Theory of unimolecular reactions induced by monochromatic infrared radiation

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A theory of unimolecular reactions induced by coherent, monochromatic infrared radiation (URIMIR) in the absence of collisions is presented. It is shown that the set of first order linear differential equations for the amplitudes of molecular *states* (Schrödinger equation) can be reduced, under specified conditions, to a much smaller set of first order linear differential equations for the coarse grained populations of *levels* for polyatomic molecules (master equation). Four limiting situations are identified in which such linear rate equations provide a reasonable approximation. Rate coefficients are obtained as a function of spectroscopic parameters (energy levels and transition moments). Solutions for the master equations are given as a function of time and at steady-state. Simple limiting cases (Strong Field Limit, Weak Field Limit, Reaction Threshold Bottleneck, etc.) are identified and very simple rate expressions are obtained for these cases. A complete statistical mechanical theory of URIMIR is formulated and the computational approaches for the quantitative treatment for any molecule are summarized. Predictions are made concerning the dependence of the unimolecular rate constant and product (state) distributions upon radiation intensity. In particular at high intensities a less than proportional increase of the rate constant with intensity is predicted. The possibility of specific pumping of reaction paths with high energy thresholds is discarded. Comparison with thermal unimolecular reactions shows that collisionless URIMIR are quite different in all respects. Fundamentally these differences are traced to the fact that the *underlying* molecular distribution functions are different. They are Boltzmann distributions for thermal reactions and "microcanonical" [without $\exp(-E/kT)$] in URIMIR. Although real distribution functions are still different in general, the *underlying* distribution functions often dominate the dynamical behavior.

I. INTRODUCTION

In the early days of the theory of unimolecular reactions it was a common view that they were induced by the interaction of isolated molecules with the radiation field.[1] This "radiation theory of chemical action" had been developed because of the supposedly experimentally established fact that unimolecular reactions were independent of total gas pressure. As F. A. Lindemann pointed out in a very brief discussion remark,[1] the *apparent* independence of the reaction rate upon the total gas pressure can be explained by assuming a two-step mechanism:

$$A + M \rightleftharpoons A^* + M \tag{1.1}$$

$$A^* \rightarrow \text{products} \tag{1.2}$$

with a finite intrinsic lifetime for the excited molecules A*. Lindemann *predicted* a dependence of the unimolecular rate constant,

$$k_{\text{uni}} = (-d\ln([A] + [A^*])/dt) , \tag{1.3}$$

upon the total gas pressure (or [M]). This prediction was later verified experimentally.

Figure 1 gives a schematic view of our present understanding of *thermal* unimolecular reactions of polyatomic molecules, which is a somewhat more complicated version of the Lindemann mechanism. The multistep excitation mechanism includes transitions between all molecular states, which are stable below the dissociation threshold and can dissociate with rate constants k_i above the threshold (assuming exponential decay). The populations p_i of molecular states move according to the rate equation (in matrix notation),

$$\dot{\mathrm{p}} = \mathrm{K}\mathrm{p} . \tag{1.4}$$

(The point denotes derivation with respect to time.) The off-diagonal matrix elements are given by

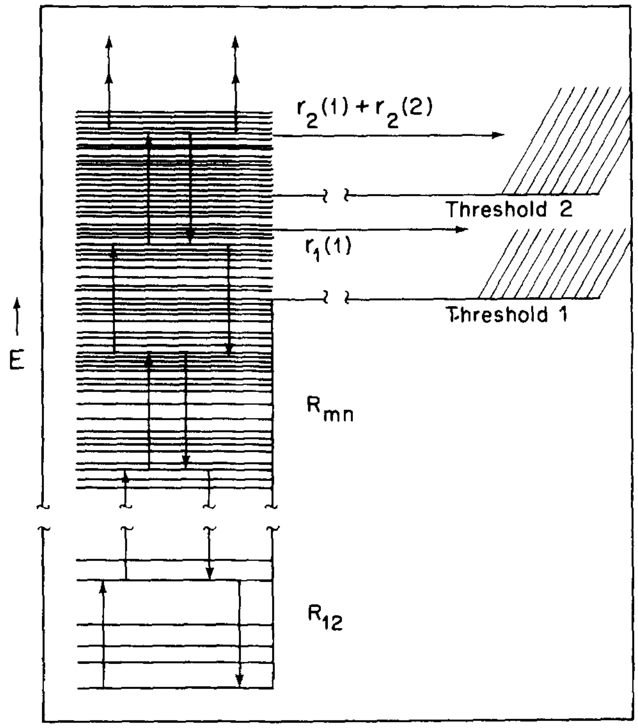

FIG. 1. A common scheme for the multistep excitation in thermal unimolecular reactions and URIMIR. R_{mn} and r_i symbolize rate processes of an unspecified nature.

