

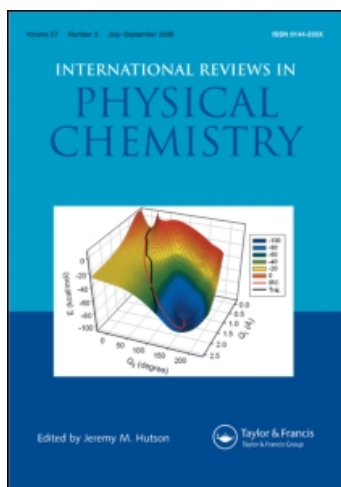
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M. Quack^a; J. Trose^a

^a Institut für Physikalische Chemie, Universität Göttingen, Göttingen, GFR

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CURRENT ASPECTS OF UNIMOLECULAR REACTIONS

M. QUACK AND J. TROE

*Institut für Physikalische Chemie, Universität Göttingen,
Tammannstr. 6, D-3400 Göttingen, GFR*

ABSTRACT

Areas of particular current interest in the field of unimolecular reactions are reviewed. New developments and experimental applications of the theory of thermal unimolecular reactions are discussed, with particular stress on simple descriptions of both the low- and high-pressure limiting ranges and the intermediate fall-off. Recent experimental studies of elementary steps in unimolecular reactions after optical (one photon) and molecular beam (chemical) activation are reviewed in relation to theory. The kinetic and mechanistic aspects of the new field of unimolecular reactions induced by monochromatic infrared radiation (URIMIR, with multiphoton excitation) are developed in some detail. Experiments in this area are summarized and their role for the interpretation of URIMIR is discussed.

INTRODUCTION

Unimolecular reactions have a long history. Since the early days of chemical kinetics important aspects of reactivity have been investigated in this field. For a long time attention focused on collision-induced thermal unimolecular reactions. This effort has led to a semiquantitative theory which, in spite of some poorly understood details, is of considerable practical use. With the advent of more specific activation techniques, the study of the elementary processes involved in unimolecular reactions has become possible. Such investigations not only help to improve the quantitative description of classical thermal unimolecular reactions, but they allow for an analysis of intra- and intermolecular processes in terms of properties of potential surfaces at a microscopic level. In this way the concept of unimolecular reactions has been widened to include any reactive process occurring on bound potential surfaces. It is the aim of the present review to describe the current status of particularly active fields related to unimolecular reactions.

In the first part we discuss aspects of thermal unimolecular reactions and identify parts of the description which are still uncertain and limit our predictive possibilities. An important problem also is the way theories should be formulated to be suitable for practical use. This section will be concluded with examples of new applications of the theory. In the second part we describe new experimental studies of isolated elementary steps in a unimolecular reaction. Modern techniques allow for the direct observation of unimolecular transformations of selectively excited species. Also, energy distributions of the products of unimolecular fragmentations and of bimolecular reactions occurring on surfaces with deep minima have been measured thoroughly. Such observations are detailed enough to be compared directly with numerical simulations of the intramolecular dynamics. In this part of our review, single-photon optical activation experiments play an important role. Multiphoton activation studies inducing unimolecular reactions in a less specific, but new and very attractive way, are reviewed in the last part of this article. In the

short time since its discovery, this type of unimolecular reaction has created wide interest. After many misunderstandings it now is becoming clearer to what extent this phenomenon resembles or differs from other unimolecular reactions.

THERMAL UNIMOLECULAR REACTIONS

Many thermal unimolecular isomerization, dissociation or the reverse recombination reactions are being studied experimentally over increasingly large temperature and pressure ranges. It has become clear that earlier attempts to characterize a reaction on the basis of a limited set of experiments have often led to wrong conclusions. On the one hand limited pressure ranges did not allow for a correct construction of the fall-off curve, on the other hand dissociation and recombination experiments had not always been combined to obtain the largest accessible temperature range.

Flexible theoretical expressions are most useful in analysing the available experimental data, localizing the experiments with respect to their position on the fall-off curves, and providing compact expressions for a full set of fall-off curves to be used in simulations of large reaction systems. An analysis of experimental data in terms of current theory should be obligatory in order to avoid misinterpretations. In this analysis, however, one must not forget that the available theories are all of a semi-quantitative nature and often fine details are not well characterized. Users of RRKM-program packages in many cases have neglected the unrealistic simplifications of the model. In order to clarify the various contributions, we have proposed an alternative version of the statistical theory of unimolecular reactions which tries to separate the effects and shows the influence of various parameters in an explicit way. We shall use this scheme in the following discussion.

Low pressure rate constants

The steady state rate constant in the low pressure range k_0 can be represented by a collision efficiency β_c and a strong collision rate constant k_0^{sc} (written as a pseudo-first order rate coefficient),

$$k_0 = \beta_c k_0^{sc} = \beta_c Z_{LJ} [M] \int \int^* f(E, J) dE dJ. \quad (1)$$

The collision efficiency β_c crucially depends on properties of intermolecular energy transfer whereas the strong collision rate constant, apart from the Lennard-Jones collision frequency Z_{LJ} and the bath gas concentration $[M]$, is given by the integral of equilibrium populations $f(E, J)$ over 'metastable molecular configurations *'. It is worthwhile to remember the origin of this integral: it enters the derivation by replacing the collisional activation flux from stable to unstable configurations, using the principle of detailed balancing, by the corresponding collisional deactivation flux. The boundaries of the integral * therefore also depend on collisional properties. Nevertheless, for practical purposes it appears sufficient to consider for the range * just a smooth continuation of stable states to energies larger than the total angular momentum J -dependent threshold energies $E_0(J)$. The understanding of a low-pressure rate constant k_0 according to Eq. (1) depends on the analysis of two components, the collisional energy transfer part $\beta_c Z_{LJ} [M]$, and the remaining statistical mechanical factor. In the following we first consider the energy transfer part. We assume that Z_{LJ} represents the adequate overall rate coefficient for inelastic energy transfer reasonably well (see Troe, 1979), and we focus attention on the properties of the collision efficiencies β_c .

Collision efficiencies

As shown earlier (Tardy and Rabinovitch, 1966, 1968; Troe and Wagner, 1966, 1967; Troe, 1973, 1977a), the collision efficiency β_c is closely related to the average energy $\langle \Delta E \rangle$ transferred per collision, or alternatively to the mean squared energy $\langle \Delta E^2 \rangle$ transferred. Additional factors such as the exact shape of the collisional transition probabilities $P(E', E)$ are only of secondary importance. This is illustrated in Fig. 1 which compares numerically computed collision efficiencies for various collision models as a function of the ratio $-\langle \Delta E \rangle / F_E kT$ where F_E is defined by

$$F_E = \frac{\int_{E_0}^{\infty} f(E) dE}{f(E_0) kT} \quad (2)$$

In order to understand the collision efficiencies, and hence the low-pressure unimolecular reactions in general, one has to solve the master equation of the reaction, see Fig. 1, and one must have sufficient information on $\langle \Delta E \rangle$ and its temperature dependence. Numerical solutions of the master equation are now obtained routinely on standard computers. New efficient algorithms have been proposed (Gaynor, Gilbert and King, 1978) which greatly reduce computer time. It should be emphasized, however, that new numerical solutions of the energy dependent master equation in the low pressure range are often not really needed since analytical solutions cover much of the physically relevant part of the problem.

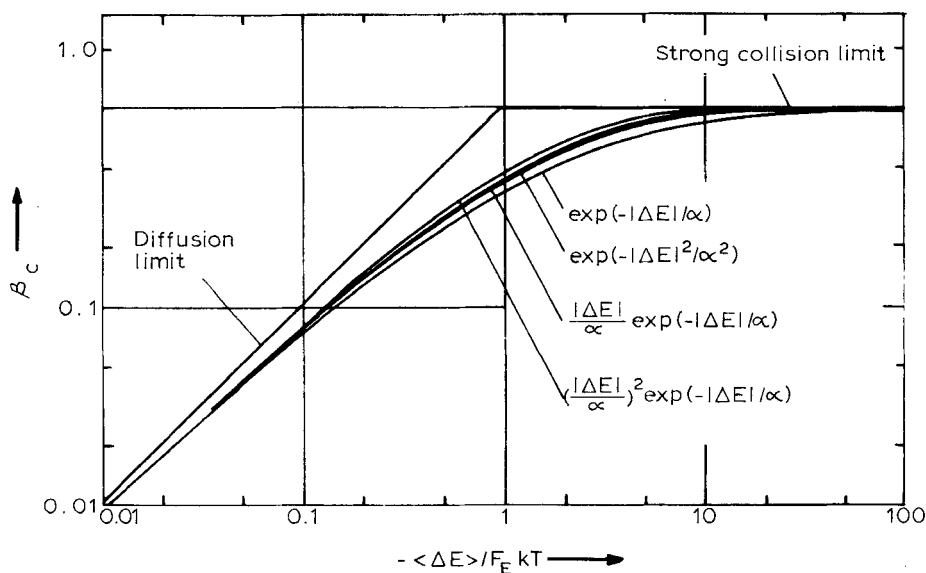


FIG. 1. Collision efficiencies in thermal unimolecular reactions at low pressure. (Numerical solutions of the master equation for various down transition probabilities at $1 \leq F_E < 2$, from Troe, 1977a).

As shown in Fig. 1:

- (i) the strong collision limit $\beta_c = 1$ is fixed;
- (ii) the weak collision 'diffusion' limit is exactly solved for arbitrary collision models;
- (iii) the intermediate case between the weak and strong collision limits has been solved exactly for exponential and stepladder collision models.

The particular deviations from the exponential model are negligibly small compared to uncertainties in $-\langle\Delta E\rangle/F_E kT$.

Our attention therefore has to concentrate on the average energies $\langle\Delta E\rangle$ transferred per collision. Information on this quantity may stem from in situ measurements in thermal unimolecular reactions, either from collision efficiency studies for one- and two-channel reactions, or from incubation time or dilution measurements (*see below*). At very high temperatures $\langle\Delta E\rangle$ can only be measured in situ in thermal unimolecular reaction systems. At lower temperatures often non-thermal activation experiments provide a much better access to $\langle\Delta E\rangle$. Finally, theoretical calculations can help to understand the properties of $\langle\Delta E\rangle$.

For an exponential collision model the simple relationship (Troe, 1977a) holds

$$\frac{\beta_c}{1 - \sqrt{\beta_c}} \approx \frac{-\langle\Delta E\rangle}{F_E kT} \quad (3)$$

as long as F_E is not much larger than unity. It has been shown that Eq. (3) remains an excellent solution when the mathematical simplifications in its derivation are realized (Troe, 1977a; Penner and Forst, 1977). Following Eq. (3), the temperature dependence of β_c is given by that of $\langle\Delta E\rangle$ and $F_E kT$, a temperature independent $\langle\Delta E\rangle$ leading to a decrease of β_c . At low temperatures, where non-thermal activation experiments can be made, $\langle\Delta E\rangle$ has been shown to vary only slightly with temperature. In the collisional deactivation of photoactivated cycloheptatriene over the temperature range 300–700 K, the bath gas He showed a small positive T-coefficient, polyatomic bath gases like C_3H_8 showed a small negative T-coefficient, whereas intermediate bath gases gave constant $\langle\Delta E\rangle$ (Luu and Troe, 1974). Since $\langle\Delta E\rangle$ values from thermal and non-thermal activation studies give a very similar picture, which is often independent of the molecular complexity and degree of excitation of the highly excited collision partner (van den Bergh, Benoit-Guyot and Troe, 1977; Quack and Troe, 1977; Tardy and Rabinovitch, 1977), this information on the magnitude and T-coefficient of $\langle\Delta E\rangle$ can be used to understand and predict β_c -values in thermal unimolecular reactions. There is agreement about the conclusion that β_c generally will decrease with increasing temperature, as predicted by Eq. (3) for T-independent $\langle\Delta E\rangle$. However, information on the amount of decline of β_c at high temperatures seems to be controversial:

- (i) The analysis of the absolute values of the low pressure rate constants for H_2O dissociation and recombination in Ar gives β_c values of the order 0.5–1 at 200–300 K, 0.06 at 2000 K and 0.01 at 6000 K (Troe, 1979). Over this large temperature range (where $1 \leq F_E \leq 1.2$ is valid), the data analysed by Eq. (3) suggest again only a small temperature coefficient for $\langle\Delta E\rangle$ of T^n with $-1 \leq n \leq 0$. Trajectory calculations of $\langle\Delta E\rangle$ were in agreement with the analysis by Eq. (3) (Stace and Murrell, 1978).
- (ii) Very precise measurements of the temperature coefficient of the $O + O_2$ recombination at 200–300 K give a stronger temperature coefficient of the rate constant than predicted by Eqs. (1)–(3) (Klais, Anderson and Kurylo, 1980). Apparently here one has a rare example where for a unimolecular reaction of a polyatomic molecule the energy transfer mechanism of the recombination is slower than the complex mechanism, such that the typical behaviour of diatomic recombinations is observed. The conclusion that energy transfer in excited O_3 is exceptionally slow is confirmed by trajectory calculations (Stace and Murrell, 1978) as well as the observation of spectra of hot O_3 at early times in the recombination (Kleindienst, Burkholder and Bair, 1980).
- (iii) Shock wave experiments on the dissociation of NO_2 , $CINO$, O_3 , and N_2O in the temperature range 800–1000 K and near 2000 K, with the rare gases, N_2 , O_2 , CO_2 ,

CF₄, and SF₆ as bath gases, have again indicated only a small T-coefficient of $\langle \Delta E \rangle \propto T^n$ in Eq. (3) with $-0.5 \leq n \leq 0.5$ for 300–2000 K (Endo, Glänzer and Troe, 1979). Most remarkably the collision efficiency found for He was larger than that of Ar at high temperatures, whereas the opposite is true at 300 K. This behaviour is consistent with the above mentioned observation in photoactivated cycloheptatriene.

- (iv) Recent high temperature measurements of β_c for larger polyatomic excited molecules have led to different results. From the analysis of the two-channel structural isomerization of 1,1-cyclopropane-d₂ by ‘collisional competitive reaction spectroscopy’ (Klein, Rabinovitch and Jung, 1978), as well as from an analysis of the fall-off curves of this reaction (Klein and Rabinovitch, 1978), Rabinovitch and coworkers derive β_c -values for cyclopropane as bath gas near unity at 770 K and near 0.5 at 973 K, whereas β_c (He) = 0.08 at 770 K and 0.01 at 973 K. At first sight these marked temperature dependences of β_c over such small temperature ranges seem to contradict the observations (i) and (iii) as well as the general analysis of many other small molecule data (Troe, 1977b).
- (v) A similar behaviour to that described in (iv) has been observed by the ‘variable encounter method’ for wall-collision activated unimolecular isomerization reactions of cyclopropane and methylcyclopropane (Kelley *et al.*, 1979, 1980a,b; Flowers *et al.*, 1980). Wall collision efficiencies β in this case have been found to decrease from 0.48 at 800 K, 0.33 at 950 K to 0.24 at 1100 K (Kelley *et al.*, 1980b). A quite similar result was obtained by Gilbert and King (1980). These data show that quite a number of high temperature VLPP studies, in which the wall was treated as a strong collider, have to be reinterpreted. With the wall collision efficiencies of the order of 0.3–0.6 in the temperature range 750–1150 K, the effective number of wall collisions often must have been overestimated.
- (vi) Shock wave studies of the thermal isomerization of substituted cycloheptatrienes in the 1000–1200 K range in Ar (Astholz, Troe and Wieters, 1979) show fall-off behaviour at pressures much higher than expected from strong collision unimolecular rate theory. This indicates either very pronounced weak collision broadening of the shape of the fall-off curve (Luther and Troe, 1979) and/or very low values of the collision efficiencies β_c for the low pressure range. For these molecules the low pressure limit was not accessible experimentally such that this question could not be answered. However, because of the dramatic shift of the fall-off curves for large molecules, at higher temperatures, shock wave experiments on more stable species can answer this question. Such experiments have been made for the dissociation of toluene and xylenes near 2000 K (Astholz *et al.*, 1981a,b), and an analysis is underway.

The experimental results (i) and (iii) on the high temperature behaviour of β_c for small polyatomic molecules seem to contradict the observations (iv)–(vi) for large polyatomic molecules. In the discussion so far, however, the dramatic increase of F_E with increasing temperature for large polyatomic species has been neglected. As noticed for substituted cycloheptatrienes (vi) (Astholz *et al.*, 1979) at temperatures above 1000 K, F_E greatly exceeds unity (values larger than 10³!) so that Eq. (3) does not apply any longer. In this case the strong energy dependence of the density of states $\rho(E)$ invalidates the analytical solution of the master equation for the exponential collision model. Since the situation is characterized by completely weak collisions, the diffusion theory (Nikitin, 1959, 1966; Keck and Carrier, 1965; Troe, 1977a) gives the required relationship for the collision efficiency. One has (*see* Eqs. (5.23) and (5.24) in Troe, 1977a)

$$\beta_c = \frac{\langle \Delta E^2(E_0) \rangle}{2(kT)^2 F_E F'(E_0)}. \quad (4)$$

with

$$F'(E_0) = \int_0^{E_0} \frac{dE f(E_0) \langle \Delta E^2(E_0) \rangle}{kT f(E) \langle \Delta E^2(E) \rangle}. \quad (5)$$

For the weak collision limit, Eqs. (4) and (5) are exact, *see* Fig. 1; the average squared energy transferred $\langle \Delta E^2 \rangle$ and $\langle \Delta E \rangle$ are related by

$$\langle \Delta E(E) \rangle = \frac{1}{2f(E)} \frac{d}{dE} (f(E) \langle \Delta E^2(E) \rangle); \quad (6)$$

the energy dependences of $\langle \Delta E(E) \rangle$ and $\langle \Delta E^2(E) \rangle$ can be accounted for correctly. Whereas $\langle \Delta E^2(E) \rangle$ is always positive, $\langle \Delta E(E) \rangle$ has to change its sign, when $f(E)$ changes the sign of its slope such as happens for relatively high energies in polyatomic molecules (*see* Hippler, Luther and Troe, 1979). With energy independent $\langle \Delta E^2(E) \rangle$, and with $f(E)$ approximated by

$$f(E) \simeq f(E_0) \exp\left(-\frac{E - E_0}{F_E kT}\right), \quad (7)$$

Eq. (4) is identical to the right hand side of Eq. (2). However, in the present case of polyatomic molecules at high temperatures this approximation is not sufficient, and $F'(E_0)$ can assume values larger than F_E . As a consequence, β_c will decrease even more strongly with temperature than given by Eq. (2). For this situation, the relationship

$$\frac{\beta_c}{1 - \sqrt{\beta_c}} \simeq \frac{\langle \Delta E^2(E_0) \rangle}{2(kT)^2 F_E F'(E_0)} \quad (8)$$

together with Eqs. (5) and (6) provides a generalization which includes the full transition from the weak toward the strong collision limit. The reason for the very pronounced decline of β_c at high temperatures for large polyatomic molecules is then found in the strong increase of F_E and of $F'(E_0)$.

More shock tube experiments at high temperatures are required to confirm this theoretical prediction.

Energy transfer studies with non-thermal activation

Optical and chemical activation experiments often produce highly excited molecules whose stepwise deactivation can be observed. Stern-Volmer curves for collisional quenching of a chemical reaction in these systems yield relative information on energy transfer versus chemical reaction. A 'calibration' of these experiments in most cases is achieved either by calculation of the specific rates of the competing chemical processes or by measurements with a presumably 'strong' collider. Unfortunately this calibration technique always retains some uncertainty since no collider is completely strong, not even the wall of a vessel and the calculations of the reference rate are imperfect anyway (*see* above). In spite of these limitations, a considerable amount of $\langle \Delta E \rangle$ values could be collected in this way (*see* summaries in Quack and Troe, 1977; Tardy and Rabinovitch, 1977). It was recently possible to put $\langle \Delta E \rangle$ measurements for photoactivated cycloheptatrienes on an absolute basis, because the reference rate of the unimolecular reaction was measured directly in time-resolved flash photoexcitation experiments and could also be deduced from thermal isomerization experiments (Troe and Wieters, 1979). In this way a table of $\langle \Delta E \rangle$ values is now available which is not influenced by calibration problems.

Bearing in mind the difficulties of the absolute calibration of $\langle \Delta E \rangle$ values in relative yield measurements, steady-state photoactivation and chemical activation experiments continue to provide very important systematic data on energy transfer. Unfortunately, for historical reasons, the evaluations of these two types of experiments are done in different ways.

Now it would appear more useful to change over to a common language. In photoactivation experiments quantum yields for product formation are used and in chemical activation dissociation over stabilization product ratios D/S are used. A common yield relationship

$$\phi \hat{=} Y \hat{=} \frac{D}{S + D} = \frac{D/S}{1 + D/S} \quad (9)$$

would reconcile these two descriptions. Furthermore, Stern–Volmer expressions for the yield–pressure dependence

$$\phi^{-1} = 1 + \frac{\gamma_c Z_{LJ}[M]}{k(E_{exc})} \quad (10)$$

describe the quenching of photoactivated reactions where $K(E_{exc})$ is the specific rate constant of the reference chemical process at the initial excitation energy E_{exc} and $\gamma_c Z_{LJ}[M]$ is the effective collisional quenching rate constant with a collision efficiency γ_c . Chemical activation experiments are often represented by plotting

$$k_a \equiv \langle k(E) \rangle \equiv Z_{LJ}[M] D/S \quad (11)$$

as a function of the pressure (see Rynbrand and Rabinovitch, 1970, 1971; Oref, Schuetzle and Rabinovitch, 1971). In the language of Eqs. (9) and (10), k_a corresponds to

$$k_a = \frac{k(E_{exc})}{\gamma_c} \quad (12)$$

Curvatures of the Stern–Volmer plots or the k_a -plots are thus completely equivalent and expressed in terms of the collision efficiency γ_c . For a strong collider, $\gamma_c \rightarrow 1$.

