the different linear absorption cross sections of isotopomers, a second non-linear mechanism (+ +). Many experiments have been reviewed [4 – 8].

b) *Intensity dependence.* The intensity dependence of the rate coefficient in IR-photochemistry has never been measured quantitatively. Qualitative, conclusive evidence has been obtained by measuring product yields with laser pulses of different average intensity but the same fluence [11, 13, 25, 44]. If  $n = 1$ , the same yield is obtained, if  $n < 1$ , less yield would be obtained, but no experiments have shown this effect, so far, if  $n > 1$ , a greater yield is obtained [11, 13, 19]. The question mark in the case of classical trajectories (and in other cases in table 3) indicates that no calculations are available concerning this point and that the outcome of such calculations is not obvious, since  $n > 1$  results at least partly from a quantum effect.

c) *Branching ratios.* Many molecular beam experiments on branching ratios in physical channels (product translational energy distributions) and chemical channels are now available [15]. Claims concerning "mode specific" pumping being reflected by unpredicted branching ratios have never been substantiated (see the reviews [8], [11], [15]).

d) *Yield enhancement by static fields.* Van den Bergh and coworkers have established an interesting enhancement of the IR-multiphoton dissociation of  $\text{CF}_2\text{HCl}$  by strong, static electric and magnetic fields [58]. This enhancement can be understood in a straightforward way only by one of the available theories [26, 59].

e) *The quantitative results for  $k(st)$*  discussed in section 4 provide the most stringent test on theories. Classical trajectory calculations will only provide good predictions, if the initial excitation in the highly quantized low energy region of polyatomic molecules is not rate determining. To what extent the simplifications of the general theory u) discussed in section 4 will lead to correct predictions in the long run remains to be tested.

An important effect missing in table 3 is the detailed frequency dependence of the IR-photochemical rates. This is partly due to the lack of experiments with continuously tunable lasers, and partly due to our lack of knowledge about IR-spectra of highly excited molecules. Qualitatively, the frequency dependence of photochemical rates observed with line tunable lasers is easily understood within any theoretical framework, similar to the isotope selectivity, which is just one manifestation of the frequency dependence. It is ironical that isotope separation, which may become an important practical application of IR-photochemistry, is the least discriminative

process in terms of a fundamental understanding. From table 3 it should be clear that future work is to be directed towards quantitative results, experimentally and theoretically. A *quantitative* understanding of the primary rate processes in IR-photochemistry will finally not be just of academic interest but will also provide the basis for any large scale technical application that may become feasible. Thus, it is meaningful "to translate the laws of the ever changing forms of the phenomena into the clearest possible formulae" [60].

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