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$$k_{fi}=\left(\frac{8kT}{\pi\mu}\right)^{1/2}\int_0^\infty\left(\frac{E}{kT}\right)\sigma_{fi}(E)\exp\left(\frac{-E}{kT}\right)\left(\frac{dE}{kT}\right)[\mathrm{M}]\,, \tag{1.5}$$

if the translational motions are thermalized in an inert heat bath. The σ_{fi} are the inelastic cross sections in collisions of reactant and heat bath molecules. The diagonal matrix elements are

$$-K_{ii}=\sum_{j\neq i}K_{ji}+k_i\,. \tag{1.6}$$

Equation (4) is a valid approximation neglecting radiation. The solutions are

$$\mathbf{p}(t)=\mathbf{Y}(t,t_0)\mathbf{p}(t_0)\,, \tag{1.7}$$

with

$$\mathbf{Y}(t,t_0)=\exp[\mathbf{K}(t-t_0)]\,. \tag{1.8}$$

The parts of a theoretical treatment of thermal unimolecular reactions can be formulated as

(i) Determination of the properties (energies ϵ_i and lifetimes) of molecular states i. This concerns the solution of the Schrödinger equation for isolated molecules (The *"diagonal"* problem in terms of an appropriate molecular Hamiltonian).

(ii) Determination of collisional cross sections σ_{fi} or rates K_{fi} (The "off-diagonal" coupling or energy transfer problem).

(iii) The solution of the kinetic equation of motion, which is a *master equation* (1.4) under the conditions specified. Difficulties arise because the σ_{fi} and the ϵ_i and k_i are difficult to obtain and because of the huge size of the matrices for polyatomic systems. The theory of thermal unimolecular reactions[2,3] has been concerned with various approximation schemes for the three parts of the problem and has, on the whole (and on a variety of levels of sophistication), been quite successful in qualitatively and quantitatively explaining and predicting experiments (i.e., k_{uni} as a function of specified experimental parameters). The reason for the possibility of neglecting *thermal* radiation in the process is the relative weakness of the interaction compared to collisional activation at normally available pressures. On the other hand true photochemical reactions have always (see, e.g., Ref. 1) been known too, using radiation which is not in thermal equilibrium with the reactive molecules. These reactions follow a mechanism which is quite different from the one shown in Fig. 1. Usually we have a one step excitation above the reaction threshold, involving excited electronic states, and subsequent reactive processes (eventually competing with collisions).[4]

In recent years photochemical reactions induced by strong ir-laser radiation have been observed, which follow a mechanism quite different from conventional photochemistry.[5-19] Indeed, the absorption of many photons is needed for reaction to occur and the excitation process follows a multistep mechanism as shown in Fig. 1. We leave the question of the *nature* of the rate processes R_{mn} open, at present, but we anticipate some similarities to thermal reactions. Although in many experiments collisions play a considerable but often ill defined role, it has been proven that unimolecular reactions can be induced by ir-lasers under molecular beam conditions where collisions do not interfere seriously with the radiative process.[18] It is this *collisionless* process which is the main concern of the present paper. The process has also been shown to be isotopically selective in certain cases.[7,8,12] In the absence of collisions the latter fact would appear to be rather less surprising, in view of the possibility of selectively pumping rovibrational transitions for specific isotopomeres with a highly monochromatic radiation.