Similar to thermal unimolecular reactions, the exact relation for the collision efficiency, γ_c , is complicated and requires the solution of the master equation for chemical reaction and step-wise collisional quenching. It can be shown that such solutions are practically equivalent to the old stochastic expression

$$\frac{S}{S + D} = \prod_{j=1}^T \frac{Z_{Lj}[M]}{Z_{Lj}[M] + k(E_j)} \quad (13)$$

if the number of steps T is given by

$$T \simeq \frac{E_{exc} - E_0}{-\langle \Delta E \rangle} \quad (14)$$

where $\langle \Delta E \rangle$ is the average energy transferred per collision. Elaborating this model in detail, leads to an approximate relationship for the collision efficiency

$$\frac{\gamma_c}{1 - \gamma_c} \simeq \frac{-0.8 \langle \Delta E \rangle}{E_{exc} - E_0} \left\{ \frac{(E_{exc} - E_0)(E_0 + C_2 - C_1)}{(E_{exc} - E_0 + C_1)(E_{exc} + C_2)} \right\} \quad (15)$$

when $k(E)$ can be represented by $k(E) \propto [(E - E_0 + C_1)/(E + C_2)]^{s-1}$ (Troe and Wieters,

1979). Equation (15) clearly shows that γ_c^{-1} is always larger than the number of steps T necessary to bring the molecule into the stable energy range.

Energy transfer in chemically activated haloethane molecules has been studied systematically by Setser *et al.* Recent work on mono- and difluoroethane (Richmond and Setser, 1980) complemented earlier work on trifluoroethane and dichloroethane. Whereas similar deactivation efficiencies were found for some colliders, differences were observed for others. So far these results are difficult to explain in detail.

New chemical activation studies, in which the influence of molecular complexity, not of the unexcited bath gas molecules, but of the highly excited molecules was monitored, have been reported by McCluskey and Carr (1978) for a series of alkylcyclopropanes. In a systematic comparison of these data for unexcited collision partners of the same molecular complexity, Carr (1980) identifies a trend toward smaller $\langle \Delta E \rangle$ values for larger excited molecules which is in accord with predictions from quasi-statistical transition mode models (Lin and Rabinovitch, 1970). It appears to us that such a conclusion is much too premature. Earlier inspections of results from triatomic up to large polyatomic excited molecules have not shown an influence of the complexity of the excited molecule (Quack and Troe, 1977). The actual scatter of all the available data, not only those shown by Carr, is too large to allow for definite conclusions. Much of this scatter has to be attributed to the above-mentioned ambiguities in the data evaluation. There have been several recent attempts to characterize the energy transfer of highly excited molecules by statistical or quasi-statistical models (Oref and Rabinovitch, 1977; Bhattacharjee and Forst, 1978; Nordholm, Freasier and Jolly, 1977). All these investigations were only partially successful. Obviously constraints due to angular momentum conservation are of great importance. Nevertheless, the small efficiency of this energy transfer observed in practice poses the serious question, whether new quasi-statistical theories lead any further than similar older approaches (Serauskas and Schlag, 1965, 1966; Keck and Kalelkar, 1968; Lin and Rabinovitch, 1970; Troe, 1973). Although an empirical 'scaling' of the collisional transition probabilities from such theories, to meet the experimental $\langle \Delta E \rangle$ values, may prove useful in practice (Troe, 1973), the general merits of quasi-statistical theories may be limited by pronounced non-randomization during the short contact times of the collision partners. We feel that the final solution of the problem can only come from complete trajectory calculations of the energy transfer, such as those started by Stace and Murrell (1978).

On the experimental side a considerable step toward the direct observation of the state-to-state collisional transfer probabilities $P(E', E)$ will be made in the near future. With optical excitation in laser flashes one can selectively prepare highly excited molecules in the vibrational quasi-continuum. With progress in the spectroscopy of molecules in this energy range, energy transfer then can be observed and analysed in direct time-resolved experiments. Fig. 2 shows the direct observation of the collisional deactivation of vibrationally very highly excited toluene molecules ($E_{exc} = 623 \text{ kJ mol}^{-1}$) in collisions with cold He at a pressure of 7.5 Torr on the microsecond time scale (Hippler *et al.*, 1981). In this case, the observed hot UV absorption signal of toluene is a direct measure of the energy content of the relaxing excited molecules. Highly vibrationally excited methyl radicals and their collisional deactivation could be followed directly by overtone IR spectra in recent experiments by Baughcum and Leone (1980). Experiments of this type with improved state-time resolutions will give a much better insight into the detailed properties of energy transfer. One can even think of doing the experiment shown in Fig. 2 in shock waves near 2000 K in order to obtain unambiguous information on the temperature dependence of $\langle \Delta E \rangle$ for large polyatomic molecules.

With pulsed laser techniques collisional energy transfer in highly excited molecular ions has been studied recently (Kim and Dunbar, 1979; Jasinski and Brauman, 1980) for

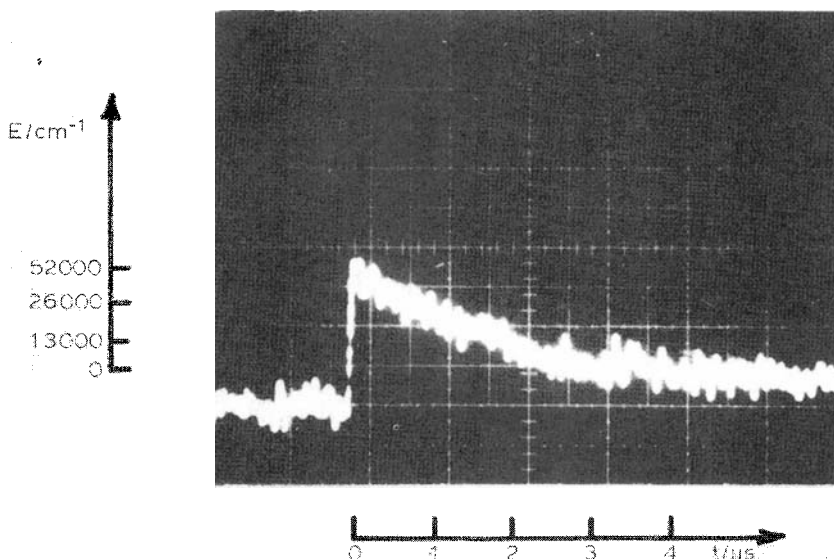


FIG. 2. Direct observation of collisional deactivation of vibrationally highly excited toluene ($E_{exc} = 52\,000\text{ cm}^{-1}$, collider = He at 7.5 Torr, $-\langle\Delta E\rangle = 2\text{ kJ mol}^{-1}$, from Hippler *et al.*, 1981).

$\text{C}_6\text{H}_5\text{Br}^+$ and CF_3O^- ions. Under the assumption that the total collision rates are adequately described by Langevin orbiting collision rate constants, the efficiencies for excited ion-bath gas collisional energy transfer were found to be low. In collisions between CF_3O^- and N_2 , maximum average energies transferred of about 4.6 kJ mol^{-1} were observed quite comparable to the corresponding values for neutral systems. Not unexpectedly, therefore, thermal unimolecular reactions of molecular ions such as thermal dissociation or combination will be governed by weak collision effects as well.

Strong collision rate constants for low pressures

The calculation of the strong collision low pressure rate constant

$$k_0^{sc} = Z_{LJ}[M] \int \int^* f(E, J) dE dJ \quad (16)$$

(see Eq. (1)) is straight-forward although some details depend on not too well known molecular quantities. The Lennard-Jones collision parameters can be estimated, even for poorly studied molecules, by several empirical relationships (Reid, Prausnitz and Sherwood, 1980). The integral over the equilibrium population $f(E, J)$ either can be computed directly, or one may choose the simplified factorized form given by Troe (1977b, 1979);

$$k_0^{sc} \simeq Z_{LJ}[M] \frac{\rho_{vib}(E_0) kT}{Q_{vib}} \exp\left(-\frac{E_0}{RT}\right) F_E F_{anh} F_{rot} F_{rotint} \quad (17)$$

where $\rho_{vib}(E_0)$ is the harmonic vibrational density of states at E_0 given by the

Whitten–Rabinovitch approximation; Q_{vib} is the vibrational partition function; F_E accounts for the energy dependence of the density of states (see Eq. (2)); and F_{anh} for anharmonicity corrections (being typically between 1 and 2). The rotational and internal rotational factors F_{rot} and F_{rotint} require information about centrifugal and internal rotational barriers. These factors are very important and one of the sources of uncertainty. Nevertheless, the agreement between experiment and theory was found to be generally good (sometimes better than a factor of two) such that Eq. (7) can well be used for predictive purposes (Troe, 1977b, 1979). However, one should be aware of the two main uncertainties in a prediction of k_0 which are the weak collision efficiencies β_c in high temperature experiments, and the rotational factors F_{rot} in low temperature experiments.

Mixture rules

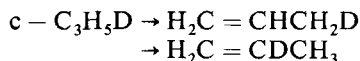
Unimolecular reactions at low pressures, which take place in a mixture of bath gases, in practice are generally treated by simple adding of the respective pseudo-first order contributions of bath gas components. While this is correct for strong colliders, weak collisions produce a nonlinear coupling such that nonlinear mixture rules are observed (Lin and Rabinovitch, 1968; Boyd, 1977; Troe, 1980). This effect can be expressed by ‘kinetic activity coefficients’ f_i , e.g. for a binary bath gas mixture by

$$k_0 = k_{01}f_1 + k_{02}f_2, \quad (18)$$

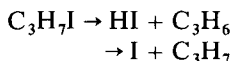
where the f_i depend on the concentrations. The effect is due to a mutual influence of the different bath gases on the non-equilibrium populations of states below E_0 and on the activation flux. By explicit solutions of the master equation for exponential collision models it was shown, however, that nonlinearities of this kind would require a higher precision for their detection than is available today (Troe, 1980).

Two-channel reactions

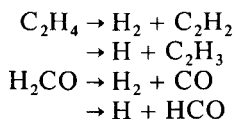
An important access to properties of energy transfer is provided by two-channel reactions for which the difference in the threshold energies ΔE_0 is only small. In the low-pressure range, the non-equilibrium depletion of molecular states below the lower threshold energy, and the small jump size for weak collisions, result in a smaller yield of reaction on the upper channel than expected in the absence of the lower channel. The branching ratio for the upper channel is a sensitive measure not only for the average energy transferred, but also for the shape of the collisional transition probability $P(E', E)$. It permits ‘collisional competitive reaction spectroscopy’ (Klein and Rabinovitch, 1978). The interest in two-channel reactions, because of this access to energy transfer, is old (Chow and Wilson, 1962; Nikitin, 1966) although only recently the experiments have been performed in a sufficiently detailed way. Among the most promising experimental examples are the isomerizations



and other isomerizations of isotopically labelled cyclopropanes (Klein *et al.*, 1977; Waage and Rabinovitch, 1970, 1972), the competitive eliminations and fragmentations of halohydrocarbons such as



(Gaynor, Gilbert and King, 1978; King *et al.*, 1971) and similar competitive eliminations and fragmentations like



(Just, Roth and Damm, 1977; Rimpel and Just, 1981).

The analysis of two-channel reactions, as in the corresponding one-channel problem, can proceed via a direct numerical solution of the master equation. The essential input parameters are the branching ratios for the specific reaction channels, the precise gap ΔE_0 between the two threshold energies and a suitable collision model $P(E', E)$. Besides this approach, the analytical solution of the problem, for an exponential collision model, provides a clear insight into the behaviour of the branching ratio (Just and Troe, 1980). The relative yield of the upper channel (2) was found to be

$$\frac{k_{02}}{k_0} = \langle V_2(E) \rangle \exp \left(-\Delta E_0 \left(\frac{1}{F_E kT} + \frac{1}{\alpha} \right) \right) \quad (19)$$

where $\langle V_2(E) \rangle$ is a suitable average of the branching ratio of the specific rate constants for the two channels, and α is the average energy transferred per down-collision. With the average energy γ transferred per up-collision given by $\gamma = \alpha F_E kT / (\alpha + F_E kT)$, Eq. (19) can also be rewritten

$$\frac{k_{02}}{k_0} = \langle V_2(E) \rangle \exp \left(-\frac{\Delta E_0}{\gamma} \right). \quad (20)$$

Obviously the yield of the upper channel is a sensitive measure of γ as long as ΔE_0 is known. When eliminations and simple bond fissions compete, rotational effects can considerably complicate the analysis (Just and Troe, 1980). The energy gap ΔE_0 will depend on the total angular momentum such that even a channel switching can occur for rotationally very hot molecules. In this case, the branching ratio will depend sensitively also on the centrifugal barrier properties. In this case, the conclusion on energy transfer properties will be much less direct than for just two competing isomerizations of isotopically labelled molecules as studied by Klein *et al.* (1978).

Rotational effects

The overall rotation of the molecules has a complicated influence on the low-pressure rate constants of a unimolecular reaction. There is at first the influence on the strong collision rate constant (16) which was treated in Eq. (17) by a separate rotational factor F_{rot} . This factor at high temperatures, for a nonlinear molecule, approaches

$$F_{rotmax} \simeq \frac{(s-1)!}{(s+\frac{1}{2})!} \left(\frac{E_0 + a(E_0)E_z}{kT} \right)^{3/2} \quad (21)$$

where s is the number of oscillators, E_z is the zero point energy, $a(E_0)$ the Whitten-Rabinovitch correction factor. For a linear molecule, the exponent 3/2 is replaced by unity, the s -factor is replaced by $1/s$. At lower temperatures, Eq. (21) gives only an upper limit, the exact relation depends on the threshold energy dependence on total

angular momentum J . It has been shown that, for simple bond fission reactions, threshold energy laws

$$E_0(J) \simeq E_0(J=0) + C_\nu [J(J+1)]^\nu \quad (22)$$

are often observed, for which a simple relation between F_{rot} (being smaller than F_{rotmax}) and the parameters C_ν and ν can be derived (Troe, 1979). For other types of unimolecular reactions like isomerizations and eliminations, generally $\nu = 1$ and $C_\nu = B^\ddagger$ is obtained, where B^\ddagger is the rotational constant of the molecule at the potential maximum between reactants and products; generally $\nu > 1$ is derived for simple bond fissions.

Whereas the contribution to the strong collision rate constant is well understood today, the influence on the collision efficiency β_c is an open problem. For its solution, the two-dimensional, E - and J -dependent master equation has to be solved with a suitable model for rovibrational energy transfer. Such a solution has been given by Troe (1977a) for a factorized exponential collision model for rotational and vibrational energy transfer and a linear threshold energy law, i.e. Eq. (22) with $\nu = 1$. The limitation of this solution is that it employed no cut-off of the energy and angular momentum at $E = 0$, and $J = 0$. With the sacrifice of being restricted to strong collision rotational energy transfer, which appears not to be realistic either (Ennen and Ottinger, 1974), the J -cut-off error has been avoided by Penner (1978b), who obtains equi-depletion lines in the E - J plane parallel to the J -axis, whereas Troe derived such lines parallel to the threshold energy line $E_0(J)$. Numerical solutions (Dove and Raynor, 1979) for a diatomic system indicate that the reality will be in between these two cases, being closer to Troe's solution at high temperatures where weak collision effects are most important. In any case, new solutions of the two-dimensional master equation are required to understand the complex relationship between the collision efficiency β_c and the properties of rovibrational energy transfer.

Incubation and relaxation phenomena

So far only unimolecular reactions proceeding at steady-state have been considered. In recent years, attention has also been directed to the transient phenomena observed during the presteady state period of the reaction. Although such transient phenomena are much more important in multi-photon dissociation experiments (*see below*), a few experimental studies are now also available for thermal unimolecular reactions. By laser schlieren techniques, the incubation period as well as vibrational relaxation have been resolved in the thermal dissociation of N_2O in shock waves (Dove, Nip and Teitelbaum, 1974). The corresponding phenomenon in wall-collision activated unimolecular reaction, occurring in a VLPP system, has been studied systematically in the 'variable encounter method' by Rabinovitch and coworkers (Kelley *et al.*, 1979, 1980a,b; Flowers *et al.*, 1980). In these experiments the number of collisions which is required to achieve a steady-state population of molecular states corresponding to the temperature of the wall is determined. The numerical simulation of the dynamics of the collisional energization process resembles completely the analysis of the incubation period of homogeneous thermal unimolecular reactions such as given by Dove and Troe (1978).

In order to describe the transient period of the reaction, quite generally the full eigenvalue spectrum of the time dependent master equation has to be calculated, the smallest non-zero eigenvalue determining the steady-state rate constant k . The length of the 'incubation period', i.e. the delay time for chemical reaction, can be characterized by an incubation time τ_{inc} related to the steady-state eigenvector of the master equation and the

initial population. For a simple exponential collision model with energy independent $\langle \Delta E \rangle$, τ_{inc} is approximately given by

$$Z_{LJ}[M] \tau_{inc} \simeq \frac{E_0}{-\langle \Delta E \rangle} \quad (23)$$

(Dove and Troe, 1978). For energy transfer, which is less efficient at low energies than at high energies, τ_{inc} exceeds the value given by Eq. (23). The experimental results for N_2O indeed indicate a factor of 20 discrepancy compared to Eq. (23); apparently τ_{inc} depends to a large extent on the comparably slow energy transfer at lower energies. The length of the incubation time τ_{inc} does not tell in which way the system relaxes towards its steady-state behaviour. This can be understood only with the knowledge of the full eigenvalue spectrum of the master equation or directly from numerical solutions of the master equation. An analytical solution of this problem for an exponential collision model with energy independent $\langle \Delta E \rangle$ has been given by Penner and Forst (1977, 1980). Although this solution is mathematically very interesting, it does not appear to be too realistic because it neglects the change of the properties of collisional energy transfer at low energies at the transition from a quasi-continuous to a discrete structure of the vibrational spectrum. Alternative to the incubation time τ_{inc} , also mean first passage times can be used to characterize the length of the incubation period (Kelley *et al.*, 1980b; Penner 1978a).

High-pressure rate constants

Experimental data

Experimental information on limiting high-pressure rate constants k_∞ is available now for a very large number of reactions. An excellent review of recent results has been given by Frey and Walsh (1978) who continued the series of comprehensive compilations of data (Benson and O'Neal, 1970; Robinson and Holbrook, 1972; Robinson, 1975) up to 1978. Only a few more recent experimental examples will be mentioned but first some general remarks must be made.

It is most important to derive, for a particular reaction, the limiting low- and high-pressure rate constants, because only in these limits inter- and intramolecular processes are separated, such that a theoretical analysis of separated phenomena can be undertaken. This poses the experimental problem that fall-off curves have to be followed to sufficiently low and high pressures. Unfortunately, often one reaches the limits of the experimental possibilities such that an analysis of the full fall-off curve has to be made (*see below*). It turns out that often in the past, measured rate constants have been attributed to the high-pressure limit although some fall-off was still present. This concerns, in particular, all experiments above temperatures of 1000 K. It has to be emphasized that, no matter how large a molecule is considered, above about 1000 K fall-off effects have always to be taken into account (Astholz, Durant and Troe, 1979), partly because of strong collision fall-off effects, partly because of weak collision efficiencies, and weak collision broadening of the fall-off curves. In a recent analysis of alkane decomposition rates at 1000–1200 K, a strong decrease of high-temperature A-factors from 300–1100 K was noticed (Tsang, 1978). The analysis of these data necessitated a revision of the heats of formation of ethyl, isopropyl and t-butyl radicals by 10–20 kJ mol⁻¹. It appears quite possible that this conclusion is not justified because fall-off effects at $T \gtrsim 1000$ K have been overlooked. Reliable high-pressure data, therefore, often are restricted to experiments below about 1000 K. For small molecules, it is easier to derive k_∞ for the recombination reaction at low temperatures with a sufficiently wide pressure range available.

For the $\text{CH}_4 = \text{CH}_3 + \text{H}$ reaction, new experimental measurements of k_∞ were reported for the recombination at 300 K (Sworski, Hochenadel and Ogren, 1980; Patrick, Pilling and Rogers, 1980) whereas high-temperature shock-wave results corresponded to the low-pressure range (Chiang, Baker and Skinner, 1980). It has again to be emphasized that earlier conclusions on k_∞ from shock-wave experiments near 2000 K were due to an oversimplified analysis of the fall-off curve and have to be revised. The dissociation $\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$ has been reexamined over the range 840–913 K by Trenwith (1979). Evaluation of the fall-off curves gives results which are consistent with RRKM calculations combined with a minimum state density criterion. However, as criticized earlier, this analysis involves a threshold energy E_0 which is below the value of ΔH_0^\ddagger for the reaction. Therefore, alternative theoretical models should be used (*see below*). A new high-pressure value for the reverse combination of CH_3 radicals at 823 K of $k_\infty = 2.2 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ has been reported (Pacey and Wimalasena, 1980a). This confirms very well the earlier conclusions on a practically temperature independent value of k_∞ over the range 300–1500 K. Over this large temperature range, theoretical models can be tested well, and the failure of conventional RRKM calculations becomes quite evident (Glänzer *et al.*, 1977; Quack and Troe, 1977). A study of the induction period in the pyrolysis of ethane (Pacey and Wimalasena, 1980b) gave new data for the dissociation of C_2H_5 and the combination $2\text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10}$; ethyl dissociation in the fall-off range at high temperatures (Pratt and Rogers, 1979a) and the reverse combination $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$ at the high-pressure limit at 300 K (Lee *et al.*, 1978) have also been reinvestigated. New studies of the pyrolysis of propane (Pratt and Rogers, 1979b; Kolke and Gardiner, 1980), n-butane (Pratt and Rogers, 1979c), isobutane (Pratt and Rogers, 1980), neopentane (Pacey and Wimalasena, 1980a), difluorocyclobutane (Conlin and Frey, 1979), dimethylvinylloxetan (Carless *et al.*, 1980), epoxytrifluoropropane (Flowers and Honeyman, 1980), azobenzene (Leiba and Oref, 1979), ethyl fluoride, propyl chloride (Okada, Tschuikow-Roux and Evans, 1980) and methyl chloride (Kondo, Saito and Murikami, 1980) have been reported. The isomerization of cyclopropene to methylacetylene was studied over a very wide pressure range by Bailey and Walsh (1978). This reaction provides a new prototype of a particularly well-behaved unimolecular reaction. The decomposition reactions of tetrafluoro-cyclobutane, (Conlin and Frey, 1980) and of vinyl- and isopropenyl-cyclobutane (Frey and Pottinger, 1978), have been shown to proceed by two channels, and the branching ratio has been measured at the high-pressure limit. Bimolecular reactions of radicals with molecules, which had been assumed to be direct exchange or abstractions, often reveal a more complex mechanism, when the conditions are varied over wide ranges of temperatures and pressure. At low temperatures and high pressures association processes may dominate. Structural rearrangements may follow the addition, fragmentation of the adducts may finally lead to the products of the 'bimolecular reaction', complicated branching patterns may arise. An analysis of these systems in terms of unimolecular rate theory appears obligatory to reveal the association-chemical activation-unimolecular rearrangement aspects of the system. Recent studies of this type were, e.g. the pressure-dependent reactions between OH and C_2H_2 (Michael *et al.*, 1980), of OH with propylene (Hoyermann and Sievert, 1979) and others.