Due to the recent discovery of unimolecular reactions induced by monochromatic infrared radiation (we shall use the acronym URIMIR hereafter), little theoretical work is available compared to thermal reactions. We should mention in particular the pioneer work by Bloembergen, Cantrell, and Larsen,[20-22] Mukamel and Jortner,[23] and Stone, Goodman, and Dows.[24] These authors have been able to explain the possibility of collisionless dissociation, the qualitative dependence upon laser power density and the isotopic selectivity. However, one may find (with apologies to these authors) that none of the proposed treatments is sufficiently general to provide a framework for a complete theory of URIMIR. They do not provide a completely realistic, quantitative description of the excitation process at high levels of molecular excitation, nor do they describe the monomolecular reaction above threshold in a quantitative manner (as would be possible using modern unimolecular rate theory[3]). We shall see below, however, that these treatments are under certain limiting conditions perfectly justified approximations for the computation of the overall dissociation rate and isotopic selectivity (provided that the spectroscopic part of the treatment is done properly[25]). Recently, it has also been proposed to use a simple rate equation of the type (1.4) for URIMIR, with phenomenological rate constants (taken to be essentially free parameters) for photoexcitation, and RRKM[2,26] rate constants for dissociation.[27,66] Although it is not at all self-evident that the use of a master equation (1.4) should be justified for a coherent laser excitation, qualitatively very satisfactory agreement of calculated and measured product translational energy distributions in molecular beam experiments was obtained.[18,27] We shall see that, indeed, the use of a master equation is justified in a limiting situation which is somewhat complementary to the situations covered by the treatments in Refs. 20–22. To do this, we need a more general theory of URIMIR, which is the subject of the present paper.

The logical development follows the one for thermal unimolecular reactions.

(i) The "diagonal" part of the problem is the same as for thermal unimolecular reactions and for (low power, high resolution) molecular spectroscopy. We *do not* start from some "convenient zero order Hamiltonian," but rather from the full molecular Hamiltonian (with certain reservations to be made below).

(ii) The molecular states are coupled by the laser field through the electric dipole interaction (neglecting other terms). This leads to equations of motion of the form

$$i\dot{\mathbf{b}}=\mathbf{H}(t)\mathbf{b}\ , \tag{1.9}$$

where $\mathbf{H}(t)$ may usually be supposed to be complex symmetric and approximately periodic in time

$$\mathbf{H}(t+\tau)=\mathbf{H}(t)\ . \tag{1.10}$$

The amplitudes in Eq. (1.9) are connected to the populations in Eq. (1.4) by

$$b_k b_k^* = p_k\ . \tag{1.11}$$

(iii) Solutions to Eq. (1.9) are considered in Sec. II. They are of the form

$$\mathbf{b}(t)=\mathbf{U}(t,t_0)\mathbf{b}(t_0)\ . \tag{1.12}$$

$\mathbf{U}$ is more difficult to obtain than $\mathbf{Y}$ (Eq. 1.8). We know, however, that Eq. (1.9) is reducible in the sense of Liapunoff.[28] The solution can be formally obtained with the aid of a Liapunoff matrix, satisfying

$$\mathbf{L}(t+\tau)=\mathbf{L}(t)\ , \tag{1.13}$$

and

$$\mathbf{U}=\mathbf{L}\mathbf{X}\ . \tag{1.14}$$

$\mathbf{X}$ satisfies a differential equation with constant coefficients $\mathbf{A}$

$$\dot{\mathbf{X}}=\mathbf{A}\mathbf{X}\ , \tag{1.15}$$

therefore ($t_0\equiv 0$)

$$\mathbf{U}=\mathbf{L}\exp(\mathbf{A}t)\ . \tag{1.16}$$

While this establishes the *form* of the solution, it does not provide an obvious practical method. Approximations will be discussed. We note that the treatment of Refs. 20–22 (and other related treatments) consisted essentially of a rotating wave approximation solution of Eq. (1.9) with only a relatively small number of molecular states being retained explicitly in highly simplified molecular models. A complete solution along these lines including all molecular states is prevented by the size of the problem (easily of the order 10^{10} and more for medium sized polyatomic molecules). Therefore we shall, in Sec. III pay particular attention to *statistical simplifications* arising when many molecular states are coupled. It will be shown in which situations master equations of the form (1.4) and of low order can be derived to be reasonable approximations to Eq. (1.9). Four typical cases will be distinguished and the matrix elements for the corresponding master equations will be connected to molecular (spectroscopic) properties. Model calculations will illustrate the results.