Theoretical models

The high-pressure rate constant for unimolecular dissociation or isomerization is conveniently expressed by

$$k_\infty = \frac{kT}{h} \frac{Q^\ddagger}{Q} \exp(-E_0/kT) \quad (24)$$

where Q^\ddagger is the pseudo-partition function of the 'activated complex.' The calculation of Q^\ddagger is a difficult task. The problem appears to be most clear for isomerization and complex dissociation or elimination processes, where both the forward and backward reaction involve high-energy barriers. In this case, Q^\ddagger corresponds close to the notation of transition state and RRKM theory, i.e. individual rovibrational channel states of the reaction all have their threshold energies E_{0i} at the same configuration near the top of the potential barrier between reactants and products. By guessing and fitting the activated complex frequencies, and the height of the potential barrier, the measured high-pressure rate constants k_∞ can be represented without too large a problem. However, it is evident from two measured parameters, the A_∞ -factor and the high-pressure activation energy, only two potential parameters can be fitted. If, for example, the height of the potential barrier is chosen to be the one parameter, the other can be either just one frequency or just one universal scaling factor which converts the reactant frequencies (one frequency excluded for the reaction coordinate) into the activated complex frequencies. It has been shown that the corresponding specific rate constants $k(E)$ are not very dependent on this arbitrariness in the fitting procedure (Astholz *et al.*, 1979). It has to be emphasized that no test of statistical theories is possible in this way as long as no ab initio calculations of the potential surface fix the parameters, in particular the barrier height. It is, for instance, conceivable that some nonstatistical character of the reaction is just hidden by this fitting procedure.

Simple bond fission and the reverse radical association reactions show the difficulties of transition state and RRKM theory in a much more pronounced way. Here, activated complexes are difficult to locate. Over the last decade, several procedures have been described which handle this problem in an approximate way (*see review by Quack and Troe, 1981*). The most detailed model appears to be the statistical adiabatic channel model (Quack and Troe, 1974) in which all individual rovibrational channel potentials are constructed, and their individual threshold energies E_{0i} used to calculate the pseudo-partition function Q^\ddagger by

$$Q^\ddagger = \sum_i \exp\left(-\frac{E_{0i} - E_0}{kT}\right). \quad (25)$$

An important aspect of this model is that it correlates reactant with product states with explicit account for angular momentum conservation. Loose coordinates, i.e. oscillators which disappear and are transformed into product rotors, contribute dominantly to Q^\ddagger , and are also most seriously governed by angular momentum coupling rules. If these coordinates are described, at fixed activated complexes in RRKM or transition state theory, by oscillators or rotors, angular momentum conservation is always violated. This defect is avoided by the statistical adiabatic channel model, although so far it has only been elaborated for crude channel potentials and the application to ab initio potential surfaces has still to come. Nevertheless, it provides a logical link between rigid RRKM and loose phase space theory which, as limiting cases, neither correspond to reality, in general.

In practical calculations of k_∞ often a simpler calculation than the detailed statistical adiabatic channel model is sufficient. Several approaches are possible.

- (i) One may construct a local free energy along the reaction coordinate which connects the values of the reactant and product species. The maximum of this free energy defines an activated complex whose position most naturally depends on the temperature (Quack and Troe, 1977). The construction of the local free energy can be done more or less equivalent to the statistical adiabatic channel model.
- (ii) One may also analyse the energy pattern of the threshold energies E_{0i} for loose coordinates in the statistical adiabatic channel model and calculate Q^\ddagger in Eq. (25)

after the separation into the contribution from all individual coordinates. It has been shown (Troé, 1981) that, for loose coordinates, the energy pattern of the threshold energies E_{0i} corresponds to the state pattern neither of harmonic oscillators, nor of free or hindered rotors. If in this approach all coordinates are separated, angular momentum coupling again is neglected and a global correction has to be applied at the end.

The two approaches (i) and (ii) have been tested for many practical cases and found to approximate well with the detailed statistical adiabatic channel model. The latter approach has the advantage that it can be used also for the calculation of specific rate constants $k(E)$.

- (iii) Compared to the limit of loose activated complex theory (i.e. phase space theory), in a real system, at their activated complexes, the loose coordinates are tightened to some extent. It has been tried by Golden and Benson (1978), to describe this phenomenon by rotors whose accessible phase space is restricted. The corresponding hindrance parameter η has to be fitted to the experiments. Since it depends on the temperature, this model involves more arbitrariness than the approaches (i) and (ii) which use only one T-independent parameter.
- (iv) It has also become customary to improve RRKM program packages by the addition of a minimum state density routine (Bunker and Pattengill, 1968; Hase, 1972, 1976; Bunker and Hase, 1973). This approach only partly avoids the basic defects of the RRKM method, since the oscillators are separated without correction for angular momentum coupling, and are not transformed properly into product rotors.

The various approaches described so far allow k_∞ to be expressed by the parameters of the reactant and the product molecules together with one extra parameter, which in the approach (ii) is the ratio α/β of the looseness parameter α and the Morse parameter β of the potential surface. The relation between these global potential parameters and fine details of the potential surface still has to be established. However, so far the theory appears to be able to reproduce experimentally observed k_∞ quite well. Unfortunately measurements of k_∞ will not be able to provide evidence against or in favour of the validity of statistical theories of unimolecular reactions.

Fall-off curves

Theoretical representations

A theoretical construction of the intermediate fall-off curve between the limiting low and high-pressure rate constants is a most difficult task. The available RRKM calculations definitely do not give a full solution of the problem since weak collision effects generally are neglected as well as the problems of activated complex positions and centrifugal barrier effects. However, for practical applications realistic fall-off expressions are urgently needed. It is, therefore, most desirable to have a formalism which on the one hand is simple and includes the known effects, and which on the other hand is flexible enough to be modified for other factors which may show up in a comparison with the experiments.

A number of such alternatives to the original RRKM formalism have been tested over the last few years. Slater's (1959) old relationship between k_∞ and $k(E)$, for cases where k_∞ is exactly given by an Arrhenius expression, has been taken up again by Forst (1972, 1979), and Pritchard and coworkers (Yau and Pritchard, 1978; Pritchard and Labib, 1976). For this case, $k(E)$ is derived from k_∞ by inverse Laplace transformation and its

calculation is reduced to a state counting problem for the initial molecule. Weak collision effects are taken into account by multiplying the collision frequency by an empirical collisional efficiency for the full pressure range as in the early theories. This approach appears to us to be a step backward since it neglects a number of details, which have been shown to be of practical importance, without gaining too much of computational simplifications as compared to RRKM theory. Strict Arrhenius forms of k_∞ are known not to be correct, the problem of collisional energy transfer is neglected, in particular with respect to its effect on the shape of the fall-off curve.

In order to simplify the calculation of the fall-off curve to a level which experimentalists should be willing to accept and which can be used in simulations of many reaction systems (Westbrook and Dryer, 1981), we have proposed an empirical representation which is based on earlier more detailed theories. This approach starts from the argument that fall-off expressions cannot be better than the limiting rate constants which are much easier to compute. Therefore, reduced expressions of k/k_∞ as a function $k_0/k_\infty = [M]/[M_c]$ should be employed where $[M_c]$ defines the centre of the fall-off curve (Buff and Wilson, 1960). The Lindeman–Hinshelwood model would then give

$$\frac{k}{k_\infty} = \frac{k_0/k_\infty}{1 + k_0/k_\infty}. \quad (26)$$

Strong collision unimolecular rate theory as elaborated by RRKM theory introduces a considerable broadening of this function which can be represented by a broadening factor

$$\frac{k}{k_\infty} = \frac{k_0/k_\infty}{1 + k_0/k_\infty} F^{SC}(k_0/k_\infty). \quad (27)$$

Guided by earlier (now superseded) reduced Kassel-integral expressions, we have analysed a large number of exactly statecounted RRKM fall-off calculations to represent F^{SC} in an empirical way. The function

$$\log F^{SC}(k_0/k_\infty) = \frac{\log F_{cent}^{SC}}{1 + \left(\frac{\log(k_0/k_\infty)}{N^{SC}} \right)^2}. \quad (28)$$

With $N^{SC} \simeq 0.75-1.27 \log F_{cent}^{SC}$ was found to give very good results (at low temperatures often $N^{SC} \simeq 1$ is sufficient). The broadening factor at the centre of the fall-off curve, F_{cent}^{SC} , is empirically related (Trope, 1979) to the two parameters

$$S_K = 1 - \frac{1}{T} \frac{\partial \ln Q^\ddagger}{\partial(1/T)} \quad (29)$$

and

$$B_K = \frac{S_K - 1}{s - 1} \left(\frac{E_0 + a(E_0)E_Z}{kT} \right) \quad (30)$$

where $a(E_0)$ is the Whitten–Rabinovitch correction. Often $a(E_0) \simeq 1$ and

$$S_K \simeq \frac{U_{vib}}{kT} \quad (31)$$

provide sufficiently good accuracy when a detailed analysis of activated complex structure appears inappropriate (U_{vib} is the thermal average vibrational energy of the reactant molecule). Weak collision effects produce an additional broadening of the fall-off curves which is handled by multiplication with an extra weak collision broadening factor $F^{WC}(k_0/k_\infty)$. To a first approximation F^{WC} is given by

$$\log F^{WC}(k_0/k_\infty) = \frac{\log F_{cent}^{WC}}{1 + (\log k_0/k_\infty)^2} \quad (32)$$

with

$$\log F_{cent}^{WC} \simeq 0.14 \log \beta_c. \quad (33)$$

Improvements of Eqs. (32) and (33) require more detailed solutions of the master equation in the fall-off range (Luther and Troe, 1979; *see also* Lawrance *et al.*, 1980). Equations (26–33) represent RRKM theory and the results of improved theoretical models in a compact form. On the other hand, these equations can also be used as simple fitting expressions for experimental data, as a next step beyond the Lindemann–Hinshelwood formula (26). In this way, they have already found an application in numerous experimental examples (*see below*).

Experimental examples

Full fall-off curves are experimentally most difficult to measure at high temperatures (above about 1200 K, *see above; see* Astholz, *et al.*, 1979). For lower temperatures a number of excellent studies are available in which, at a given temperature, the pressure was varied over up to six orders of magnitude. The classical examples still are the isomerization of methyl isocyanide (Schneider and Rabinovitch, 1962), ethyl isocyanide (Maloney and Rabinovitch, 1969), cyclopropane, cyclobutane and others; a nice new example is that of cyclopropene (Bailey and Walsh, 1978). Because of their importance for atmospheric chemistry, a large number of low-temperature dissociation and recombination fall-off curves have been measured. Among these are the dissociation of N_2O_5 (Viggiano *et al.*, 1981), $HO_2 NO_2$ (Graham, Winer and Pitts, 1978), and the recombinations $OH + NO_2$ (Anastasi and Smith, 1976; Wine, Kreutter and Ravishankara, 1979), $ClO + NO_2$ (Baulch *et al.*, 1980; Molina, Molina and Ishiwata, 1980), $CH_3 + NO$, $CH_3O_2 + NO_2$, $CH_3O_2 + CH_3O_2$ (Sander and Watson, 1980; Ravishankara *et al.*, 1980), $HO_2 + NO_2$ (Cox and Patrick, 1979), $BrO + NO_2$ (Sander, Ray and Watson, 1980) and others (*see* Baulch *et al.*, 1980). Because of their compact form, Eqs. (27) and (28) (often with $N^{SC} \simeq 1$ and with a constant F_{cent}^{SC} parameter over a limited temperature range) have here found a systematic application (*see* Baulch *et al.*, 1980; Viggiano *et al.*, 1981; Sander *et al.*, 1980; Ravishankara *et al.*, 1980; Zellner, 1978; Sander and Watson, 1980).

A recent application of thermal unimolecular rate theory to ion-molecule reactions should be particularly mentioned since it helped to rationalize quite a number of experimental observations (Chang and Golden, 1980). The pressure dependence of the addition of ions to molecules could well be analysed by fall-off expressions as provided by unimolecular rate theory for reactions like the formation of proton-bound dimers of NH_3 , CH_3NH_2 and $(CH_3)_2NH$ (Olmstead *et al.*, 1977; Neilson *et al.*, 1978), and the formation of proton-bound dimers of H_2O , H_2S and of $(C_3H_6)_2^+$ (Jasinski *et al.*, 1979). The application of unimolecular rate theory to calculate the temperature coefficients of thermolecular ion-molecule addition reactions was also quite successful (Bates, 1979a,b).

SPECIFIC RATE CONSTANTS OF UNIMOLECULAR PROCESSES

Absolute values of $k(E, J)$ *Theoretical models*

The specific rate constants of unimolecular reactions can be calculated theoretically by various techniques. In the following section we shall review briefly recent activities in the statistical approach, and in trajectory calculations, which have led to progress in practical applications.

In the statistical theory of unimolecular reactions, $k(E, J)$ is calculated from the relation

$$k(E, J) \leq \frac{W(E, J)}{h\rho(E, J)} \quad (34)$$

where W is the number of open reaction channels at the energy E and the angular momentum J , ρ is the corresponding density of states. Strictly, from theory the inequality applies in Eq. (34) (Quack and Troe, 1981; Quack, 1981c), but in practical work the equality is currently used. For isomerization and the complex dissociation process with a well-localized activated complex at the potential energy barrier, the practical problem then is that of state counting (apart from the ambiguities of assigning activated complex frequencies, *see above*). Since the advent of the Beyer–Swinehart–Stein–Rabinovitch exact counting algorithm (Beyer and Swinehart, 1973; Stein and Rabinovitch, 1973), this problem is solved satisfactorily for molecules of any complexity. Technically one can still think of modifications which save computer time. One such modification is to retain only the very fast Beyer–Swinehart algorithm for harmonic oscillators, and to handle anharmonicity effects and the contributions from free or hindered rotors separately. It has been proposed to treat internal rotors classically at first and to use their density of states to construct the starting array for the Beyer–Swinehart counting (Astholz *et al.*, 1979). In this way densities of state, e.g. for molecules of more than 100 oscillators at excitation energies of 800 kJ mol⁻¹ have been calculated with negligible computing efforts.

As discussed above, simple bond fission reactions are much more difficult to treat. The detailed statistical adiabatic channel model (Quack and Troe, 1974) has dealt with the problem of angular momentum coupling and transformation of ‘loose’ oscillators into product external rotations. In this way, in particular, the J -dependence of the specific rate constants has been demonstrated. A recent simple analysis of this model (Troe, 1981) has concentrated on the inherent energy pattern of channel threshold energies for the loose coordinates. It was found that, if represented classically, loose coordinates in this model contribute to $W^\ddagger(E, J)$ number-of-state-functions

$$W^\ddagger(E) \approx \left(\frac{E}{\varepsilon}\right)^x \quad (35)$$

where x is nearly independent of energy and has a value between 0.5 and 1, and ε is an energy between the reactant oscillator quantum and the product rotational constant. The exact values of x and ε depend, in first approximation, only on the ratio α/β of the looseness parameter α and the Morse parameter β . Loose coordinates as characterized by Eq. (35) can be convoluted with harmonic oscillators by the Beyer–Swinehart algorithm as discussed above. Separation of coordinates, however, always introduces errors because of inadequate angular momentum coupling. This has to be corrected for a posteriori by a

correction close to the angular momentum factors from the loose limit of the adiabatic channel model which is identical to the phase space theory of unimolecular processes.

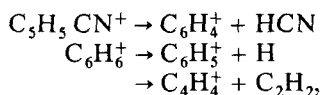
Angular momentum constraints are most easily taken into account in the phase space theory which has been elaborated in detail in relation particularly to ion fragmentation (Klots, 1971, 1972, 1976; Chesnavich and Bowers, 1979). Although the angular momentum coupling pattern here is handled adequately, phase space theory nevertheless has been shown to overestimate the rates, because some 'rigidity' in the potential, which is present in reality, is neglected. For k_{∞} values of neutral molecules, the errors by phase space theory generally were of the order of a factor of 4 (Quack and Troe, 1977). Apart from the statistical adiabatic channel model, Worry and Marcus (1977) have incorporated angular momentum constraints into RRKM theory in relation with product energy distribution measurements.

Extensive trajectory calculations of unimolecular reactions have been performed over the last years by the late Don Bunker (1971), by Hase and their coworkers (Grant and Bunker, 1978; Santamaria, Bunker and Grant, 1978; Hase *et al.*, 1979; Wolf and Hase, 1979, 1980a,b). A major point of interest in these studies is the question which potentials and excitations lead to nonstatistical specific rate constants and product energy distributions. It was found that late barrier surfaces of the Morse type produced statistical behaviour, whereas early barrier surface with potential maxima between reactants and products gave non statistical effects for the $\text{HCC} \rightarrow \text{H} + \text{C}=\text{C}$ bond fission (Wolf and Hase, 1980a). High degrees of excitation apparently more often show non-statistical reaction patterns than low excitations above threshold energy (Grant and Bunker, 1978; Hase and Wolf, 1979). The effects of localized initial excitations in C_2H_6 indicate time scales for internal energy exchange of the order of picoseconds (Bunker, 1977; Santamaria *et al.*, 1978). The existence of quasi-periodic trajectories above the threshold energy has been suggested by Wolf and Hase (1980b) for the HCC species. In classical trajectory calculations there appears to be a relatively sharp transition from predominantly quasi-periodic trajectories to stochastic behaviour at energies which are about one half of the threshold energy for reaction. This behaviour, which was observed earlier for relatively artificial potential energy surfaces, recently has been reconfirmed also for realistic potential surfaces of triatomic molecules like SO_2 and O_3 (Farantos and Murrell, 1981). Suitable potential energy functions for such calculations have been designed over the years by Murrell and coworkers (*see* summary by Murrell, 1978). On the other hand, exact quantum mechanical calculations do not show an energetic threshold for the transition from quasi-periodic to stochastic behaviour (Waite and Miller, 1980). It appears rather that the quasi-periodic, mode specific reaction behaviour is characteristic of weak coupling between oscillators, whereas strong coupling destroys mode specificity, independent of the energy. Apparently, van der Waals complexes on the one side, and strongly bound 'normal' molecules on the other side, mark extremes of the spectrum between mode specific, non-randomized and completely stochastic, randomized reaction behaviour. Non-randomization effects in normal molecules have been notoriously difficult to find experimentally, except for processes occurring on picosecond time scales (*see* review by Oref and Rabinovitch, 1979).

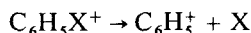
A systematic investigation of tunnelling contributions to the specific rate constants at energies below the classical threshold for pronounced potential barriers has been undertaken by Miller and coworkers (Miller, 1979; Gray *et al.*, 1980) for the complex bond fission reaction $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$, and the isomerization $\text{HNC} \rightarrow \text{HCN}$. It was shown that specific rate constants can be as high as 10^5 s^{-1} at 30 kJ mol^{-1} below the top of the potential energy barrier. However, the tunnelling rate decreases dramatically with decreasing energy such that the spontaneous $\text{HNC} \rightarrow \text{HCN}$ conversion of cold HNC molecules is completely negligible for interstellar matter.

Direct experimental observations of specific rate constants

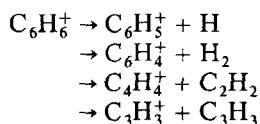
In recent years considerable progress has been made in the direct, time resolved measurement of specific rate constants $k(E)$ for selectively prepared neutral molecules and molecular ions. The first experiments of this type were studies of the molecular ion fragmentations



where the ions were prepared by charge exchange at selected internal energies, and the specific rate constants were measured by time-of-flight techniques (Andlauer and Ottinger, 1971, 1972). It turned out later that these experiments had to be corrected slightly by a shift in the energy scale because of momentum transfer in the charge exchange process (Eland and Schulte, 1975). In later experiments by Baer and coworkers on the fragmentation of halobenzene ions



(X = Cl, Br, I), and on other reactions, the very elegant photoion-photoelectron coincidence technique of selective ion preparation was combined with time-of-flight measurements for $k(E)$ (Werner and Baer, 1975; Baer *et al.*, 1975, 1976, 1978, 1979; Tsai, Werner and Baer, 1975). Particularly detailed studies have been performed for the fragmentation of C_6H_6^+ ions



where C_6H_6^+ was prepared from benzene, 2,4- and 1,5-hexadiyne (Baer *et al.*, 1979). It was shown that at low energies the various C_6H_6^+ isomers all rearrange to a common dissociative state and that the various dissociation pathways are competitive. The reaction is well described by statistical unimolecular rate theory. This result is opposite to earlier conclusions on the reaction. At high energies, however, the isomerization preceding ion fragmentation is not fast enough to produce a common dissociative C_6H_6^+ state. The application of unimolecular rate theory to ion fragmentations has been reviewed (*see e.g.* Lifshitz, 1978; Meisels *et al.*, 1979).

A major problem in the interpretation of specific rate constant measurements for ion fragmentation is still the lack of precise information on the molecular parameters, although progress in the spectroscopy of molecular ions in the future will fill this gap. For this reason, measurements of $k(E)$ for neutral molecules in their electronic ground state are of particular value. In this case, the frequencies of the reactants and products as well as the thermochemistry and the dissociation barriers (from thermal unimolecular reaction studies) are well established. The difficulty here is to find suitable techniques to prepare highly excited reactive states selectively. Three techniques are now in use.

- (i) One-photon excitation of high overtones in the electronic ground state.
- (ii) One-photon excitation of electronically excited states followed by fast internal conversion to the electronic ground state.
- (iii) The second mechanism (ii) followed by a fast isomerization to form new highly excited molecules with selected energy.