In Sec. IV we shall investigate some dynamical limiting cases which lend themselves to simple approximations. We shall introduce some new concepts in URIMIR (strong field limit, weak field limit, early bottleneck, reaction threshold bottleneck, etc.). Some of these have a correspondence to similar concepts in thermal unimolecular reactions (high pressure limit, low pressure limit, strong collision assumption, etc.) which we shall discuss. However, some differences are also noted. Simple approximation formulas and model calculations are presented. In Sec. V a complete statistical theory of URIMIR is presented, including consideration of all constants of motion, following recent developments in statistical unimolecular rate theory. Finally, in the Conclusion the more important qualitative conclusions and predictions from the present treatment are summarized. Again differences and similarities to thermal unimolecular reactions are noted. A flow chart is given for the approximate computational procedures to follow for a realistic quantitative treatment of URIMIR using results of the present paper and of previous authors.

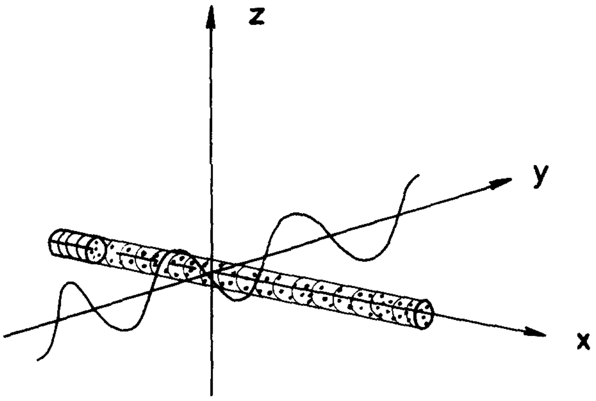


FIG. 2. The ideal experiment: a z-polarized laser beam crossing a molecular beam.

II. EQUATIONS OF MOTION OF MULTILEVEL SYSTEMS (POLYATOMIC MOLECULES) SUBJECT TO STRONG MONOCHROMATIC ir-LASER RADIATION AND METHODS OF SOLUTION

We shall derive here useful equations for the time-dependent populations of molecular states subject to coherent, monochromatic radiation. Great care will be taken to clearly point out the physical assumptions and approximations at each stage.

A. Precise formulation of the idealized problem

We consider a sample of diluted gas molecules subjected to strong ir-laser radiation. For the typical strong fields used in URIMIR the field can be treated classically to a very good approximation, indeed[29–31] (the number of photons per mode is easily 10^{15} and more). We assume the field to be z polarized, monochromatic with frequency ω, and propagating in the y direction (Fig. 2). We then have for the real part of the electric field

$$E_Z(y,t)=\mathrm{Re}\{E_0\exp[i(\omega t-k_\omega y)]\}\ . \tag{2.1}$$

In a molecular beam experiment, as in Ref. 18, which is particularly useful for theoretical idealization, we may furthermore assume that the y component of the molecular velocities is negligible, if the molecular beam propagates in the x direction (see Fig. 2). The local field for each molecule with coordinate y at time t is then given by Eq. (2.1). If the y components of molecular velocities are not zero, we have to introduce a Doppler shift $k_\omega v_y$ (k_ω is the wave number of the field and v_y is the y component of molecular velocities), and eventually average over an ensemble at the end of the calculation. Usually, the beam diameter d is much larger than the wavelength λ (say, typically, $d = 1$ mm) and we would have to average the phases $k_\omega y$ at the end of the calculation. This phase average is of a trivial nature for the present problem and we omit the phases for brevity of notation.

For a more general light source we have to use Eq. (2.2)

$$E_z(y,t) = \mathrm{Re}\left\{\sum_n E_{0n} f_n(y,t) \exp[i(\omega t - k_\omega y + \eta_n)]\right\} . \qquad (2.2)$$

Here the $f_n(y,t)$ are slowly varying over one wavelength or period.[31] Although present day CO_2-laser pulses often vary appreciably during the time scales relevant for URIMIR, and therefore the use of Eq. (2.2) would be necessary for a realistic description, most often the experimental parameters needed for Eq. (2.2) are not sufficiently characterized anyway. Therefore we shall restrict most of our considerations to the more ideal case of Eq. (2.1), with the understanding that this case can be approximated by an appropriate experimental setup *or* that it can be generalized to Eq. (2.2) by means of numerical simulation.