The high overtone excitation technique has been applied extensively by Berry and coworkers (Reddy and Berry, 1977, 1979a,b; Bray and Berry, 1979a), to study the effect of mode-specific excitation on unimolecular isomerizations. In Stern–Volmer quenching experiments, only little, if any mode-specific reaction effects were detected. From lineshapes, information on intramolecular energy redistribution was obtained (Bray and Berry, 1979; Dübal and Quack, 1980). A direct observation of the specific rate constant $k(E)$ with the technique of high overtone excitation was only recently undertaken by Cannon and Crim (1980) who followed the formation of electronically excited acetone from the dissociation of tetramethyldioxetane by chemiluminescence measurements. With the techniques (ii) and (iii), i.e. selective electronic excitation followed by fast internal conversion (and fast isomerization (iii)), a number of isomerization and simple bond fission reactions could be studied, for which the corresponding thermal unimolecular reactions as well as steady state photoisomerization experiments are also available. For the isomerization reactions of substituted cycloheptatrienes (Hippler *et al.*, 1978, 1979; *see also* Atkinson and Thrush, 1970) and cyclooctatetraene (Dudek, Glänzer and Troe, 1979) one-photon electronic absorption followed by fast internal conversion was used to prepare the reacting, vibrationally highly excited electronic ground state molecules. Hot UV absorption spectra were used to follow the disappearance of the reactants and the appearance of the products. This is illustrated for the isomerization of ethyl-cycloheptatriene in Fig. 3. Hot UV-spectra have also been used to detect highly excited molecules after multiphoton-IR excitation where broad distributions of excited molecules are produced (Kudriavtsev and Letokhov, 1980). A systematic investigation of the hot UV spectra observed in Fig. 2 has

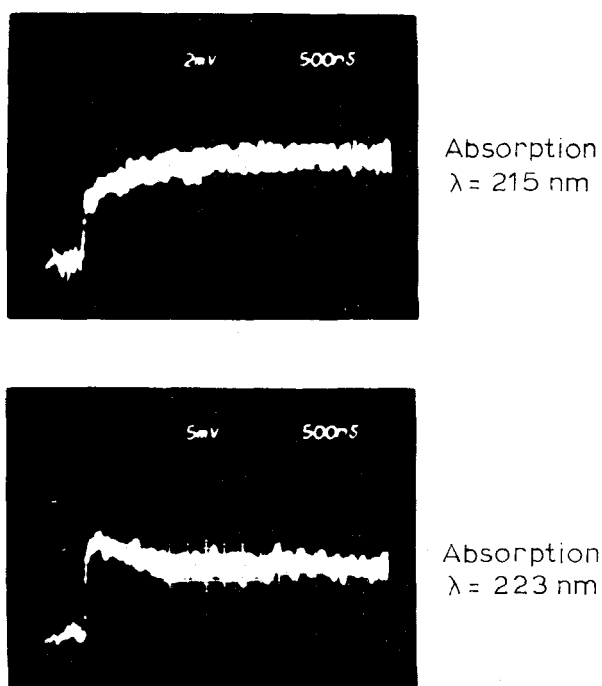


FIG. 3. Direct observation of unimolecular isomerization of ethylcycloheptatriene to methylethylbenzene (laser excitation at 265 nm, reactant disappearance observed at 223 nm, product appearance observed at 215 nm, from Hippler *et al.*, 1981).

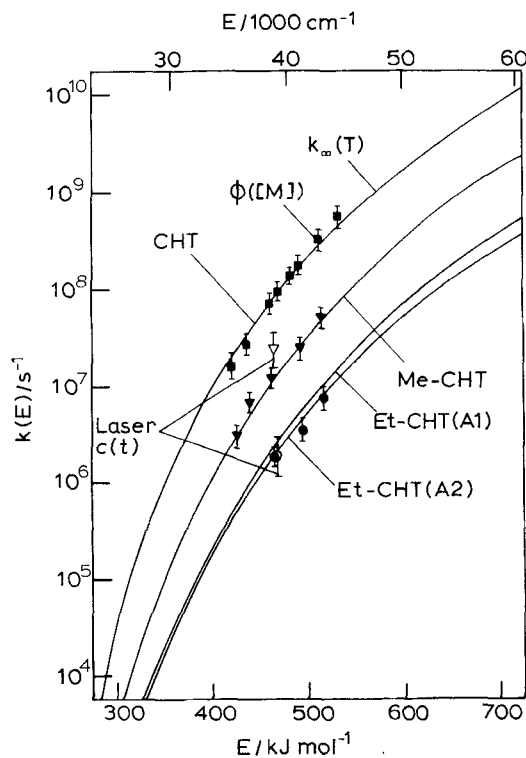
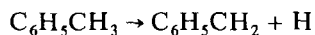


FIG. 4. Specific rate constants for isomerization of cycloheptatriene, methyl-, and ethylcycloheptatriene ($k_{\infty}(T)$ from thermal isomerization (Astholz *et al.*, 1979); ϕ ($[M]$): Stern–Volmer quenching experiments (Troe and Wieters, 1979); $c(t)$: Laser flash photolysis (Hippler *et al.*, 1978, 1980)).

been made in shock waves (Astholz *et al.*, 1981) in order to understand ‘canonically hot’ and ‘microcanonically hot’ UV spectra of thermally and laser excited molecules. New perspectives open also from the observation of hot CARS spectra of laser excited molecules (Luther and Wieters, 1980), since these spectra show a detailed structure and can be recorded with very short time resolution down into the picosecond range. The specific rate constants derived from Fig. 3 agree very well with the RRKM analysis of thermal isomerization experiments and the results from the analysis of Stern–Volmer quenching curves from steady-state photoisomerization experiments, *see* Fig. 4.

A direct access to simple bond fission reactions of substituted benzenes is provided by the use of fast isomerizations of cycloheptatrienes as illustrated in Fig. 5 for the cycloheptatriene-toluene system. In this case the specific rate constant for the reaction



was measured directly by following the hot UV spectrum of the forming benzyl radicals (Hippler *et al.*, 1981). A comparison with thermally averaged values of $k(E)$ from the thermal recombination $\text{H} + \text{C}_6\text{H}_5\text{CH}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}_3$ and the reverse dissociation gave a consistent picture. The substituted cycloheptatrienes and the substituted benzenes are now particularly good model reactions for isomerization and simple bond fission processes.

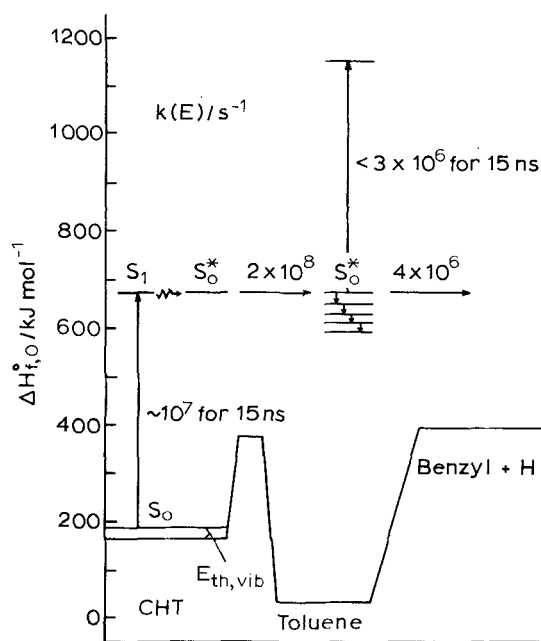


FIG. 5. Energy diagram for preparation and unimolecular bond fission of excited toluene (Hippler *et al.*, 1981).

Relative values of $k(E, J)$: product and product state distributions

Theoretical models

Statistical models have been devised and applied to a number of reactions, and recent reviews concentrating on the general treatment of neutral systems (Quack and Troe, 1981) and on phase space theory for ions (Chesnavitch and Bowers, 1979) are available. The statistical adiabatic channel model still appears to be the most detailed, purely statistical model (including phase space theory as a limiting case, *see* Quack and Troe, 1977). Recent formulations allow for the calculation of product translational energy distributions in large polyatomic systems, where it has been noted that by convoluting the difficult part with detailed correlation of channels from strongly changing coordinates with the simple part from essentially not changing coordinates one can treat systems of any size with exact count (Quack 1979c). An interesting 'semistatistical' development is the successful combination of classical trajectory calculations with phase space theory applied to the reaction $D^+ + H_2$ (Gerlich *et al.*, 1980).

Statistical models for product and product energy distributions really apply in their simple version only to vibrational predissociation on a bound surface with no large barrier for the reverse combination reaction. It has been known for some time, for instance, that elimination of HX from haloalkanes in chemical activation may lead to 'non-statistical' inversions in the HX molecule (Holmes and Setser, 1980). Photodissociation is another situation, where in many cases direct mechanisms or Franck-Condon dominated electronic predissociation determine the distributions of products. Dynamic models for these have been developed (Simons, 1977). Statistical models may still serve as a *diagnostic tool* indicating whether the above-mentioned mechanism applies in comparing experiment and theory (Quack and Troe, 1975). Another diagnostic tool, which has also

been suggested for predictive purposes is surprisal theory (Nesbet, 1981) or the information theoretical approach, which has been applied recently to unimolecular elimination reactions (Zamir and Levine, 1980). Linear surprisals were found for the examples shown. We may recall, however, that nonlinear surprisals were found in a comparison of detailed statistical distributions and the so-called prior distributions. Also, it had already been shown that the currently used prior distribution may not be adequate theoretically (Quack and Troe, 1976). For the true understanding of molecular reaction dynamics, it would appear useful to have approaches, possibly invoking statistical concepts, that can be related to molecular interaction potentials, as they have been formulated for the elimination reactions, for instance, by Kato and Morokuma (1980).

Metastable intermediates produced by collisions

If there is a deep minimum in the interaction potential of two collision partners, corresponding to a bound intermediate, reactive collisions may or may not involve a metastable intermediate. In agreement with current concepts, complex formation results in nearly statistical product state distributions. It is now well established that direct and complex mechanisms often compete and that this competition depends upon the collision energy, the complex mechanism being preferred at low energies. Recent examples in ion molecule reactions being given by the reactions $D^+ + H_2 \rightarrow HD + H^+$ (Gerlich *et al.*, 1980), $N^+ + CO$ (Ottinger and Zimmermann, 1980), and $H_3O^+ + D_2O$ (Ryan *et al.*, 1980). Much discussion has centred around the question, whether in substitution reactions of halogen atoms with unsaturated hydro(halo)carbons the complex mechanism actually does lead to statistical distributions:



This question has been reviewed by Rice (1975) and has been addressed again in experiments by Buss *et al.* (1979a,b).

In a reevaluation of the experiments, it has been suggested that most of these reactions actually do give practically statistical distributions (Quack, 1980a) even if the statistical lifetime of the intermediate is only a ps or less. The issue is complicated, since detailed statistical calculations are somewhat cumbersome, whereas simplifications often give misleading results as also discussed by Klots (1976) in connection with phase space theory. The possibility of fundamental deviations from statistical theory has been investigated with a simple Pauli equation model (Quack, 1981c). It has been suggested that a very simple fit formula may be helpful in a first evaluation of experimental data:

$$P(E_t, E) = CE_t^n \rho(E - E_t).$$

$P(E_t, E)$ is the product translational energy distribution and ρ is the combined internal density of states of the products, with $0 \leq n \leq 3$ as a fit parameter in the 'statistical' range. Fig. 6 shows two examples of such evaluations (Quack, 1980a) and it is noted in particular that the large relative shift from the small system (C_2H_3Cl) to the large system (C_6H_3F) is well reproduced by the statistical fit formula. Another recent example with the possibility of complex formation is the interesting reaction of $O(^3P)$ atoms with C_6H_6 leading in part to the very long lived species C_6H_6O (Sibener *et al.*, 1980) and in part to H-atom elimination.

Photodissociation

The interesting photodissociation of $NO_2 \rightarrow NO + O$ has been reinvestigated in the near UV (at $29\,965\text{ cm}^{-1}$) by laser photofragment spectroscopy (Zacharias *et al.*, 1981).

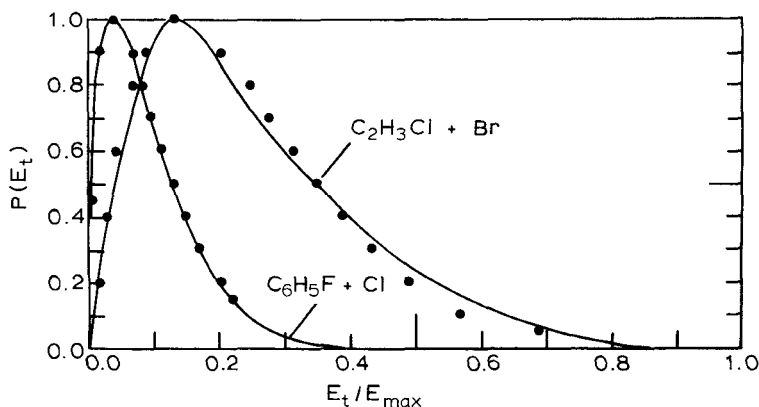


FIG. 6. Experimental product translational energy distributions for the reactions $\text{Cl} + \text{C}_2\text{H}_3\text{Br} \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{Br}$ and $\text{F} + \text{C}_6\text{H}_5\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{F} + \text{Cl}$ (full lines, from Buss *et al.*, 1979 and from Shobatake *et al.*, 1973). The points give the fits from the simple fit formula with $n = 1$ ($\text{C}_2\text{H}_3\text{Cl}$) and $n = 0.5$ ($\text{C}_6\text{H}_5\text{F}$). More detailed statistical calculations give similar results (Quack, 1980a). Note how well the relative shifts of the distributions are reproduced by the statistical calculations.

Inversion has been found in the NO-vibrational populations, indicating a clearly nonstatistical decay mechanism, whereas earlier results of Busch and Wilson (1972) at $28\,810\text{ cm}^{-1}$ were reasonably consistent with a statistical distribution calculated from the adiabatic channel model, without adjustable parameters but assuming strong mixing with the electronic ground state (Quack and Troe, 1975). Also high-pressure photolysis experiments were consistent with such an interpretation (Gaedtke and Troe, 1975). A most intriguing question is now, whether the finding of Zacharias *et al.* (1981) is restricted to certain wavelengths, or whether it is general. Experiments at other wavelengths, in particular at $28\,810\text{ cm}^{-1}$ would appear to be most interesting. They should not be too difficult to obtain with the tunable laser sources available.

As already mentioned above, photodissociation is very often characterized by non-statistical product state distributions. This is amply illustrated by the vacuum ultraviolet photodissociation of the cyanogen halides (Ashfold *et al.*, 1981; McPherson and Simons, 1979), of CS_2 and CSe_2 (Ashfold *et al.*, 1980), of methyl nitrite (Lahmani, Lardeux and Solgadi, 1980), or of CF_2CINO (Johnson and Wright, 1980). On the other hand, the detailed experimental reinvestigation of the energy disposal in the dissociation of CH_3^+ and CD_4^+ , created by photoionization, appears to agree with results from approximate phase space theory calculations (Powis, 1979). For a detailed treatment of ionic systems we refer to the review by Lifshitz (1978).

UNIMOLECULAR REACTIONS INDUCED BY MONOCHROMATIC INFRARED RADIATION (URIMIR)

The excitation of polyatomic molecules with intense IR-radiation from laser light sources (CO_2 -laser, HF-laser, etc.) can induce unimolecular reactions with threshold energies much higher than the energy of the light quantum, even in the absence of important collisional processes. These reactions constitute a relatively new area of research. The

phenomenon might have been surmised in 1966 (Bordé *et al.*, 1966); it had been postulated experimentally in 1971 (Isenor and Richardson, 1971; Isenor *et al.*, 1973) and since then, in a rapid sequence of many investigations, it has been established beyond any reasonable doubt by its isotopic selectivity in 1974 (Ambartzumian and Letokhov, 1977; Lyman, Rockwood and Freund, 1977, and references quoted therein) and finally by molecular beam experiments (Coggiola *et al.*, 1977; Brunner *et al.*, 1977; Diebold *et al.*, 1977). URIMIR consists of two parts.

- (i) The multiphoton process with monochromatic IR-radiation interacting with the highly complex spectral structures of polyatomic molecules is a fundamental, new problem in spectroscopy and molecular dynamics which has now become amenable to experiment and theory for the first time. Many exciting results have emerged within a few years and new theoretical concepts are required.
- (ii) On the other hand, the subsequent unimolecular reaction after excitation is expected to be more closely related to conventional phenomena in unimolecular reactions, although this expectation has been questioned in the early stages of the field. New problems arise here because of the interaction between excitation process and the monomolecular reaction step.

Reviews dealing with various aspects of URIMIR are already available (Letokhov and Moore, 1976; Ambartzumian and Letokhov, 1977; Zare, 1977; Frey and Walsh, 1978; Bloembergen and Yablonovitch, 1978; Grunwald, Dever and Keehn, 1978; Cantrell, Freund and Lyman, 1979; Schulz, Shen and Lee, 1979; Lyman, Quigley and Judd, 1980; Ashfold and Hancock, 1981a; Golden *et al.*, 1980). The more fundamental aspects of the theoretical treatment of the multiphoton excitation process have been summarized just recently (Quack, 1981b). Therefore, in the present brief review we shall direct our attention to simpler, mechanistic kinetic concepts of the excitation process and to the relationship to ordinary unimolecular reactions. This discussion should be useful to the kineticist entering or already working in this extremely active field as well as to those who are interested as spectators in the current development of concepts for URIMIR. The list of molecules, for which URIMIR have been observed now exceeds a hundred with a correspondingly larger number of experimental and theoretical publications. We shall restrict our discussion to a selection of those experiments that have provided evidence for the understanding of the phenomenon of URIMIR and to theories that can lead to realistic applications of a qualitative, conceptual or quantitative, computational nature.

Preliminary kinetic considerations for URIMIR and definitions

In a typical experiment in URIMIR, a gaseous substance is irradiated with intense IR-radiation ($\tilde{\nu} \approx 1000 \text{ cm}^{-1}$ $h\nu = 12 \text{ kJ mol}^{-1}$, intensity I in the MW cm^{-2} range and times usually less than $1 \mu\text{s}$). Let us assume for conceptual simplicity that the irradiation is uniform in space and time (step function at the limits) and can be characterized by its intensity I , and time t or by the fluence (the pulsed time step function irradiation has been accomplished experimentally just recently; Ashfold, Atkins and Hancock, 1981b; Hancock, 1981)

$$F = \int_0^t I(t') dt' \quad (36)$$

which in this case would be $F = I \times t$. These are then three independent variables of the experiment with two degrees of freedom. The measured dependent variable would be the

time dependent concentration of reactants and products, say in a reduced form by reactants:

$$c_R/c_R^0 = F_R = 1 - F_P = f(F, I, t). \quad (37)$$

F_R is the remaining fraction of reactant after irradiation with I during t and can be probed during the laser pulse. This is possible, for instance, with the laser induced fluorescence technique, using a short probe pulse in the visible or UV with well-defined delays (Ashfold *et al.*, 1979; King and Stephenson, 1979; Campbell, Hancock and Welge, 1976) or by time resolved absorption spectroscopy (Duperrex and van den Bergh, 1979a), or time resolved chemiluminescence of products (Yahav and Haas, 1978). In bulk experiments without time resolution or in beam experiments there may be dissociation after the pulse of all those molecules that have been excited above the reaction threshold. The corresponding quantities will be called F_R^* ($\leq F_R$) and F_P^* ($\geq F_P$). In practice there may be further complications due to collisional quenching in bulk or flight time effects in beams (Brunner and Proch, 1978).

In kinetics one is furthermore interested in a differential quantity, the rate coefficient:

$$-\frac{d \ln F_R}{dt} = k(F, I, t) \quad (38)$$

and again the corresponding starred quantity $k^*(F, I, t)$ from F_R^* . The rate coefficient in Eq. (38) may be compared to the rate coefficient in thermal unimolecular reactions $k_{uni}^{(t)} = f(T, [M], t)$, which depends upon three parameters with three degrees of freedom. Usually the time dependence is unimportant, giving $k_{uni}(T, [M])$ at steady state. $[M]$ can be compared to the intensity I as the exciting medium. The temperature T has no correspondence in Eq. (38). Although the initial state and therefore the initial temperature does influence the effective rates in URIMIR (Duperrex and van den Bergh, 1979b; Quack *et al.*, 1980; Chou and Grant, 1980), a temperature cannot be defined during and after irradiation in general. On the other hand, it has been found that in URIMIR steady state is attained rather late, for some typical situations after a third of the reaction has taken place (Quack 1978), therefore both intensity (I) and time or fluence (F) dependence have to be retained explicitly during this period. Under appropriate conditions (long times, large F or high yields) steady state can be attained in URIMIR and then the steady state rate coefficient depends only upon one degree of freedom, intensity. The concept of steady state is thus of crucial importance for the unambiguous investigation of the role of radiation intensity in URIMIR. At steady state the influence of intensity on yields and rates can be expressed in an instructive, approximate way

$$-\ln(F_R/F_R^{(S)}) = k(st)(t - t_s) \quad (39a)$$

$$= cI^n(t - t_s) \quad (39b)$$

$$= cI^{n-1}(F - F_s) \quad (39c)$$

We have written here the intensity dependence of the steady state rate coefficient $k(st)$ by a power law with the exponent n , for illustrative purposes. If $n = 1$ the yield will not really depend upon intensity, but upon fluence. If $n > 1$ there will be a larger yield the higher the intensity at a given fluence and inversely for $n < 1$. The situation is quite similar before steady state (Quack, 1979b) and we shall make use of these considerations below. It has also been shown that one has at steady state $k^*(st) = k(st)$, which is important for the evaluation of experiments measuring F_R^* (Quack, 1979d).

Fundamental experimental facts concerning the kinetics of URIMIR

The first qualitatively important observation is the isotope selectivity. This phenomenon indicates selective, monochromatic excitation and a truly unimolecular, photochemical process without collisional heating. Table 1 gives a summary of some of the isotopes separated with URIMIR. The collision free nature of URIMIR is also established by beam experiments (*see* Schulz *et al.*, 1979 for a review). The second qualitative experimental rule is that product and product state distributions favour the lowest channels on the electronic ground state surface. Competition between several reaction channels has been observed, when expected (Colussi *et al.*, 1977; Krajnovitch *et al.*, 1979; Golden *et al.*, 1980). Electronic excitation has also been observed sometimes (Makarov *et al.*, 1980). Still, the chemical evidence suggests primary *vibrational* excitation in the electronic ground state, qualitatively similar to thermal unimolecular reactions (differences will be discussed below).

TABLE 1 Some examples for isotope separations in URIMIR

Element	Reaction	Authors
H	$\text{CH}_2\text{DCH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{DCI}$	Colussi <i>et al.</i> , 1977
H	$\text{CH}_3\text{OD} \rightarrow \text{CH}_3 + \text{OD}$	McAlpine <i>et al.</i> , 1979
H	$\text{CDF}_3 \rightarrow \text{CF}_2 + \text{DF}$	Marling <i>et al.</i> , 1980
H	$\text{HDCO} \rightarrow \text{HD} + \text{CO}$	Koren <i>et al.</i> , 1976
B	$\text{BCl}_3 \rightarrow ?$	Ishikawa <i>et al.</i> , 1980; Ambartzumian <i>et al.</i> , 1976
C	$\text{CF}_3\text{I} \rightarrow \text{CF}_3 + \text{I}$	Bittenson and Houston, 1977
N	$\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$	Hartford and Tuccio, 1979; Kleinermanns and Wagner, 1977
O	$\text{UO}_2(\text{HFACAC})_2 \cdot \text{THF}$ (elim. of THF)	Cox <i>et al.</i> , 1979; Kaldor <i>et al.</i> , 1979
Si	$\text{SiF}_4 \rightarrow ?$	Lyman and Rockwood, 1976
S	$\text{SF}_6 \rightarrow \text{SF}_5 + \text{F}$	Ambartzumian <i>et al.</i> , 1976; Campbell <i>et al.</i> , 1976; Lyman <i>et al.</i> , 1977; Lin <i>et al.</i> , 1978
Cl	$\text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_2\text{Cl} + \text{Cl}$	Huie <i>et al.</i> , 1978
Se	$\text{SeF}_6 \rightarrow ?$	Tiee and Wittig, 1978
Br	$\text{CF}_3\text{Br} \rightarrow \text{CF}_3 + \text{Br}$	de Mévergnes and del Marmol, 1980
Mo	$\text{MoF}_6 \rightarrow ?$	Freund and Lyman, 1978
Os	$\text{OsO}_4 \rightarrow ?$	Ambartzumian <i>et al.</i> , 1977
U	$\text{U}(\text{OCH}_3)_6 \rightarrow ?$	Miller <i>et al.</i> , 1979
U	$\text{UO}_2(\text{HFACAC})_2 \cdot \text{THF}$ (elim. of THF)	Cox <i>et al.</i> , 1979; Kaldor <i>et al.</i> , 1979

The next, more quantitative bit of evidence concerns the role of fluence, intensity and time in yields and rates. In the early days, it had almost been taken for granted that the many photons required for URIMIR would lead to a high power law in intensity as it was known from the multiphoton ionization of atoms (Bebb and Gold, 1966). This has led to the experimental postulate of an *intensity threshold* of about 20–30 MW cm⁻² occurring in the URIMIR of SF₆ (Ambartzumian *et al.*, 1976b), which was also supported theoretically (Goodman, Stone and Downs, 1976; Mukamel and Jortner, 1976). More quantitatively one could write assuming *steady state* for the product yield $F_p \ll 1$ [$\ln(1-x) \simeq -x$] (*see* Eq. (39)):

$$-\ln F_p \simeq F_p = k(st) \cdot t \quad (40a)$$

$$= cF^n/t^{n-1} \quad (40b)$$

$$\log F_p = n \log F + \text{const} \quad (40c)$$

where we have assumed constant pulse duration t . By plotting the logarithm of the product yield as a function of the logarithm of the fluence one would thus obtain as slope n , the power law in intensity (all this had been similarly used in the multiphoton ionization of atoms). Typically for small F_p a value of n between 3 and 7 was found. This reasoning is historically at the origin of the still most popular presentation of experimental data in $\log F_p$ vs. $\log F$ form. The difficulties in the discussion are twofold. The two degrees of freedom in the experiments had not been varied independently (fluence and intensity being varied in a parallel manner). Also it is known now from theory (Quack, 1978) that steady state does not apply for small $F_p < 0.3$, in general.

The question concerning the true role of intensity and fluence has been asked experimentally by varying the two degrees of freedom separately, in particular by measuring yields at a given fluence but changing the average intensity as illustrated in Fig. 7. Kolodner, Winterfeld and Yablonovich (1977) have investigated SF_6 dissociation with a 0.5 and a 150 ns pulse and did not find truly significant changes in yield at the same fluence (the yield was slightly larger for the shorter pulse, though). This points to an essentially linear intensity dependence of the multiphoton excitation process ($n = 1$), and similar evidence comes from related experiments on SF_6 (Lyman *et al.*, 1977; Gower and Billman, 1977). In the elimination of tetrahydrofuran from a large volatile uranyl compound (see Table 1) it was found that at the same fluence short pulse irradiation and longer CW-laser irradiation gave the same yields, pointing to strict linearity of the process in this case (Cox *et al.*, 1979; Kaldor *et al.*, 1979).

In a very elegant experiment on the dissociation of CH_3NH_2 , Ashfold *et al.* (1979) have been able to investigate separately the role of fluence and intensity by probing the product yields at different times during the laser pulse, and for pulses of different intensities (see Fig. 7, flashes indicating probing times). Consistently higher yields were found for higher average intensity, indicating nonlinearity with $n > 1$. Similar results have been obtained with a similar technique for the URIMIR of CF_2HCl by King and Stephenson (1979). Further nonlinearities have been shown to exist in the URIMIR of CF_3I (Rossi *et al.*, 1979) and $(\text{CF}_3)_2\text{CO}$, when pumped off resonance (Naaman and Zare, 1979). There is also some less direct evidence for nonlinearity in the dissociation of CF_2HCl , based upon the shape of the logarithmic reactant-fluence plot to be discussed below (Quack *et al.*, 1980). Thus, at present, cases are known where the URIMIR are linear in intensity

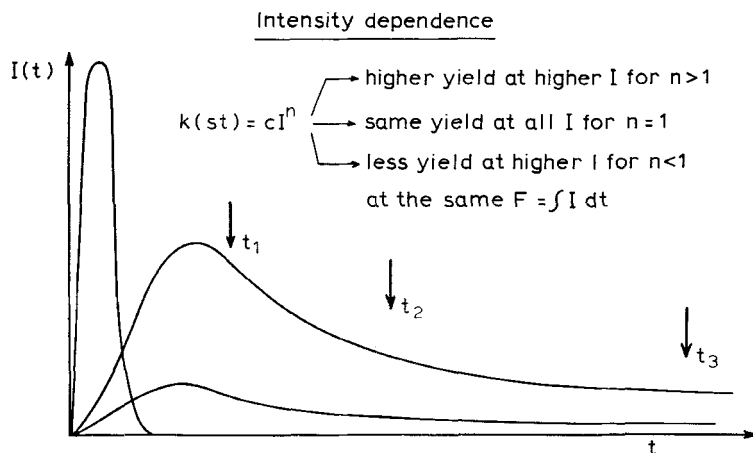


FIG. 7. Irradiation with pulses of the same fluence but different average intensity and the consequences for yields (see discussion in the text).

(fluence dependence, no intrinsic intensity dependence of yields) and where there are truly nonlinear effects (nonlinear intensity dependence of $k(st)$ giving an intrinsic intensity, not just fluence dependence of the yields). The interpretation of this important evidence is to be discussed now.

Mechanistic concepts for URIMIR

We shall summarize here the models and theories that have been suggested for the multiphoton absorption process in URIMIR. Mentioning the early molecular explosion model (implying excitation very high above all reaction thresholds), the diatomic model of Pert (1973) and perturbative models related to the theory of multiphoton ionization of atoms (Faisal, 1976), we shall be interested mainly in those concepts that are still being used. We shall briefly present five of them and discuss their merits and failures with respect to the fundamental *experimental* evidence of the previous section. The theoretical merits have been discussed elsewhere (Quack, 1981b). We omit a discussion of classical trajectory calculations (Noid *et al.*, 1977; Poppe, 1980). A rather general description of excitation and reaction is given in Fig. 8, which can apply both to URIMIR and to thermal, collisional unimolecular reactions, as long as the rate processes R_{mn} are of an

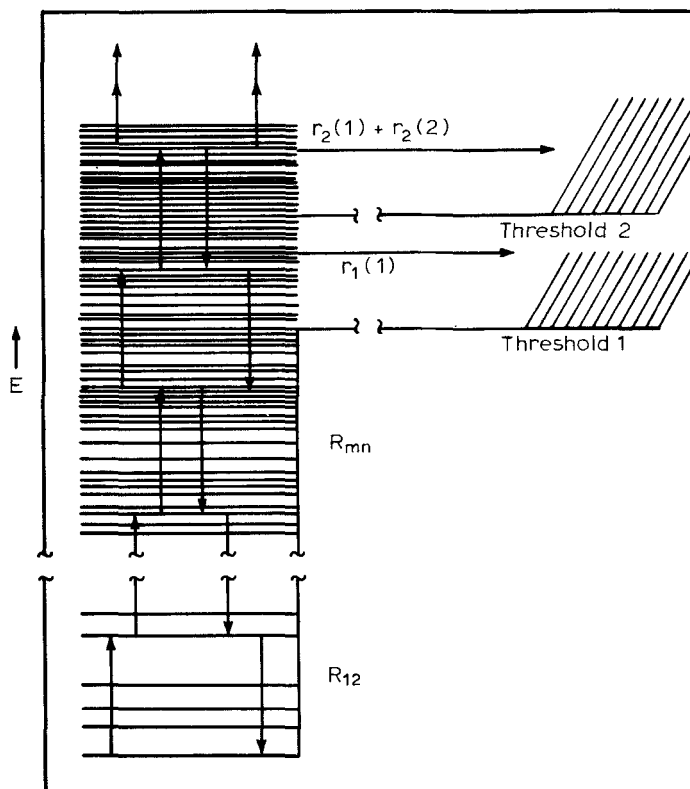


FIG. 8. Multistep excitation in unimolecular reactions of polyatomic molecules. The R_{mn} indicate rate processes of an unspecified nature. (Reproduced by permission from *J. Chem. Phys.*, 69, 1282 (1978))

unspecified nature. An understanding of the true nature of the important rate processes is needed for a qualitative and quantitative description of URIMIR.

The stepwise rate equation model with Einstein coefficients or cross sections

In this model (Grant *et al.*, 1978; Lyman, 1977) the transitions in Fig. 8 are assumed to be stepwise transitions between energy levels separated by the energy $h\nu$ of one laser photon and with rates K_{MN} from the Einstein coefficients for stimulated emission and absorption (spontaneous emission can be neglected for short times in this model) or in terms of a phenomenological absorption cross section σ_M (independent of intensity)

$$K_{M+1,M} = \sigma_M \cdot I/h\nu \quad (41a)$$

$$K_{M,M+1}/K_{M+1,M} = \rho_M/\rho_{M+1} \quad (41b)$$

ρ_M is the level degeneracy or density of states at that excitation energy. Dissociation above threshold can be treated by unimolecular rate theory as usual. We stress that σ_M is merely a constant of proportionality and not the true (small signal) molecular absorption cross section at the laser frequency. In practice σ_M has been chosen to fit experiments. This model *can qualitatively explain* isotope selection, by reasonably allowing for different σ in different isotopomers, it furthermore can explain the fluence dependence of URIMIR and the roughly linear intensity dependence of $k(st)$. It is quite successful in predicting product and product state distributions after reaction using approximate RRKM-models (Schulz *et al.*, 1979). It *cannot* explain the nonlinear intensity effects discussed on page 126.

The two ladder–three regions model

This model appears to be the most popular model for the qualitative description of URIMIR and is reproduced in Fig. 9 (after Bloembergen and Yablonoitch, 1977, *see also* Mukamel and Jortner, 1976, and an extension by Dai, Kung and Moore, 1980). It combines a direct, high-order multiphoton process at low energies (region I) with intramolecular energy transfer and sequential pumping at intermediate energies (region II) and finally dissociation (region III). Qualitatively this model explains everything, the isotope selectivity through the shift of multiphoton resonances, the nonlinear intensity dependence by the power law for the multiphoton process, the product and product state distribution by making the same assumption as the rate equation model in the quasicontinuum. The linear regime of URIMIR can be explained by assuming the quasicontinuum to start at low energies. A critique of this model must be theoretical (Quack, 1981b). An estimate of the rate for a high-order multiphoton process gives much too low rates as compared to experiments. Fundamental conceptual difficulties are associated with the intramolecular energy transfer, which is postulated to change its rate between regions I and II. The model cannot be used for quantitative estimates (and it has not). In spite of its popularity it cannot be considered to be a good description of reality. The nonlinear intensity dependence can be explained by mechanisms other than the inefficient coherent multiphoton transition.

Intramolecular relaxation and the pumping dumping model

This model is somewhat related to the previous model and is shown in Fig. 10. The pumping is described by the interaction of one molecular mode with the radiation field. This increases E_{mode} , however, at the same time there is coupling to the ‘bath’ (the other modes of the molecule) whose energy increases steadily until reaction in an arbitrary mode

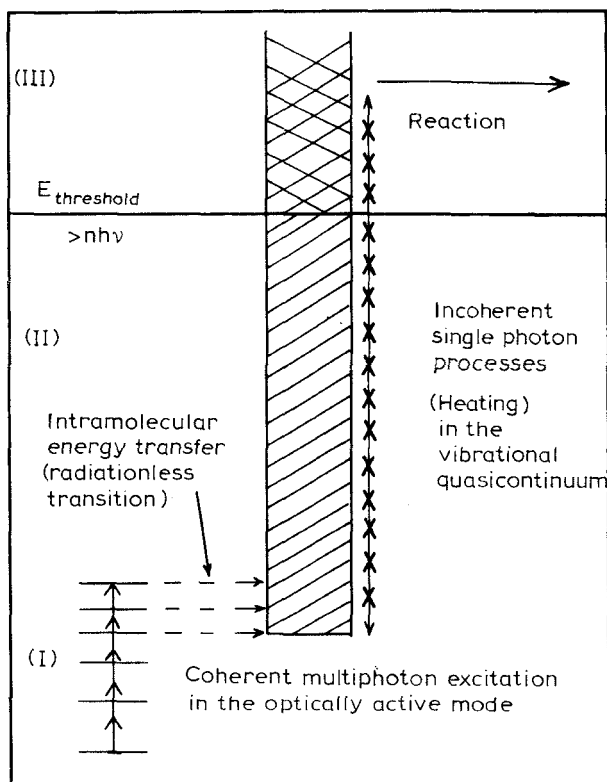


FIG. 9. The two ladder, three regions model for URIMIR (after Bloembergen and Yablonovitch, 1977).

of the bath is possible. Again this model explains everything. It is distinguished, however, by a quantitative statistical mechanical formulation for the equations of motion of the reduced density matrix of the pumped mode (Hodgkinson and Briggs, 1976, 1977, and elaborations by Stone and Goodman, 1978, 1979; Friedman, 1979, Cantrell *et al.*, 1979). A critique of this model is again theoretical (Quack, 1981b), a brief discussion being given below.

The two ensembles model

It has been suggested that one combines the rate equation model for one subensemble of molecules (characterized, for instance, by rotational quantum number) with a completely nonreactive, second subensemble of molecules. By making the relative partitioning between these two subensembles intensity dependent in an arbitrary manner, one can allow for the nonlinear effects missing in the simple rate equation model (*see*, for instance, Bagratashvili *et al.*, 1979; Schulz *et al.*, 1980). Again, difficulties arise mainly in a quantitative sense, the description being too 'permissive' (in terms of arbitrary parameters) on the one hand and too restrictive on the other hand, since the assumption of one subset of molecules, which are completely nonreactive at a given, constant intensity, may be questioned (Quack *et al.*, 1980). A better description involves a reducible rate coefficient

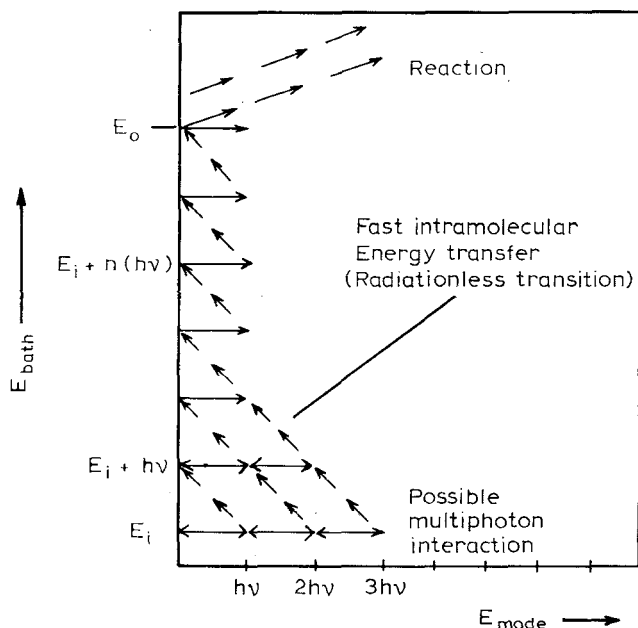


FIG. 10. Scheme for the pumping-dumping model (Friedmann, 1979). — indicate *radiative* processes, ---- indicate *radiationless* (vibrational) transitions. The reaction is to be interpreted as occurring in the 'third axis', out of the plane, since the reactive mode and the pumped mode do not coincide, in general.

matrix, allowing for nonlinear intensity dependencies within each subset, as discussed below (Quack, 1979b, 1981a).

Coarse-grained, unified master equation including nonlinearity

It has been shown (Quack, 1978, 1979a) that nonlinear effects can be included in a stepwise master equation by making use of the statistical mechanics of case C without invoking multiphoton transitions. A simple, approximate unified treatment has been elaborated (Quack, 1981a) and is described in Fig. 11. Case B (Pauli equation) has the same linear intensity dependence as the rate equation model, the rate coefficients being now defined in terms of average square coupling matrix elements. We note in particular the intensity independent ratio $K_{M+1,M}/K_{M,M+1}$, equivalent to Eq. (41b), in essence. However, in case C this ratio is intensity dependent (Quack, 1978), which leads to a power law with $n > 1$ for $k(st)$, depending upon the number of steps, for which case C applies (Quack, 1979a). Note the *fast* down pumping rates in Case C, which increases with the square root of intensity (width of the arrows in Fig. 11). The transition between case B and case C can be simply described by taking the maximum value from either case C or case B for $K_{M,M+1}$, which can be computed from spectroscopic parameters (line spacings and strengths) in both cases. No explicit reference is made in this treatment to intramolecular relaxation processes. Although this treatment invokes unusual concepts, such as an intensity dependent detailed balancing $K_{M+1,M}/K_{M,M+1}^C$ and may appeal less to intuition, it is well founded theoretically on measurable, spectroscopic properties of the molecules themselves, and allows for qualitative and possibly quantitative explanations and

The mechanism of excitation

Case B (Pauli)

ρ_3
 ν
 ρ_2
 ν
 ρ_1

$\propto I$
 $\propto I$

$$\frac{K_{M+1,M}}{K_{M,M+1}^B} = \frac{\rho_{M+1}}{\rho_M}$$

Case C

$\propto \sqrt{I}$
 $\propto \sqrt{I}$

$$\frac{K_{M+1,M}}{K_{M,M+1}^C} = \frac{\rho_{M+1}}{\rho_M} \cdot g$$

$$g = \frac{\pi}{2} \sqrt{3} |V| \rho_{M+1}$$

Unified : $K_{M,M+1}^{B,C} = \text{Max} \{ K_{M,M+1}^B, K_{M,M+1}^C \cdot f_c \}$

$$K_{M+1,M} = 2\pi \langle |V_{M+1,M}|^2 \rangle \rho_{M+1}^\omega$$

$$\frac{dp_N}{dt} = \sum_{M \neq N} K_{NM} p_M - (k_N + \sum_{M \neq N} K_{MN}) p_N$$

FIG. 11. The stepwise, unified master equation including non-linear effects (after Quack, 1981a, see the detailed discussion in the text).

predictions of experimental observations. Isotope selectivity is provided for by *two* mechanisms, a linear and a nonlinear one (case B and case C), which gives some predictions that may be subject to future experimental test (Quack, 1981a). The nonlinear intensity dependence can be estimated semiquantitatively for every molecule and the transition to the linear regime can be made without making artificial assumptions. The relationship to exact quantum mechanical solutions has been established and a nonlinear intensity effect as observed in experiments is shown in Fig. 12 from such a calculation.

Of the mechanistic concepts discussed, two (intramolecular relaxation and the coarse-grained unified master equation) have been approximately derived from first principles. Intramolecular relaxation invokes the concept of a finite rate of intramolecular energy transfer, the other does not, being entirely based upon spectroscopic properties. Fig. 13 shows, in terms of spectroscopy, under which conditions the two alternatives provide simple and useful descriptions. If the vibrational absorption is essentially continuous, many states carrying oscillator strength in the range of the homogenous width Γ_h^ω (created by intramolecular coupling), both models can be applicable. The intramolecular relaxation model will be simple, if the bandwidth Δ of the excitation (both polychromaticity of the light and 'power' width) is large compared to Γ_h^ω . The coarse-grained model will give a simple description if $\Delta < \Gamma_h^\omega$ for which there is some spectroscopic evidence (Dübal and Quack, 1980). In this sense the two treatments are complementary. However, if Γ_h^ω (or the 'rate of intramolecular relaxation' $k_r = \Gamma_h^\omega$ is fast compared to the rate of optical transitions) the intramolecular relaxation treatment becomes meaningless (not simply incorrect) as well as in the situation where the number of lines within the width Γ_h^ω is small (no quasicontinuous absorption). In fact, a reduced density matrix description is not well suited to small molecules at moderate excitation energies. The coarse-grained treatment is insensitive to all these difficulties, although the simple expressions for rate coefficients have to be amended under many conditions, including sometimes quantum mechanical solutions at low energies (Quack, 1978).

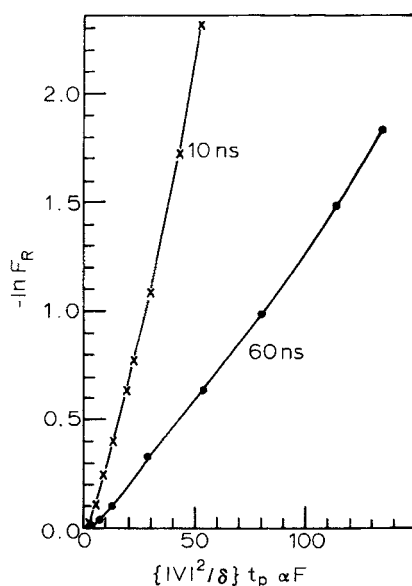


FIG. 12. Example for intensity dependent yields in a multilevel system with off resonant pumping, from an exact solution of the quantum mechanical equations of motion. The times indicate irradiation times with the same fluence. (Reproduced by permission from *J. Chem. Phys.*, 73, 247 (1980).)

With appropriate amendments all of the above models are able to provide qualitative explanations of the major experimental facts (that is, why so many different models survive in the literature). More quantitative experiments are needed in the future to provide more severe tests. On the other hand, few models, so far, have provided quantitative predictions.