The molecular Hamiltonian can now be represented in the form

$$\hat{H} = \hat{H}_0 + \hat{H}_1 . \qquad (2.3)$$

$\hat{H}_0$ is the molecular Hamiltonian, neglecting the field. For practical purposes we shall exclude the coupling with nuclear spin and with molecular states which are not accessible (isomers separated by high barriers) but we stress that $\hat{H}_0$ is otherwise completely general including all interactions. For $\hat{H}_1$ we can use the electric dipole approximation for the problem at hand,

$$\hat{H}_1 = -\boldsymbol{\mu}\mathbf{E}(y,t) . \qquad (2.4)$$

$\boldsymbol{\mu}$ is the molecular dipole moment operator $(\sum_i e_i \mathbf{r}_i)$.

We consider the "diagonal" molecular problem to be solved (experimentally this is the problem of high resolution molecular spectroscopy[32,33])

$$\hat{H}_0 \varphi_k = \hbar\omega_k \varphi_k . \qquad (2.5)$$

Expanding the time dependent wave function in this basis (Schrödinger picture), we obtain

$$\psi(t) = \sum_k b_k \varphi_k . \qquad (2.6)$$

From the time dependent Schrödinger equation

$$i\hbar\dot{\psi} = \hat{H}\psi , \qquad (2.7)$$

we obtain in a standard way[29] the set of linear equations

$$i\dot{b}_k = \omega_k b_k + \cos\omega t \sum_j V_{kj} b_j . \qquad (2.8)$$

The V_{kj} contain the space dependent part of the electric dipole interaction

$$V_{kj} \equiv -\langle\varphi_k|\boldsymbol{\mu}\mathbf{e}_z|\varphi_j\rangle |E_0|/\hbar . \qquad (2.9)$$

$\mathbf{e}_z$ is the unit vector in the z direction (laboratory frame, Fig. 2).

At low energies these matrix elements can be computed using the usual approximations of molecular spectroscopy[32-34] for the z component of the transition moment $\langle J, \tau, M, v_1, v_2, \ldots |\boldsymbol{\mu}_z| J', \tau', M', v_1', v_2' \ldots\rangle$. In matrix notation Eq. (2.8) becomes

$$i\dot{\mathbf{b}} = \{\mathbf{W} + \cos(\omega t)\mathbf{V}\}\mathbf{b} , \qquad (2.10)$$

which is a special case of Eq. (1.9).

Rewriting (2.7) in the form (2.10) is completely standard. The implicit assumptions concern only the space and time dependence of the field [Eq. (2.1)] and the nonessential use of the electric dipole approximation. Furthermore, the Hamiltonian Eq. (2.3) is not exact due to the classical approximation to the field and to the neglect of interactions with surrounding molecules (collisions). This is justified if collisional transition times and lifetimes for spontaneous infrared emission are long compared to the time scale of the experiment (this is usually the case for URIMIR). In order to properly define the spectrum of $\hat{H}_0$, strictly speaking, we must require that nondegenerate molecular states are well separated with respect to their natural width (say 1 kHz), or collisional width, if collisions are present. Even for polyatomic molecules this is fulfilled up to quite high energies (see Table I). Even if this is not the case, we believe that the treatment remains approximately valid.

We shall allow the diagonal matrix $\mathbf{W}$ to be complex, namely,

$$W_{kk} = \mathrm{Re}(\omega_k) - i\gamma_k/2 , \qquad (2.11)$$

if there is monomolecular decay of an unstable state into a continuum (or quasicontinuum). The real widths γ_k(FWHM) represent effective decay rates. This is not exact if the line shape is not Lorentzian.[29] We shall discuss the actual approximations involved and how to obtain the γ_k in more detail below. We can take furthermore $\mathbf{V}$ to be real symmetric without loss of generality. With all the appropriate reservations in mind, Eq. (2.10) is a valid representation of the physical problem.

For later use we define a statistical matrix $\mathbf{P}$ in the basis φ_k,

$$P_{kj} = b_k b_j^* , \qquad (2.12)$$

with the additional definition

$$p_k = P_{kk} = |b_k|^2 . \qquad (2.13)$$

For real $\mathbf{W}$, $\mathbf{P}$ is a density matrix. Equation (2.10) in particular provides us with the time dependent populations p_k of molecular states. We shall hereafter consider Eq. (2.10) to be a problem of finite (possibly very large) order N. This is reasonable, since in any actual experiment only a finite number of molecular states will have nonvanishing b_k during a finite reaction time and since we have eliminated any continua, using complex energies.[29] The matrices $\mathbf{W}$ and $\mathbf{V}$ can be obtained by solving the time independent Schrödinger equation for the molecule alone. They also can be obtained experimentally, using information from high resolution spectroscopy and molecular beam scattering. Practically, one would of course construct some molecular model using as much information as possible from these sources, from thermochemistry and from bulk kinetics. In the present paper we shall not make any particular model assumptions, but rather investigate the general nature of the solutions of Eq. (2.10) making some very broad assumptions about **W** and **V** and considering dynamical limiting cases.

Surprisingly, in spite of the apparent simplicity of Eq. (2.10) and its formal solution Eqs. (1.12)–(1.16), an actual exact solution presents an exceedingly difficult problem. Already the case with just two coupled equations has a literature of its own, with a variety of techniques available, none of which appears to be very suitable for extension to large N.[35–41] We shall therefore consider realistic approximations below. We note, however, one particular case for which exact solutions can be easily found, namely if **W** and **V** commute. Since W is diagonal it must then be a constant for any general (nonzero) off-diagonal V. The solution of Eq. (2.10) is then

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

$$\mathbf{U}(t,0)=\exp(-i\,\mathbf{W}t)\exp\left[-i\frac{\mathbf{V}}{\omega}\sin(\omega t)\right]\ . \tag{2.14}$$

This involves only diagonalisation of **V**, which is easy to do for moderate order N. We shall use this below for comparison. If **W** were not strictly constant but had a range of values $\ll V_{kj}$ then we could use Eq. (2.14) as a starting point for a perturbation treatment. However, just the opposite is the case for our problem.

B. Weak field approximation (quasiresonant or rotating wave approximation)

We substitute into Eq. (2.10) the interaction picture amplitudes

$$c_k=b_k\exp(i\omega_k t)\ . \tag{2.15}$$

We introduce furthermore the matrix

$$D_{kj}=\omega_k-\omega_j-\omega \text{ for } \omega_k>\omega_j\ ,$$

$$D_{kj}=\omega_k-\omega_j+\omega \text{ for } \omega_k<\omega_j\ . \tag{2.16}$$

We now obtain from Eq. (2.10)

$$i\dot{c}_k=\frac{1}{2}\sum_j V_{kj}c_j\exp(itD_{kj})[1+\exp(\pm 2i\omega t)]\ . \tag{2.17}$$

If D_{kj} and V_{kj} are much smaller than ω, we can estimate the relative contribution from the terms in the parenthesis by integrating over a short time interval $\Delta t \ll V_{kj}^{-1}$, $\Delta t\ll D_{kj}^{-1}$, i.e., $c_j\simeq$const., but with $\Delta t\gg\omega^{-1}$. The average *relative* contribution of the high frequency term is given by

$$|f(\Delta t)|\leqslant(\Delta t\omega)^{-1}\ . \tag{2.18}$$

Since by assumption $\Delta t\omega\gg 1$, we can neglect the high frequency term

$$i\dot{c}_k=\frac{1}{2}\sum_j V_{kj}c_j\exp(itD_{kj})\ . \tag{2.19}$$

The conditions of validity obviously are

$$V_{kj}\ll\omega\ , \tag{2.20}$$

$$D_{kj}\ll\omega\ . \tag{2.21}$$

The first can always be made to be fulfilled by a proper choice of the field strength, whereas the second is strictly *never* fulfilled for a quasicontinuous multilevel spectrum. For the two level case, for which this approximation was originally developed, Eq. (2.21) can be made to be fulfilled by a proper choice of ω.[42] In the multilevel case we can make a further simplification, to the extent that we can neglect transitions far off resonance altogether, by introducing a level scheme with integer n_k