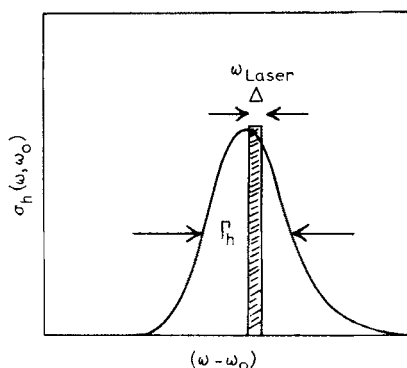


FIG. 13. Illustration of the applicability of various treatments as a function of vibrational spectroscopic coarse structure in the cross section σ (rotation is omitted for simplicity). Γ is implied here to be in units of the circular frequency ($= \Gamma_h^\omega$ in the text). This width is to be interpreted as due to *vibrational* structure in the spectrum of a highly excited molecule at initial energy $h\omega_0$ (see Quack, 1978; Dübal and Quack, 1980).

The quantitative theoretical treatments

Most of the quantitative theoretical treatments have been based upon a master equation for the population vector p of molecular states (in matrix notation, the point denotes derivative with respect to time, *see also* Fig. 11).

$$\dot{p} = Kp \quad (42)$$

With rate coefficients proportional to radiation intensity, as originally proposed on phenomenological grounds (Grant *et al.*, 1978) and as justified in several theoretical treatments (Quack, 1978; Schek and Jortner, 1979; Carmeli and Nitzan, 1980; Carmeli *et al.*, 1980; Mukamel, 1979). As discussed above, extensions to a nonlinear intensity dependence are possible (Quack, 1978, 1981a). Solutions of Eq. (42) have been based either on the exponential form, Eq. (43) (Quack, 1978):

$$p(t) = \exp(Kt) p(0) \quad (43)$$

or on numerical stepwise procedures, such as Gear's algorithm (Lyman, 1977; Baldwin *et al.*, 1979) or stochastic simulations (Barker, 1980), or closed expressions for continuous, approximate models (Fuss, 1979; Troe, 1980). The model of Fuss (1979) and a simplified 'thermal' model of Shultz and Yablonovitch (1978) and Black *et al.* (1979) have been critically analysed by Barker (1980). It is not entirely clear, how helpful the oversimplified models are, since exact solutions can be obtained in a simple manner. Particularly noteworthy are the many detailed simulations of molecular beam results using Eq. (42) with specific rate coefficients for the monomolecular reaction step from RRKM-models (*see* the review by Schulz *et al.*, 1979). Some simulations have included collisional energy transfer (Baldwin and van den Bergh, 1981; Stone, Thiele and Goodman, 1980).

As compared to the thermal unimolecular reactions the kinetics of URIMIR are distinguished by the relative importance of the pre-steady-state or incubation period (Quack, 1978). It is not generally possible to base a quantitative description on the steady state eigenvalue and the incubation time alone (both of these are steady state properties). An expansion in terms of the higher eigenvalues of K has been discussed also in connection with the evaluation of experiments (Quack, 1979b). Several authors have tried simple approximate expressions to fit the exact results for either rates or yields (or both) during the incubation period. The first of these was an 'activation equation' for the time dependent rate coefficient (Quack, 1979e)

$$k(t) = k(st) \exp[-(\Theta/t)^2] \quad (44)$$

with the activation time Θ as an additional parameter. Troe (1980) has suggested the equation

$$k(t) = k(st) [1 - \exp(-t/\Theta')]^n \quad (45)$$

with $n = 10$. Product yields can be obtained by elementary integration from these rate coefficients. Barker (1980) has suggested a log-normal distribution for product yields, which appears to give a good fit to exact results for a variety of conditions (*see also* Golden *et al.*, 1980; Baldwin and Barker 1981a,b):

$$F_p = \int_0^t (t' \sigma \sqrt{2\pi})^{-1} \exp[-(\ln t' - \mu)^2 / 2 \sigma^2] dt'. \quad (46)$$

The rate coefficient can be obtained from this by differentiation of $-\ln(1 - F_p)$ with respect to time. Although the two parameter expression in Eq. (46) is somewhat cumbersome, its use is facilitated by the fact that plotting F_p as a function of $\ln t$ on

probability paper, Eq. (46) yields a straight line (Barker, 1980). We note that such approximate expressions for $k(t)$ or $F_p(t)$ can, in principle, be of some use also for the description of the incubation period in thermal unimolecular reactions (see page 108). However, in view of the availability of the exact expansion for $k(t)$ and F_p (Quack, 1979b) one should establish some performance criteria for the approximate expressions. Clearly, there is only one exact solution, but an infinity of approximations.

The above expressions all assume irradiation with constant intensity and measurement as a function of time. The conditions, under which this time dependence can be transformed exactly or approximately to a fluence dependence have been derived by Quack (1979b). This is of some importance for the evaluation of experiments, in which intensity at present cannot be controlled although this remains a major experimental goal for the future.

The presentation of quantitative experimental data and rate constants for URIMIR

The difficulty in the quantitative evaluation of current experiments is mainly related to the incomplete control of the two degrees of freedom, say intensity and fluence. If both of them are important, but only one of them is controlled, a quantitative evaluation is impossible. Often, not even spatial control is achieved experimentally. Theory can help, if only fluence is important (Quack, 1979b). Then the question remains, how yield data should be reported as a function of F . A popular presentation is $\log F_p = f(\log F)$, which is not well founded theoretically any more. Even if the intensity dependence were taken seriously, a more logical presentation would be $\log(-\ln F_R) = f(\log F)$ (see page 125). For true fluence dependence the best kinetic evaluation appears to be from plots of $-\ln F_R$ vs. F , which corresponds to an ordinary unimolecular plot, since F corresponds then to the time scale. From such plots, steady state rate coefficients can be obtained from the limiting slope (Quack, 1979d), even if in fact F_R^* (without time resolution, see page 124) is measured, because one has $k^*(st) = k(st)$. This is an exact relationship if either $I = \text{const}$ or $k(st) \propto I$, which is implied by the assumption of pure fluence dependence anyway. An example of such a presentation is shown in Fig. 14 and details in connection with experiments have been discussed (Quack *et al.*, 1980), where one can find also a table of rate coefficients from experiments. This method has been used now in a variety of circumstances, including the URIMIR of negative ions in ICR (CH_3OH^- , Rosenfeld, Jasinski and Brauman, 1980) and laser induced desorption of CH_3F from solid surfaces (Heidberg *et al.*, 1980, 1981). Another presentation of experimental data is connected to Barker's (1980) log-normal distribution. A plot of experimental data on probability paper often appears to yield linear presentation (Golden *et al.*, 1981; Baldwin and Barker, 1981). This method of evaluation is, however, less well founded theoretically. Many other presentations are possible and have been used. We stress that in the presence of intrinsic intensity effects a complete table of the primary experimental data remains the best presentation of data, although unfortunately it is rarely used.

Distribution functions and unimolecular decay

In connection with unimolecular reactions induced by collisions and unimolecular reactions induced by one-photon activation one is also interested in the particulars of the distribution over molecular energy levels created by the multiphoton excitation process in URIMIR. Thermal unimolecular reactions create thermal Boltzmann distributions in the high-pressure limit with deviations at lower pressures (Troe and Wagner, 1967; Troe, 1977a). One-photon activation creates monoenergetic distributions, with some width if thermal energy from the ground state is conserved in the photoactivation. URIMIR create

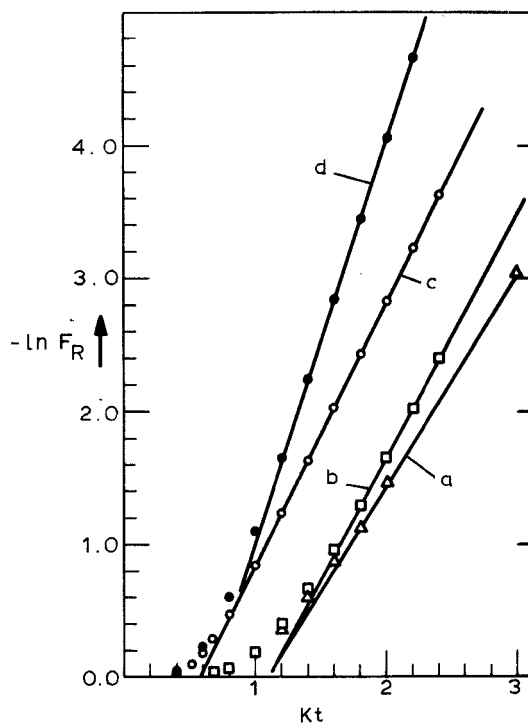


FIG. 14. Logarithmic reactant fluence plot for the evaluation of experiments, Kt is proportional to fluence. The function b corresponds to a measurement of F_R with constant intensity (time being the independent variable). The limiting slope gives the rate coefficient exactly. The function c is for the measurement of F_R^* with the same limiting slope, practically independent of either intensity or time variation (Reproduced by permission from *Ber. Bunsenges. Phys. Chem.*, 83, 757 (1979).)

non-thermal distributions that can in the limit be characterized as 'quasimicrocanonical' (proportional to the density of states alone) or by an infinite temperature (i.e. 'Boltzmann without $\exp(-E/kT)$ ', Quack, 1978). In practice the distributions are, however, strongly determined kinetically, even at steady state, and also by the nonlinear properties in case C. An example for time and intensity dependence is shown in Fig. 15. The population is characterized by two maxima, one at low, one at high energies, with some population above the reaction threshold. In the linear regime of URIMIR there is only the high-energy maximum. There appears to be some qualitative evidence on such distribution functions from photoionization of multiphoton heated SF_6 (Sudbo *et al.*, 1979). Otherwise, the distribution functions are poorly known experimentally (*see also* Kudriavtsev and Letokhov, 1980). This is unfortunate, since the calculated average energy absorbed per molecule is a strong function of the distribution function assumed and a number of erroneous conclusions have been drawn from comparing experimental results with theory. The distribution above threshold determines the rates of dissociation after irradiation, which have been measured by Duperrex and van den Bergh (1979a). For large molecules the major fraction of molecules can reside above threshold at and even before steady state. In principle, one can then follow the unimolecular decay of the corresponding ensemble without further irradiation.

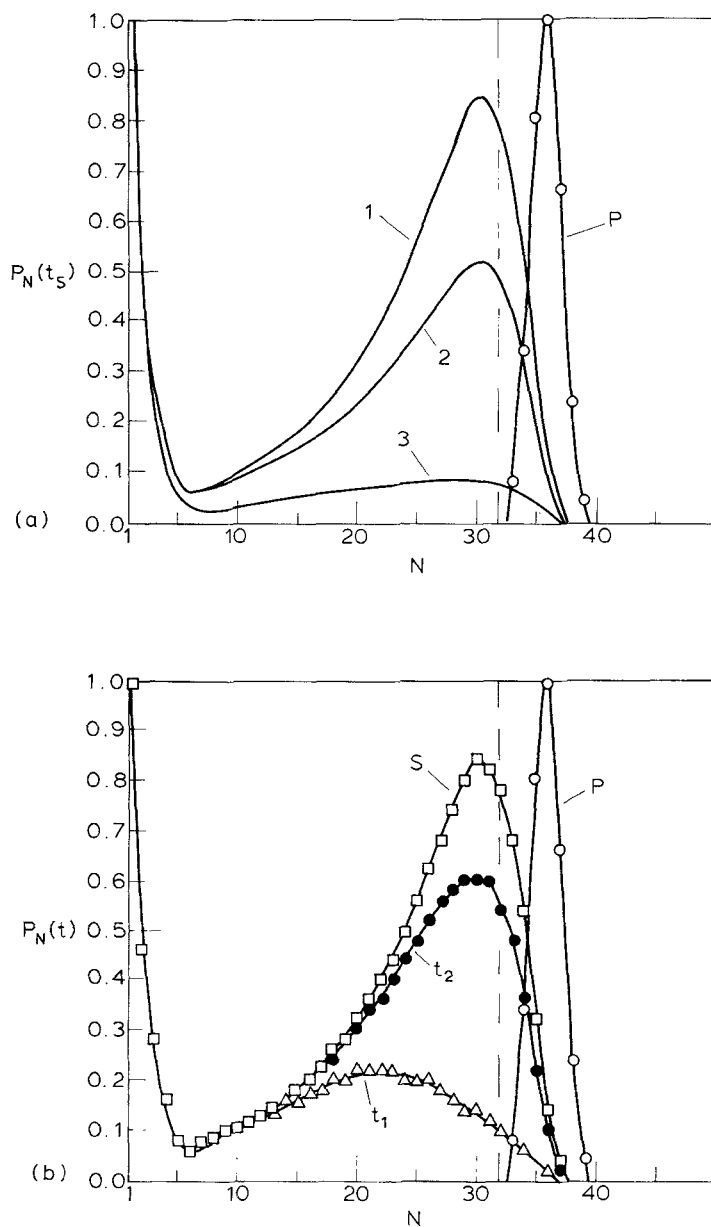


FIG. 15. Relative populations P_N of levels (index N , being equivalent to the number of IR-photons absorbed by the molecule). All functions are individually normalized to their respective maximum values. The dashed line indicates the reaction threshold. P(O) indicates the product energy distributions. (a) Populations at steady state in early bottleneck situations (moderate intensity, *decreasing* qualitatively in the order 1, 2, 3). (b) Establishment of the steady state population for the condition 1 of (a) as a function of time. Note that steady state is rapidly established for the low levels, where the three functions coincide (Reproduced by permission from *Ber. Bunsenges. Phys. Chem.*, 83, 757 (1979); see also Quack, 1981a.)

Special experimental effects of current interest

In a new field of research being still in its exploratory phase a variety of new experimental effects are easily found. Sometimes, these effects fit neatly into available theoretical considerations, sometimes more detailed investigations have still to be carried out, sometimes there appear to be strange contradictions and difficulties in reproducibility, sometimes theory predicts effects still to be confirmed experimentally. All of this happens in URIMIR as in other new fields. We shall mention here briefly such experimental effects without detailed, critical discussion.

Mode or bond selectivity

Because of the monochromatic excitation one may hope to have mode selectivity in addition to isotope selectivity, since in general IR-absorption is attributed to certain modes or even bonds within a molecule. In practice this selectivity may not become apparent because of fast energy scrambling in the molecule on the ns timescale of excitation. All the early reports on mode selectivity in URIMIR have been refuted in the review of Schulz *et al.* (1979). Nevertheless, further examples appear at a steady rate (e.g. Lesiecki and Guillory, 1977; de Hemptinne and DeKeuster, 1980; Hall and Kaldor, 1979). Some of these have been discussed by Ashfold and Hancock (1981a). To our knowledge, no experimental proof of mode-selective chemistry is available. This does not imply that mode-selective chemistry is absent, only that the right experiments have not been done. Mode selectivity is expected on short time scales. The mere observation of different product yields when pumping the same molecule at two different frequencies is *no evidence at all* for mode selective chemistry (Quack, 1978).

Luminescence

Luminescence from fragments in URIMIR has been observed in the very first experiments (Isenor and Richardson, 1971). More detailed evidence has become available subsequently for the URIMIR of vinyl cyanide (Yu *et al.*, 1979), tetramethyldioxetane (Yahav and Haas, 1978) and $C_2F_4S_2$ (Plum and Houston, 1980). Luminescence from the parent molecule has been observed for COF_2 (Hudgens *et al.*, 1979), CrO_2Cl_2 (Karny *et al.*, 1979), and OsO_4 (Makarov *et al.*, 1980). In the case of CrO_2Cl_2 emission may come from fragments (Puretzky and Schröder, 1981). Theoretical models for the luminescence have been suggested (Nitzan and Jortner, 1979), although many details remain to be explained. Hancock and coworkers have recently investigated the emission from OsO_4 with their rectangular, shaped pulses, providing most important information on the intrinsic intensity dependence (Hancock, 1981; Ashfold *et al.*, 1981b).

IR-excitation after UV-excitation

In several experiments the reactant molecule was first excited by visible or UV light with possible subsequent internal conversion or intersystem crossing and finally IR pumping. Such cases include NO_2 (Feldmann, Zacharias, and Welge, 1980), CrO_2Cl_2 (Heller and West, 1980) and biacetyl (Tsao *et al.*, 1980). These experiments add to the many possibilities of optical excitation. To some extent they also provide information about the IR-absorption of highly excited species, which has also been probed directly after multiphoton excitation in the electronic ground state (Lyman *et al.*, 1980; Fuss 1979; Stafast, Schmid and Kompa, 1977). IR-excitation in the triplet state of propynal has been reported recently (Stafast *et al.*, 1981).

Excitation of ions

Of course, IR-multiphoton excitation and reaction is not restricted to neutral molecules but can also be found in ions. Sometimes very low pressures have been used with long time scales and CW-laser excitation (Woodin, Bomse and Beauchamp, 1979). Nevertheless, collisions and spontaneous emission must be taken into account if the exciting power is too low. Ions that have been dissociated include CF_3I^+ (Coggiola, Cosby and Peterson, 1980), SF_5^+ (Von Hellfeld, Feldmann and Welge, 1979) and the negative ion CF_3OH^- (Rosenfeld *et al.*, 1980; Jasinski and Brauman, 1980). Also electron detachment from the benzyl-anion has been observed, which may be the first clear-cut IR-multiphoton ionization without collisions (Rosenfeld *et al.*, 1979).

The effects of collision

Early investigations of the effect of collisions on URIMIR have shown both collisional quenching (Bado and van den Bergh, 1978; Duperrex and van den Bergh, 1979c) and collisional enhancement (Quick and Wittig, 1978). Both effects are qualitatively understood and have been demonstrated also in investigations on CF_2HCl (Duperrex and van den Bergh, 1979a) and CF_2CFCI (Stone *et al.*, 1980). The results of the former are shown in Fig. 16. Yahav *et al.* (1980) have considered the effect of collisions on incubation phenomena in URIMIR. The current procedure in the theoretical treatment of collisional effects is to add collisional terms to a master equation (Stone *et al.*, 1980; Baldwin and van den Bergh, 1980; Yahav *et al.*, 1980). Although operationally attractive, this procedure still needs a satisfactory theoretical justification.

The effects of initial temperature

The initial state before irradiation influences the mechanisms and rates of URIMIR in several ways. Correspondingly substantial effects of initial temperature on the rates and

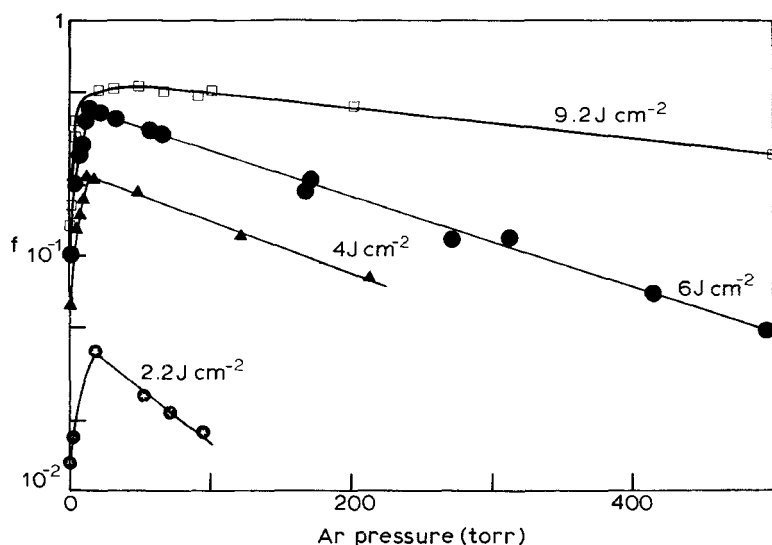


FIG. 16. The effect of inert gas pressure in the URIMIR of CF_2HCl at various fluences (indicated in J cm^{-2}). f is the fraction dissociated (F_p^*). Note the initial rise and subsequent slow decrease. (Reproduced by permission from *J. Chem. Phys.*, 71, 3613 (1979), Duperrex and van den Bergh, 1979a.)

yields as a function of fluence have been found for SF_6 (Duperrex and van den Bergh, 1979b), CF_2HCl (Quack *et al.*, 1980), and CF_2Cl_2 (Chou and Grant, 1981). Even more drastic effects have been seen in the URIMIR of ions that were created with various amounts of initial internal energy (Rosenfeld *et al.*, 1980).

The effects of static external fields

Van den Bergh and coworkers have found interesting enhancements of yields at a given fluence in the URIMIR of CF_2HCl by applying strong, static external electric and magnetic fields (Duperrex and van den Bergh, 1980; Gozel and van den Bergh, 1981). The effects are shown in Fig. 17. Such effects had been surmised on qualitative grounds by Sazonov (1978). They are probably best explained quantitatively through a breakdown of angular momentum selection rules and a corresponding transition from case C to case B (Quack, 1981a; Quack and van den Bergh, 1981). Other explanations are possible, in principle and more experimental data of this kind are urgently needed.

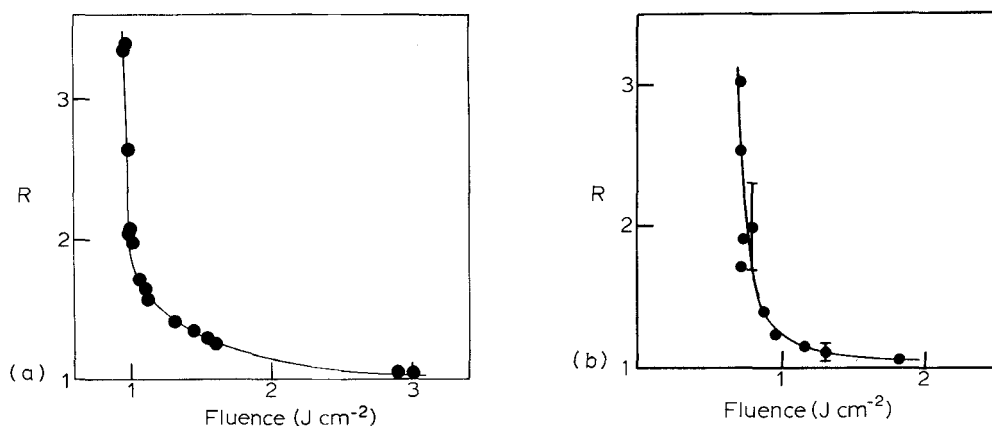


FIG. 17. The effect of static external fields on yields in the URIMIR of CF_2HCl in terms of the enhancement factor R . (a) Effect of a magnetic field of 14 kGauss (Reproduced by permission from *J. Chem. Phys.*, 73, 585 (1980), Duperrex and van den Bergh, 1980.) (b) Effect of an electric field of 4.2 kv/cm (Reproduced by permission from *J. Chem. Phys.*, 74, 1724 (1981), Gozel and van den Bergh, 1981.)