$$\omega_k=n_k\omega+x_k\ , \tag{2.22}$$

$$-\omega/2<x_k<\omega/2\ , \tag{2.23}$$

$$D_{kj}=(n_k-n_j\pm 1)\omega+x_k-x_j\ . \tag{2.24}$$

Equation (2.19) may now be rewritten

$$i\dot{c}_k=\frac{1}{2}\sum_{j,\,|n_k-n_j|=1}V_{kj}c_j\exp[i(x_k-x_j)t]$$

$$+\frac{1}{2}\sum_{j,\,|n_k-n_j|=0;\,2}V_{kj}c_j\exp[i(x_k-x_j)t]\exp(\pm i\omega t)$$

$$+\text{terms with }\exp(\pm mi\omega t);\ m=2,3,\ldots\ . \tag{2.25}$$

Since by definition $|x_k-x_j|\ll\omega$ we find by the same argument as above that the terms with $\exp(\pm mi\omega t)$, ($m=1,2,\ldots$) can be safely neglected. By making the substitution

$$a_k=\exp(-ix_kt)c_k\ , \tag{2.26}$$

we finally obtain the system with constant coefficients ($X_{kk}\equiv x_k$)

$$i\dot{\mathbf{a}}=\{\mathbf{X}+\tfrac{1}{2}\mathbf{V}\}\mathbf{a}\ . \tag{2.27}$$

We note that $p_k(t)=|b_k|^2=|c_k|^2=|a_k|^2$. The matrix $\{\mathbf{X}+\frac{1}{2}\mathbf{V}\}$ may be considered to act as a time independent (possibly complex) "effective Hamiltonian"[23] for the problem. In the definition of a level scheme it is implicitly assumed that the spread of initial energies $\Delta_a\ll\omega$, say, for a thermal situation $kT\ll\hbar\omega$. This third condition for the validity of Eq. (2.27) can however be relaxed by approximately superposing solutions of several independent systems for each of which we have $\Delta_a\ll\omega$.

This so-called rotating wave approximation has been used in one or another form by previous authors treating the problem (see Refs. 20–24 and related papers). We have tried here to clearly point out the conditions of validity, namely Eqs. (2.20) *and* (2.21) [usually in connection with Eqs. (2.22)–(2.25)]. If only Eq. (2.20) is satisfied but not (2.21) the approximation breaks down even for the two-level case. This can be easily seen by comparing with the exact solution for the degenerate case, Eq. (2.14). Equation (2.27) is easily solved,[42] obtaining for the initial condition $p_1(0)=1$

$$p_2^{(a)}(t)=[V^2/(D^2+V^2)]\{\sin[(t/2)(V^2+D^2)^{1/2}]\}^2\ . \tag{2.28}$$

From the exact solution, Eq. (2.14), one obtains

$$p_2^{(b)}(t)=\{\sin[(V/\omega)\sin(\omega t)]\}^2\ . \tag{2.29}$$

For the degenerate case we have $D^2=\omega^2$, and with $V\ll\omega$ we obtain from the rotating wave approximation ($\sin x\simeq x$)

$$p_2^{(a)}(t) \simeq (V^2/\omega^2)[\sin(\omega t/2)]^2 , \qquad (2.30)$$

whereas from the exact solution we get

$$p_2^{(b)}(t) \simeq (V^2/\omega^2)[\sin(\omega t)]^2 , \qquad (2.31)$$

which differs by a factor of 2 in the period of motion. In a multilevel situation there are of course many levels even further off resonance. However, the time averaged populations of these are estimated to be of the order of $[V^2/(D^2+V^2)]$ which becomes very small if D is large. Therefore one does not expect appreciable contributions from those states anyway. This consideration does, however, not apply to true multiphoton resonances.[36] The application of Eq. (2.27) is not justified if there are no appreciable molecular transitions close to the laser frequency. So far in those cases no URIMIR has been observed; usually strong transitions were close to resonance, with V_{kj} in the GHz region, that is much less than ω for a CO_2-laser. Therefore, the use of Eq. (2.27) would appear to be justified in those cases. This can, indeed, be tested by numerical computations (see below). A terminology which stresses the conditions of validity (Eqs. 2.20 and 2.21) would be weak field (i.e., small V_{kj}), quasiresonant (i.e., small D_{kj}) approximation, which we shall use hereafter (with the abbreviation WF-QRA). In order to get a more complete picture, we shall now treat the case of strong fields as well.