Theoretically predicted effects

Only few quantitative theories have so far been used for definite predictions. For instance, with the help of simple model assumptions, that do not depend too sensitively upon the so-far-unknown spectroscopic properties of highly excited molecules, a number of rules have been derived for the dependence of rates in URIMIR upon molecular parameters such as threshold energies, band strengths, etc. (Quack, 1979e, 1981a). Some of these results could be well reproduced by simple closed expressions from solvable models (Troë, 1980). Although a large body of experimental data does exist and has been reviewed (Lyman *et al.*, 1980), only a few of the data are quantitative enough for comparison with theory. A more fundamental prediction that has not yet been verified (or falsified) experimentally is the transition to case D and fall-off effects at high radiation intensities (Quack, 1978). The consequence is that $k(st)$ will depend with a power $n < 1$ upon intensity. This implies that under these conditions irradiation with the *higher* intensity (at a

given fluence, whether or not steady state is reached), will give *lower* product yields. This striking prediction has until now not been subjected to experimental test, although the intensities needed would be available experimentally.

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REFERENCES

- ADACHI, H., BASCO, N. and JAMES, D. G. L. (1980). *Int. J. Chem. Kin.*, **12**, 949.
- AMBARTZUMIAN, R. V. and LETOKHOV, V. S., (1977). *Acc. Chem. Res.*, **10**, 61.
- AMBARTZUMIAN, R. V., CHEKALIN, N. V., GOROKHOV, YU. A., LETOKHOV, V. S., MAKAROV, G. N. and RYABOV, E. A. (1976). *Opt. Commun.*, **18**, 121.
- AMBARTZUMIAN, R. V. GOROKHOV, Y. A., LETOKHOV, V. S., MARKAROV, G. N. and PURETSKII, A. A., (1976b). *JETP Lett.*, **23**, 22.
- AMBARTZUMIAN, R. V., FURZIKOV, N. P., GOROKHOV, Y. A., LETOKHOV, V. S., MAKAROV, G. N. and PURETZKY, A. A. (1977). *Optics Letters*, **1**, 22.
- ANASTASI, C. and SMITH, I. W. M. (1976). *J.C.S. Faraday Trans. II*, **72**, 459.
- ANDLAUER, B. and OTTINGER, CH. (1971). *J. Chem. Phys.*, **55**, 1471.
- ANDLAUER, B. and OTTINGER, CH. (1972). *Z. Naturforsch.*, **27a**, 293.
- ASHFOLD, M. N. R. and HANCOCK, G. (1981a). In: *Gas Kinetics and Energy Transfer* (Ed. R. Donovan and P. G. Ashmore), vol. 4. London: The Chemical Society.
- ASHFOLD, M. N. R., ATKINS, C. G. and HANCOCK, G. (1981b) *Chem. Phys. Lett.*, **80**, 1.
- ASHFOLD, M. N. R., HANCOCK, G. and KETLEY, G. (1979). *Faraday Disc. Chem. Soc.*, **67**, 204.
- ASHFOLD, M. N. R., QUINTON, A. M. and SIMONS, J. P. (1980). *J.C.S. Faraday Trans. II*, **76**, 905.
- ASHFOLD, M. N. R., GEORGIU, A. S., QUINTON, A. M. and SIMONS, J. P. (1981). *J.C.S. Faraday Trans. II*, **77**, 259.
- ASTHOLZ, D. C., DURANT, J. E. and TROE, J. (1981a). *18th Int. Symp. on Combustion* (The Combustion Institute).
- ASTHOLZ, D. C., BROUWER, L. and TROE, J. (1981b). *Ber. Bunsenges. Physik. Chem.*, (in press).
- ASTHOLZ, D. C., BROUWER, L. and TROE, J. (1981). *Ber. Bunsenges. Physik. Chem.*, (in press).
- ASTHOLZ, D. C., TROE, J. and WIETERS, W. (1979). *J. Chem. Phys.*, **70**, 5107.
- BADO, P. and VAN DEN BERGH, H. (1978). *J. Chem. Phys.*, **68**, 4188.
- BAER, T., SMITH, D., TSAI, B. P. and WERNER, A. S. (1978). In: *Adv. Mass. Spectrom.*, **7**.
- BAER, T., TSAI, B. P. SMITH, D. and MURRAY, P. T. (1976). *J. Chem. Phys.*, **64**, 2460.
- BAER, T., WERNER, A. S. and TSAI, B. P. (1975). *J. Chem. Phys.*, **62**, 2497.
- BAER, T., WILLETT, G. D., SMITH, D. and PHILLIPS, J. S. (1979). *J. Chem. Phys.*, **70**, 4076.
- BAGRATASHVILI, V. N., DOLJIKOV, V. S., LETOKHOV, V. S. and RYABOV, E. A. (1979). In: *Laser Induced Processes in Molecules* (ed. K. L. Kompa and S. D. Smith) p. 179. Berlin: Springer.
- BAILEY, I. M. and WALSH, R. (1978). *J.C.S. Faraday Trans. I*, **74**, 1146.
- BALDWIN, A. C. and BARKER, J. R. (1981a). *J. Chem. Phys.*, **74**, 3813.
- BALDWIN, A. C. and BARKER, J. R. (1981b). *J. Chem. Phys.*, **74**, 3823.
- BALDWIN, A. C. and VAN DEN BERGH, H. (1981). *J. Chem. Phys.*, **74**, 1012.
- BALDWIN, A. C., BARKER, J. R., GOLDEN, D. M., DUPERREX, R. and VAN DEN BERGH, H. (1979). *Chem. Phys. Lett.*, **62**, 178.
- BARKER, J. R. (1980). *J. Chem. Phys.*, **72**, 3686.
- BATES, D. R. (1979a). *J. Chem. Phys.*, **71**, 2318.
- BATES, D. R. (1979b). *J. Phys. B., Atom. Molec. Phys.*, **12**, 4135.
- BAUGHUM, S. L. and LEONE, S. R. (1980). *J. Chem. Phys.*, **72**, 6531.
- BAULCH, D. L., COX, R. A., HAMPSON, R. F., KERR, J. A., TROE, J. and WATSON, R. T. (1980). *J. Phys. Chem. Ref. Data*, **29**, 295.
- BEBB, H. B. and GOLD, A. (1966). *Phys. Rev.*, **143**, 1.
- BENSON, S. W. and O'NEAL, H. E. (1970). *NSRDS—NBS 21*.

- BEYER, T. and SWINEHART, D. F. (1973). *Commun. ACM* 16, 379.
- BHATTACHARGIE, R. C. and FORST, W. (1978). *Chem. Phys.*, 30, 217.
- BLACK, J. G., KOLODNER, P., SCHULTZE, M. J., YABLONOVITCH, E. and BLOEMBERGEN, N. (1979). *Phys. Rev.*, A19, 704.
- BITTENSON, S. and HOUSTON, P. L. (1977). *J. Chem. Phys.*, 67, 4819.
- BLOEMBERGEN, N. and YABLONOVITCH, E. (1977). In: *Laser Spectroscopy* (Ed. Hall and Carlsten) vol. III, p. 86. Berlin: Springer Verlag.
- BLOEMBERGEN, N. and YABLONOVITCH, E. (1978). *Physics Today*, 31, 23.
- BORDÉ, M. C., HENRY, ANNE, HENRY, M. L. and KASTLER, A. (1966). *C.R. Acad. Sci, Paris*, 263 B, 619.
- BOYD, R. K. (1977). *Can. J. Chem.*, 55, 802.
- BRAY, R. G. and BERRY, M. J. (1979). *J. Chem. Phys.*, 71, 4909.
- BRUNNER, F. and PROCH, D. (1978). *J. Chem. Phys.*, 68, 4936.
- BRUNNER, F., COTTER, T. P., KOMPA, K. L. and PROCH, D. (1977). *J. Chem. Phys.*, 67, 1547.
- BUFF, F. P. and WILSON, D. J. (1960). *J. Chem. Phys.*, 32, 677.
- BUNKER, D. L. and PATTENGILL, M. (1968). *J. Chem. Phys.*, 48, 772.
- BUNKER, D. L. (1971). In: *Methods in Computational Physics* (ed. B. Alder), vol. 10, New York: Academic Press.
- BUNKER, D. L. (1977). *Ber. Bunsenges. Phys. Chem.*, 81, 155.
- BUNKER, D. L. and HASE, W. (1973). *Q CPE*, 13, 234.
- BUSS, R. J. and LEE, Y. T. (1979). *J. Phys. Chem.*, 83, 34.
- BUSS, R. J., COGGIOLA, M. J. and LEE, Y. T. (1979). *Faraday Disc. Chem. Soc.*, 67, 221.
- CAMPBELL, J. D., HANCOCK, G. and WELGE, K. H. (1976). *Chem. Phys. Lett.*, 43, 581.
- CANNON, B. D. and CRIM, F. F. (1980). *J. Chem. Phys.*, 73, 3013.
- CANTRELL, C. D., FREUND, S. M. and LYMAN, J. L. (1979). In: *Laser Handbook* (ed. E. L. Stitch), vol. IIIb. Amsterdam: North Holland.
- CARLESS, H. A. J., MAITRA, A. K., POTTINGER, R. and FREY, H. M. (1980). *J.C.S. Faraday Trans. I*, 76, 1849.
- CARMELI, B. and NITZAN, A. (1980). *J. Chem. Phys.*, 72, 2054, 2070.
- CARMELI, B., SCHEK, I., NITZAN, A. and JORTNER, J. (1980). *J. Chem. Phys.*, 72, 1928.
- CARR, R. W. (1980). *Chem. Phys. Lett.*, 74, 437.
- CHANG, J. S. and GOLDEN, D. M. (1980). *J. Amer. Chem. Soc.*, (in press).
- CHESNAVITCH, W. J. and BOWERS, M. T. (1979). In: *Gas Phase Ion Chemistry*, vol. 1. New York: Academic Press.
- CHIANG, C.-C., BAKER, J. A. and SKINNER, G. B. (1980). *J. Phys. Chem.*, 84, 939.
- CHOU, J. S. and GRANT, E. R. (1981). *J. Chem. Phys.*, 74, 384.
- COGGIOLA, M. J., SCHULZ, P. A., LEE, Y. T. and SHEN, R. (1977). *Phys. Rev. Lett.*, 38, 17.
- COGGIOLA, M. J., COSBY, P. C. and PETERSON, J. R. (1980). *J. Chem. Phys.*, 72, 6507.
- COLUSSI, A. J., BENSON, S. W. and HWANG, R. J. (1977). *Chem. Phys. Lett.*, 52, 349.
- CONLIN, R. T. and FREY, H. M. (1979). *J.C.S. Faraday Trans. I*, 75, 2556.
- CONLIN, R. T. and FREY, H. M. (1980). *J.C.S. Faraday Trans. I*, 76, 322.
- COX, R. A. and PATRICK, K. (1979). *Int. J. Chem. Kin.*, 11, 635.
- COX, D. M., HALL, R. B., HORSLEY, J. A., KRAMER, G. M., RABINOVITCH, P. and KALDOR, A. (1979). *Science*, 205, 390.
- DAI, H. L., KUNG, A. H. and MOORE, C. B. (1980). *J. Chem. Phys.*, 73, 6124.
- DE HEMPTINNE, X. and DE KEUSTER, D. (1980). *J. Chem. Phys.*, 73, 3170.
- DIEBOLD, G. J., ENGELKE, F., LUBMAN, D. M., WHITEHEAD, J. C. and ZARE, R. N. (1977). *J. Chem. Phys.*, 67, 5407.
- DOVE, J. E., NIP, W. S. and TEITELBAUM, H. 15. *Int. Symp. on Combustion* (The Combustion Institute, Pittsburgh, 1974), p. 903.
- DOVE, J. E. and RAYNOR, S. (1979). *J. Phys. Chem.*, 83, 127.
- DOVE, J. E. and TROE, J. (1978). *Chem. Phys.*, 35, 1.
- DÜBAL, H. R. and QUACK, M. (1980). *Chem. Phys. Lett.*, 72, 342.
- DUDEK, D., GLÄNZER, K. and TROE, J. (1979). *Ber. Bunsenges. Phys. Chem.*, 83, 788.
- DUPERREX, R. and VAN DEN BERGH, H. (1979a). *J. Chem. Phys.*, 71, 3613.
- DUPERREX, R. and VAN DEN BERGH, H. (1979b). *J. Chem. Phys.*, 70, 5672.

- DUPERREX, R. and VAN DEN BERGH, H. (1979c). *Chem. Phys.*, **40**, 275.
- DUPERREX, R. and VAN DEN BERGH, H. (1980). *J. Chem. Phys.*, **73**, 585.
- ELAND, J. H. D., FREY, R., SCHULTE, H. and BREHM, B., (1976). *Int. J. Mass Spectrom. Ion Phys.*, **21**, 209.
- ELAND, J. H. D. and SCHULTE, H. (1975). *J. Chem. Phys.*, **62**, 3835.
- ENDO, H., GLÄNZER, K. and TROE, J. (1979). *J. Phys. Chem.*, **83**, 2083.
- ENNEN, G. and OTTINGER, CH. (1974). *Chem. Phys.*, **3**, 404.
- FAISAL, F. H. M. (1976). *Optics Commun.*, **19**, 404.
- FARANTOS, S. C. and MURRELL, J. N. (1981). *Chem. Phys.*, (in press).
- FELDMAN, D., ZACHARIAS, H. and WELGE, K. H. (1980). *Chem. Phys. Lett.*, **69**, 466.
- FLOWERS, M. C. and HONEYMAN, M. R. (1980). *J.C.S. Faraday Trans. I*, **76**, 2290.
- FLOWERS, M. C., WOLTERS, F. C., BARTON, B. D. and RABINOVITCH, B. S. (1980). *Chem. Phys.*, **47**, 189.
- FORST, W. (1972). *J. Phys. Chem.*, **76**, 342.
- FORST, W. (1979). *J. Phys. Chem.*, **83**, 100.
- FORST, W. and PENNER, A. P. (1980). *J. Chem. Phys.*, **72**, 1435.
- FREUND, S. M. and LYMAN, J. L. (1980). *Chem. Phys. Lett.*, **55**, 435.
- FREY, H. M. and POLTINGER, R. (1978). *J.C.S. Faraday Trans. I*, **74**, 1827.
- FREY, H. M. and WALSH, R. (1978). In: *Gas Kinetics and Energy Transfer*, vol. 3, p. 1. London: The Chemical Society.
- FRIEDMANN, H. (1979). In: *Laser Induced Processes in Molecules* (ed. K. L. Kompa and S. D. Smith), p. 149 Berlin: Springer-Verlag.
- FUSS, W. (1979). *Chem. Phys.*, **36**, 135.
- GAEDTKE, H. and TROE, J. (1975). *Ber. Bunsenges. Phys. Chem.*, **79**, 184.
- GAYNOR, B. J., GILBERT, R. G. and KING, K. D. (1978). *Chem. Phys. Lett.*, **55**, 40.
- GAYNOR, B. J., GILBERT, R. G. and KING, K. (1978). *Chem. Phys. Lett.*, **58**, 591.
- GERLICH, D., NOWOTNY, U., SCHLIER, CH. and TELOY, E. (1980). *Chem. Phys.*, **47**, 245.
- GILBERT, R. G. and KING, K. D. (1980). *Chem. Phys.*, **49**, 367.
- GLÄNZER, K., QUACK, M. and TROE, J. (1977). *16th Symp. Int. Combustion*, 949.
- GOLDEN, D. M. and BENSON, S. W. (1978). In: *Physical Chemistry. An Advanced Treatise*, vol. VII, p. 57. New York: Academic Press.
- GOLDEN, D. M., ROSSI, M. J., BALDWIN, A. C. and BARKER, J. R. (1981). *Acc. Chem. Res.*, **14**, 56.
- GOODMAN, M. F., STONE, J. and DOWNS, D. A. (1976). *J. Chem. Phys.*, **65**, 5052, 5062.
- GOWER, M. C. and BILLMAN, K. W. (1976). *Appl. Phys. Lett.*, **30**, 514.
- GOZEL, P. and VAN DEN BERGH, H. (1981). *J. Chem. Phys.*, **74**, 1724.
- GRAHAM, R. A., WINER, A. M. and PITTS, J. N. (1978). *J. Chem. Phys.*, **68**, 4505.
- GRANT, E. R., SCHULZ, P. A., SUDBO, A. S., SHEN, Y. R. and LEE, Y. T. (1978). *Phys. Rev. Lett.*, **40**, 115.
- GRANT, E. R. and BUNKER, D. L. (1978). *J. Chem. Phys.*, **68**, 628.
- GRAY, S. K., MILLER, W. H., YAMAGUCHI, Y. and SCHAEFER, H. F. (1980). *J. Chem. Phys.*, **73**, 2733.
- GRUNWALD, E. R., DEVER, D. F. and KEEHN, P. M. (1978). *Megawatt Infrared Laser Chemistry*, New York: John Wiley.
- HALL, R. B. and KALDOR, A. (1979). *J. Chem. Phys.*, **70**, 4027.
- HANCOCK, G. (1981). Private communication.
- HARTFORD, A. and TUCCIO, S. A. (1979). *Chem. Phys. Lett.*, **60**, 431.
- HASE, W. L. (1972). *J. Chem. Phys.*, **57**, 730.
- HASE, W. L. (1976). *J. Chem. Phys.*, **64**, 2442.
- HASE, W. L. and BUNKER, D. L. (1973) *QCPE*, **12** (1980), 234.
- HEIDBERG, J., STEIN, H., RIEHL, E. and NESTMANN, A. (1980). *Z. Phys. Chem. N.F.*, **121**, 145.
- HEIDBERG, J., STEIN, H. and RIEHL, E. (1981). In: *Proceedings EPS Conference 'Vibrations at Surfaces', Namur 1980*. New York: Plenum Press: (in press).
- HELLER, D. F. and WEST, G. A. (1980). *Chem. Phys. Lett.*, **69**, 419.
- HIPPLER, H., LUTHER, K. and TROE, J. (1979). *Faraday Disc. Chem. Soc.* **67**, 173.
- HIPPLER, H., LUTHER, K., TROE, J. and WALSH, R. (1978). *J. Chem. Phys.*, **68**, 323.
- HIPPLER, H., TROE, J. and WENDELKEN, H. J. (1981). *J. Chem. Phys.*, (in press).
- HODGKINSON, D. P. and BRIGGS, J. S. (1976). *Chem. Phys. Lett.*, **43**, 451.

- HODGKINSON, D. P. and BRIGGS, J. S. (1977). *J. Phys. B*, *10*, 2583.
- HOLMES, B. E. and SETSER, D. W. (1980). In: *Physical Chemistry of Fast Reactions* (ed. I. W. M. Smith), vol. 3. New York: Wiley.
- HOYERMANN, K. and SIEVERT, R. (1979). *Ber. Bunsenges. Physik. Chem.*, *83*, 933.
- HUDGENS, J. W., DURANT, J. L., BOGAN, D. J. and COVELESKIE, R. A. (1979). *J. Chem. Phys.*, *70*, 5906.
- HUIE, R. E., HERRON, J. T., BRAUN, W. and TSANG, W. (1978). *Chem. Phys. Lett.*, *56*, 193.
- ISENOR, N. R. and RICHARDSON, M. C. (1971). *Appl. Phys. Lett.*, *18*, 225.
- ISENOR, N. R., MERCHANT, V., HALLSWORTH, R. S. and RICHARDSON, M. C. (1973). *Can. J. Phys.*, *51*, 1281.
- ISHIKAWA, YO-ICHI, KURIHARA, O., NAKANE, R. and ARAI, S. (1980). *Chem. Phys.*, *52*, 143.
- JASINSKI, J. M. and BRAUMAN, J. I. (1980). *J. Chem. Phys.*, *73*, 6191.
- JASINSKI, J. M., ROSENFELD, R. N., GOLDEN, D. M. and BRAUMAN, J. I. (1979). *J. Amer. Chem. Soc.*, *101*, 2259.
- JOHNSON, C. A. F. and WRIGHT, H. J. (1980). *J. Chem. Soc. Faraday Trans. II*, *76*, 1409.
- JUST, TH., ROTH, P. and DAMM, R. (1977). *16th Int. Symp. on Combustion* (The Combustion Institute, Pittsburgh), p. 961.
- JUST, TH. and TROE, J. (1980). *J. Phys. Chem.*, *84*, 3068.
- KALDOR, A., HALL, R. B., COX, D. M., HORSLEY, J. A., RABINOVITCH, P. and KRAMER, G. M. (1979). *J. Am. Chem. Soc.*, *101*, 4465.
- KARNY, Z., GUPTA, A., ZARE, R. N., LIN, S. T., NIEMAN, J. and RONN, A. M. (1979). *Chem. Phys.*, *37*, 15.
- KATO, S. and MOROKUMA, K. (1980). *J. Chem. Phys.*, *73*, 3900.
- KECK, J. C. and CARRIER, G. (1965). *J. Chem. Phys.*, *43*, 2284.
- KECK, J. C. and KALELKAR, A. (1968). *J. Chem. Phys.*, *49*, 3211.
- KELLEY, D. F., BARTON, B. D., ZALOTAI, L. and RABINOVITCH, B. S. (1979). *J. Chem. Phys.*, *71*, 538.
- KELLEY, D. F., KASAI, T. and RABINOVITCH, B. S. (1980b). *J. Chem. Phys.*, *73*, 5611.
- KELLEY, D. F., ZALOTAI, L. and RABINOVITCH, B. S. (1980a). *Chem. Phys.*, *46*, 379.
- KIM, M. S. and DUMBAR, R. C. (1979). *Chem. Phys. Lett.*, *60*, 247.
- KING, K., GOLDEN, D. M., SPOKES, G. N. and BENSON, S. W. (1971). *Int. J. Chem. Kinet.*, *3*, 411.
- KING, D. S. and STEPHENSON, J. C. (1979). *Chem. Phys. Lett.*, *66*, 33.
- KLAIS, O., ANDERSON, P. C. and KURYLO, M. J. (1980). *Int. J. Chem. Kin.*, *12*, 469.
- KLEIN, I. E. and RABINOVITCH, B. S. (1978). *Chem. Phys.*, *35*, 439.
- KLEIN, I. E., RABINOVITCH, B. S. and JUNG, K. H. (1977). *J. Chem. Phys.*, *67*, 3833.
- KLEINDIENST, T., BURKHOLDER, J. B. and BAIR, E. J. (1980). *Chem. Phys. Lett.*, *70*, 117.
- KLEINERMANN, C. (1978). *Bericht 12/1978*, Max-Planck-Institut für Strömungsforschung, Göttingen, ISSN 0436—1199.
- KLEINERMANN, C. and WAGNER, H. GG. (1977). *Ber. Bunsenges. Physik. Chem.*, *81*, 1283.
- KLOTS, C. E., (1971). *J. Phys. Chem.*, *75*, 1526.
- KLOTS, C. E. (1972). *Z. Naturforsch.*, *A 27*, 553.
- KLOTS, C. E. (1976). *J. Chem. Phys.*, *64*, 4269.
- KOLKE, T. and GARDINER, W. C. (1980). *J. Phys. Chem.*, *84*, 2005.
- KOLODNER, P., WINTERFELD, C. and YABLONOVITCH, E. (1977). *Opt. Commun.*, *20*, 119.
- KONDO, O., SAITO, K. and MURAKAMI, I. (1980). *Bull. Chem. Soc. Japan*, *53*, 2133.
- KOREN, G., OPPENHEIM, U. P., TAL, D., OKON, M. and WEIL, R. (1976). *Appl. Phys. Lett.*, *29*, 40.
- KRAJNOVITCH, D. J., GIARDINI-GUIDONI, A., SUDBO, A. S., SCHULZ, P. A., SHEN, Y. R. and LEE, Y. T. (1979). In: *Laser Induced Processes in Molecules* (ed. K. L. Kompa and S. D. Smith), p. 176. Berlin: Springer-Verlag.
- KUDRIAVTSEV, YU. A. and LETOKHOV, V. S. (1980). *Chem. Phys.*, *50*, 353.
- LAHMANI, F., LARDEUX, C. and SOLGADI, D. (1980). *J. Chem. Phys.*, *73*, 4433.
- LAWRANCE, W. D., GILBERT, R. G. and KING, K. D. (1980). *Chem. Phys. Lett.*, *76*, 113.
- LEE, J. H., MICHAEL, J. V., PAYNE, W. A. and STIEF, L. J. (1978). *J. Chem. Phys.*, *68*, 1817.
- LEIBA, A. and OREF, I. (1979). *J.C.S. Faraday Trans. I*, *75*, 2694.
- LESIECKI, M. L. and GUILLORY, W. A. (1977). *J. Chem. Phys.*, *66*, 4317.
- LETOKHOV, V. S. and MOORE, B. S. (1976). *Sov. J. Quantum Electron.*, *6*, 129, 259.
- LIFSHITZ, CH. (1978). In: *Adv. Mass Spectrom.*, *7A*, p. 3.

- LIN, S. T., LEE, S. M. and RONN, A. M. (1978). *Chem. Phys. Lett.*, **53**, 260.
- LIN, Y. N. and RABINOVITCH, B. S. (1968). *J. Phys. Chem.* **72**, 1726.
- LIN, Y. N. and RABINOVITCH, B. S. (1970). *J. Phys. Chem.*, **74**, 3151.
- LUTHER, K. and TROE, J. (1979). *17th Int. Symp. on Combustion* (The Combustion Institute, Pittsburgh), p. 535.
- LUTHER, K. and WIETERS, W. (1980). *J. Chem. Phys.*, **73**, 4131.
- LUU, S. H. and TROE, J. (1974). *Ber. Bunsenges. Phys. Chem.*, **78**, 766.
- LYMAN, J. L. (1977). *J. Chem. Phys.*, **67**, 1868.
- LYMAN, J. L. and ROCKWOOD, S. D. (1976). *J. Appl. Phys.*, **47**, 595.
- LYMAN, J. L., ROCKWOOD, S. D. and FREUND, S. M. (1977). *J. Chem. Phys.*, **67**, 4545.
- LYMAN, J. L., QUIGLEY, G. P. and JUDD, O. P. (1980). In: *Multiple Photon Excitation and Dissociation of Polyatomic Molecules* (ed. C. Cantrell), Berlin, Heidelberg: Springer.
- MACPHERSON, M. T. and SIMONS, J. P. (1979). *J. Chem. Soc. Faraday Trans. II*, **75**, 1572.
- MAKAROV, A. A., MAKAROV, G. N., PURETZKY, A. A. and TYAKHT, V. V. (1980). *Appl. Phys.*, **23**, 391.
- MALONEY, K. M. and RABINOVITCH, B. S. (1969). *J. Phys. Chem.*, **73**, 1642.
- MARLING, J. B., HERMANN, I. P. and SCOTT, J. T. (1980). *J. Chem. Phys.*, **72**, 5603.
- MCALPINE, R. D., EVANS, D. K. and MCCLUSKY, F. K. (1979). *Chem. Phys.*, **39**, 263.
- MCCLUSKY, R. J. and CARR, R. W. (1978). *J. Phys. Chem.*, **82**, 2637.
- MEISELS, G. G., VERBOOM, G. M. L., WEISS, M. J. and HSIEH, T. C. (1979). *J. Amer. Chem. Soc.*, **101**, 7189.
- MICHAEL, J. V., NOVA, D. F., BORKOWSKI, R. P., PAYNE, W. A. and STIEFF, L. J. (1980). *J. Chem. Phys.*, **73**, 6108.
- MILLER, W. H. (1979). *J. Amer. Chem. Soc.*, **101**, 6810.
- MILLER, S. S., DEFORD, D. D., MARKS, T. J. and WEITZ, E. (1979). *J. Am. Chem. Soc.*, **101**, 1036.
- MOLINA, M. J., MOLINA, L. T. and ISHIWATA, T. (1980). *J. Phys. Chem.*, **84**, 3100.
- MUKAMEL, S. and JORTNER, J. (1976). *J. Chem. Phys.*, **65**, 5204.
- MURRELL, J. N. (1978). In: *Gas Kinetics and Energy Transfer*, vol. 3, p. 200. London: The Chemical Society.
- NAAMAN, R. and ZARE, R. N. (1979). *Faraday Disc. Chem. Soc.*, **67**, 242.
- NEILSON, P. V., BOWERS, M. T., CHAU, M., DAVIDSON, W. R. and AUE, D. H. (1978). *J. Amer. Chem. Soc.*, **100**, 3649.
- NÈVE DE MEVERGNIES, M. and DEL MARMOL, P. (1980). *J. Chem. Phys.*, **73**, 3011.
- NESBET, R. K. (1981). In: *Theoretical Chemistry, Advances and Perspectives* (ed. D. Henderson), vol. 6B. New York: Academic Press.
- NIKITIN, E. E. (1959). *Zhurnal Fizicheskoy Khimii*, **33**, 573.
- NIKITIN, E. E. (1966). *Theory of Thermally Induced Gas Phase Reactions*. Indiana University Press, Bloomington.
- NITZAN, A. and JORTNER, J. (1979). *Chem. Phys. Lett.*, **60**, 1.
- NOID, D. W., KOSZYKOWSKI, M. L., MARCUS, R. A. and MCDONALD, J. D. (1977). *Chem. Phys. Lett.*, **51**, 540.
- NORDHOLM, S. (1978). *Chem. Phys.*, **29**, 55 (1978).
- NORDHOLM, S., FREASIER, B. C. and JOLLY, D. L. (1977). *Chem. Phys.*, **25**, 433.
- OKADA, K., TSCHUIKOW-ROUX, E. and EVANS, P. J. (1980). *J. Phys. Chem.*, **84**, 467.
- OLMSTEAD, W. N., LEV-ON, M., GOLDEN, D. M. and BRAUMAN, J. I. (1977). *J. Amer. Chem. Soc.*, **99**, 992.
- OREF, I. and RABINOVITCH, B. S. (1977). *Chem. Phys.*, **26**, 385.
- OREF, I. and RABINOVITCH, B. S. (1979). *Acc. Chem. Res.*, **12**, 166.
- OREF, I., SCHUETZLE, D. and RABINOVITCH, B. S. (1971). *J. Chem. Phys.*, **54**, 575.
- OTTINGER, CH. and ZIMMERMANN, S. (1980). *Chem. Phys.*, **53**, 293.
- PACEY, P. D. and WIMALASENA, J. H. (1980a). *J. Phys. Chem.*, **84**, 2221.
- PACEY, P. D. and WIMALASENA, J. H. (1980b). *Chem. Phys. Lett.*, **76**, 433.
- PATRICK, R., PILLING, M. J. and ROGERS, G. J. (1980). *Chem. Phys.*, **53**, 279.
- PENNER, A. P. (1978a). *Mol. Phys.*, **35**, 357.
- PENNER, A. P. (1978b). *Mol. Phys.*, **36**, 1373.
- PENNER, A. P. and FORST, W. (1977). *J. Chem. Phys.*, **67**, 529.
- PERT, G. J. (1973). *IEEE J. of Quantum Electron.*, **9**, 435.

- PLUM, C. N. and HOUSTON, P. L. (1980). *Chem. Phys.*, **45**, 159.
- POPPE, D. (1980a). *Chem. Phys.*, **45**, 371.
- POPPE, D. (1980b). *Chem. Phys. Lett.*, **75**, 264.
- POWIS, I. (1979). *J.C.S. Faraday Trans. II*, **75**, 1294.
- PRATT, G. L. and ROGERS, D. (1979a). *J.C.S. Faraday Trans. I*, **75**, 1089.
- PRATT, G. L. and ROGERS, D. (1979b). *J.C.S. Faraday Trans. I*, **75**, 1101.
- PRATT, G. L. and ROGERS, D. (1979c). *J.C.S. Faraday Trans. I*, **75**, 2688.
- PRATT, G. L. and ROGERS, D. (1980). *J.C.S. Faraday Trans. I*, **76**, 1694.
- PRITCHARD, H. O. and LABIB, N. I. (1976). *Can. J. Chem.*, **54**, 329.
- PURETZKY, A. A. and SCHRÖDER, H. (1981). *Abstr. Eur. Conf. Atom. Phys.*, Heidelberg, 1981.
- QUACK, M. (1978). *J. Chem. Phys.*, **69**, 1282.
- QUACK, M. (1979a). *Chem. Phys. Lett.*, **65**, 140.
- QUACK, M. (1979b). *Ber. Bunsenges. Phys. Chem.*, **83**, 757.
- QUACK, M. (1979c). *J. Phys. Chem.*, **83**, 150.
- QUACK, M. (1979d). *J. Chem. Phys.*, **70**, 1069.
- QUACK, M. (1979e). *Ber. Bunsenges. Phys. Chem.*, **83**, 1287.
- QUACK, M. (1980a). *Chem. Phys.*, **51**, 353.
- QUACK, M. (1981a). *Ber. Bunsenges. Phys. Chem.*, **84**, 318.
- QUACK, M. (1981b). *Adv. Chem. Phys.*, (in press).
- QUACK, M. (1981c). *Il Nuovo Cimento (Suppl.)*, **63b**, 358.
- QUACK, M. and TROE, J. (1974). *Ber. Bunsenges. Phys. Chem.*, **78**, 240.
- QUACK, M. and TROE, J. (1975). *Ber. Bunsenges. Phys. Chem.*, **79**, 469.
- QUACK, M. and TROE, J. (1976). *Ber. Bunsenges. Phys. Chem.*, **80**, 1140.
- QUACK, M. and TROE, J. (1977). *Ber. Bunsenges. Phys. Chem.*, **81**, 329.
- QUACK, M. and TROE, J. (1977). In: *Gas Kinetics and Energy Transfer* vol. 2. (ed. P. G. Ashmore and R. J. Donovan), London: The Chemical Society.
- QUACK, M. and TROE, J. (1981). In: *Theoretical Chemistry, Advances and Perspectives*, **6B**, 199 (ed. D. Henderson) New York: Academic Press.
- QUACK, M. and VAN DEN BERGH, H. (1981). To be published.
- QUACK, M., HUMBERT, P. and VAN DEN BERGH, H. (1980). *J. Chem. Phys.*, **73**, 247.
- QUICK, C. R. and WITTIG, C. (1978). *J. Chem. Phys.*, **69**, 4201.
- RAVISHANKARA, A. R., EISELE, F. L. and WINE, P. H. (1980). *J. Chem. Phys.*, **73**, 247.
- REDDY, K. V. and BERRY, M. J. (1977). *Chem. Phys. Lett.*, **52**, 111.
- REDDY, K. V. and BERRY, M. J. (1979a). *Faraday Disc. Chem. Soc.*, **67**, 188.
- REDDY, K. V. and BERRY, M. J., (1979b). *Chem. Phys. Lett.*, **66**, 223.
- REID, R. C., PRAUSNITZ, I. M. and SHERWOOD, T. K. (1980). *The Properties of Gases and Liquids*, 3rd Edition. New York: McGraw-Hill Co.
- RICE, S. A. (1975). In: *Excited States* (ed. E. C. Lim). New York: Academic Press.
- RICHMOND, G. and SETSER, D. W. (1980). *J. Phys. Chem.*, **84**, 2699.
- RIMPEL, G. and JUST, TH. (1981). *Ber. Bunsenges. Phys. Chem.*, (in press).
- ROBINSON, P. J. and HOLBROOK, K. A. (1972) *Theory of Unimolecular Reactions*. London: Wiley.
- ROBINSON, P. J. (1975). In: *Reaction Kinetics*, vol. 1, p. 93. London: The Chemical Society.
- ROSENFELD, R. N., JASINSKI, J. M. and BRAUMAN, J. I. (1979). *J. Chem. Phys.*, **71**, 1030.
- ROSENFELD, R. N., JASINSKI, J. M. and BRAUMAN, J. I. (1980). *Chem. Phys. Lett.*, **71**, 400.
- ROSSI, M., BARKER, J. R. and GOLDEN, D. M. (1979). *Chem. Phys. Lett.*, **65**, 523.
- RYAN, P. W., BLAKELEY, C. R., VESTAL, M. L. and FUTRELL, J. H. (1980). *J. Phys. Chem.*, **84**, 561.
- RYNBRAND, J. D. and RABINOVITCH, B. S. (1970). *J. Phys. Chem.*, **74**, 4175.
- RYNBRAND, J. D. and RABINOVITCH, B. S. (1971). *J. Phys. Chem.*, **75**, 2164.
- SAZONOV, V. N. (1978). *Sov. J. Quantum Electron.* **8**, 324.
- SANDER, S. P., RAY, G. W. and WATSON, R. T. (1980). *J. Phys. Chem.*, (in press).
- SANDER, S. P. and WATSON, R. T. (1980). *J. Phys. Chem.*, **84**, 1664.
- SANTAMARIA, J., BUNKER, D. L. and GRANT, E. R. (1978). *Chem. Phys. Lett.*, **56**, 170.
- SCHEK, I. and JORTNER, J. (1979). *J. Chem. Phys.*, **70**, 3016.
- SCHNEIDER, F. W. and RABINOVITCH, B. S. (1962). *J. Amer. Chem. Soc.*, **84**, 4215.
- SCHULZ, P. A., SUDBO, A. S., KRAJNOVITCH, D. J., KWOK, H. S., SHEN, Y. R. and LEE, Y. T. (1979). *Ann. Rev. Phys. Chem.*, **30**, 379.

- SCHULZ, P. A., SUDBO, A. S., GRANT, E. R., SHEN, Y. R. and LEE, Y. T. (1980). *J. Chem. Phys.*, **72**, 4985.
- SERAUSKAS, R. V. and SCHLAG, E. W. (1965). *J. Chem. Phys.*, **42**, 3009; **43**, 898.
- SERAUSKAS, R. V. and SCHLAG, E. W. (1966). *J. Chem. Phys.*, **45**, 3706.
- SHOBATAKE, K., LEE, Y. T. and RICE, S. A. (1973). *J. Chem. Phys.*, **59**, 1435.
- SIBENER, S. J., BUSS, R. J., CASAVECCHIA, P., HIROOKA, T. and LEE, Y. T. (1980). *J. Chem. Phys.*, **72**, 4341.
- SIMONS, J. P. (1977). In: *Gas Kinetics and Energy Transfer* (ed. P. G. Ashmore and R. J. Donovan), vol. 2, p. 58. London: The Chemical Society (Specialist Periodical Report).
- SLATER, N. B. (1959). *Theory of Unimolecular Reactions*. London: Methuen.
- STACE, A. J. and MURRELL, J. N. (1978). *J. Chem. Phys.*, **68**, 3028.
- STAFAST, H., SCHMID, W. E. and KOMPA, K. L. (1977). *Optics Commun.*, **21**, 121.
- STAFAST, H., OPITZ, J. and HUBER, J. R. (1981). *Chem. Phys.*, **56**, 63.
- STEIN, S. E. and RABINOVITCH, B. S. (1973). *J. Chem. Phys.*, **58**, 2348.
- STONE, J. and GOODMAN, M. F. (1978). *Phys. Rev. A*, **18**, 2618, 2642.
- STONE, J. and GOODMAN, M. F. (1979). *J. Chem. Phys.*, **71**, 408.
- STONE, J., THIELE, E. and GOODMAN, M. F. (1980). *J. Chem. Phys.*, **73**, 2259.
- SUDBO, A. S., SCHULZ, P. A., KRAJNOVITCH, D. J., LEE, Y. T. and SHEN, Y. R. (1979). *Optics Letters*, **4**, 219.
- SWORSKI, T. J., HOCHANADEL, C. J. and OGREN, P. J. (1980). *J. Phys. Chem.*, **84**, 129.
- TARDY, D. C. and RABINOVITCH, B. S. (1966). *J. Chem. Phys.*, **45**, 3720.
- TARDY, D. C. and RABINOVITCH, B. S. (1968). *J. Chem. Phys.*, **48**, 1282.
- TARDY, D. C. and RABINOVITCH, B. S. (1977). *Chem. Rev.*, **77**, 369.
- TIEE, J. J. and WITTIG, C. (1978). *J. Chem. Phys.*, **69**, 4756.
- TRENWITH, A. B. (1979). *J.C.S. Faraday Trans. I*, **75**, 614.
- TROE, J. (1973). *Ber. Bunsenges. Phys. Chem.*, **77**, 665.
- TROE, J. (1975a). In: *Physical Chemistry, an Advanced Treatise* (ed. W. Jost), vol. VI B. New York: Academic Press.
- TROE, J. (1975b). In: *International Review of Science*, (ed. D. Herschbach), London: Butterworths.
- TROE, J. (1977a). *J. Chem. Phys.*, **66**, 4745.
- TROE, J. (1977b). *J. Chem. Phys.*, **66**, 4758.
- TROE, J. (1978). *Annu. Rev. Phys. Chem.*, **29**, 223.
- TROE, J. (1979). *J. Phys. Chem.*, **83**, 114.
- TROE, J. (1980a). *Ber. Bunsenges. Phys. Chem.*, **84**, 829.
- TROE, J. (1980b). *J. Chem. Phys.*, **73**, 3205.
- TROE, J. (1981). *J. Chem. Phys.*, (in press).
- TROE, J. and WAGNER, H. GG., (1966). In: *Recent Advances in Aerothermochemistry*, p. 21. Oslo: AGARD.
- TROE, J. and WAGNER, H. GG., (1967). *Ber. Bunsenges. Phys. Chem.*, **71**, 937.
- TROE, J. and WIETERS, W. (1979). *J. Chem. Phys.*, **71**, 3931.
- TSANG, W. (1978). *Int. J. Chem. Kinet.* **10**, 821.
- TSAI, B. P., WERNER, A. S. and BAER, T. (1975). *J. Chem. Phys.*, **62**, 4384.
- TSAO, J. Y., BLACK, J. G., YABLONOVITCH, E. and BURAK, I. (1980). *J. Chem. Phys.*, **73**, 2076.
- VAN DEN BERGH, H., BENOIT-GUYOT, N. and TROE, J. (1977). *Int. J. Chem. Kinet.*, **9**, 223.
- VIGGIANO, A. A., DAVIDSON, J. A., FEHSENFELD, F. C. and FERGUSON, E. E. (1981). *J. Chem. Phys.*, (in press).
- VON HELLFELD, A., FELDMANN, D. and WELGE, K. H. (1979). *Optics Commun.*, **30**, 193.
- WAAGE, E. V. and RABINOVITCH, B. S. (1970). *Chem. Rev.*, **70**, 377.
- WAAGE, E. V. and RABINOVITCH, B. S. (1972). *J. Chem. Phys.*, **76**, 1695.
- WAITE, B. A. and MILLER, W. H. (1980). *J. Chem. Phys.*, **73**, 3713.
- WERNER, A. S. and BAER, R. (1975). *J. Chem. Phys.*, **62**, 2900.
- WESTBOOK, C. K. and DRYER, F. L. (1981). *18th Int. Symp. on Combustion* (The Combustion Institute, Pittsburgh).
- WINE, P. H., KREUTTER, N. M. and RAVISHANKARA, A. R. (1979). *J. Chem. Phys.*, **83**, 3191.
- WOLF, R. J. and HASE, W. L. (1979). *J. Chem. Phys.*, **71**, 2911.
- WOLF, R. J. and HASE, W. L. (1980a). *J. Chem. Phys.*, **72**, 316.

- WOLF, R. J. and HASE, W. L. (1980b). *J. Chem. Phys.*, *73*, 3779.
- WOODIN, R. L., BOMSE, D. S. and BEAUCHAMP, J. L. (1979). *Chem. Phys. Lett.*, *63*, 630.
- WORRY, G. and MARCUS, R. A. (1977). *J. Chem. Phys.*, *67*, 1336.
- YAHAV, G. and HAAS, Y. (1978). *Chem. Phys.*, *35*, 41.
- YAHAV, G., HAAS, Y., CARMELI, B. and NITZAN, A. (1980). *J. Chem. Phys.*, *72*, 3410.
- YAU, A. W. and PRITCHARD, H. O. (1978). *Can. J. Chem.*, *56*, 1389.
- YU, M. H., REISLER, H., MANGIR, M. and WITTIG, C. (1979). *Chem. Phys. Lett.*, *62*, 439.
- ZACHARIAS, H., GEILHAUPT, M., MEIER, K. and WELGE, K. H. (1981). *J. Chem. Phys.*, *74*, 218.
- ZARE, R. N. (1977). *Scientific American*, *236*, 86.
- ZELLNER, R. (1978). *Ber. Bunsenges. Phys. Chem.*, *82*, 1172.