C. Short time (strong field) approximation

We reconsider the linear system Eq. (2.10). Let us now assume that all relevant $V_{kj} \gg \omega$. The time evolution of the populations will be appreciable for times which are short compared to a period of the field. We may therefore seek a short time expansion. Expanding $\cos(\omega t)$ and neglecting quadratic and higher terms we simply obtain

$$i\dot{\mathbf{b}} = \{\mathbf{W}+\mathbf{V}\}\mathbf{b} . \qquad (2.32)$$

We can extend the justification for the validity of (2.32) and also obtain a somewhat improved approximation by using the first terms of a Magnus expansion.[43,44] The Magnus expansion solves Eq. (2.10) in the form

$$\mathbf{U}(t, t_0) = \exp(\mathbf{\Omega}) ,$$

$$\mathbf{\Omega} = \sum_{n=0}^{\infty} \mathbf{\Omega}_n . \qquad (2.33)$$

The convergence of this series has been discussed.[43] $\mathbf{\Omega}_n$ contains integrals over commutators of $\mathrm{H}(t)$ of complexity n. The first two terms of Eq. (2.10) are obtained through

$$i\mathbf{\Omega}_0 = \int_{t_0}^{t} dt'\mathrm{H}(t') , \qquad (2.34)$$

$$i\mathbf{\Omega}_1 = -\frac{1}{2}\int_{t_0}^{t} dt''\left\{\int_{t_0}^{t''} dt'[\mathrm{H}(t'), \mathrm{H}(t'')]\right\} , \qquad (2.35)$$

$$i(\mathbf{\Omega}_0 + \mathbf{\Omega}_1) = \mathbf{W}t + \mathbf{V}[\sin(\omega t)/\omega] + \tfrac{1}{2}[\mathbf{W}, \mathbf{V}] \times \{(4/\omega^2)[\sin(\omega t/2)]^2 - t\sin(\omega t)/\omega\} . \qquad (2.36)$$

If we now expand $\sin x \simeq x$, we obtain

$$\mathbf{U}(t, 0) = \exp[-it(\mathbf{W}+\mathbf{V})] . \qquad (2.37)$$

This is the same as the solution of Eq. (2.32). We note that the expansion $\sin x \simeq x$ is somewhat better than $\cos x \simeq 1$, valid for about one-tenth of a period. To this order all $\mathbf{\Omega}_{n\geq 1}$ vanish, i.e., the series terminates after the first term.[43] The use of Eq. (2.36) leads to a further improvement at somewhat longer times. We should mention, however, that such a short time expansion of a "monochromatic" perturbation is somewhat artificial, since in order to define the time zero for the perturbation to within $\delta t \ll \omega^{-1}$ one must have a pulse with a very sharp rise, and therefore very high frequency components as well. In the weak field limit this problem is much less serious. Nevertheless, we think that Eq. (2.37) gives a sufficiently correct qualitative picture of the strong field limiting situation in order to proceed. We note, that in both limiting situations we can reduce the system with time dependent coefficients, Eq. (2.10), to systems with constant coefficients, Eqs. (2.27) and (2.32). This will be our starting point in the next section.

We conclude the present section by noting that Eqs. (2.34)–(2.36) also provide a good starting point for numerical (stepwise) integration of the system (2.10). We find, indeed, that the Magnus expansion is more suitable to be adapted to multilevel systems than any of the previously proposed methods.[36-41] The computational effort of any stepwise integration scheme is further alleviated by the use of Eqs. (1.13)–(1.16), and the simple relationship (2.38)

$$\mathbf{U}(t, t_0) = \mathbf{U}(t, t_1)\mathbf{U}(t_1, t_0) . \qquad (2.38)$$

Therefore we need to integrate only over one period of the field (actually, for symmetry reasons, one-half period is sufficient as well) in order to obtain solutions of Eq. (2.10) at all times, eventhough, at very long times (much longer than one period of the field) errors accumulate in the higher matrix products and no stepwise numerical integration scheme can circumvent this problem. Therefore it must be stressed that an analytical solution of Eq. (2.10) would be extremely desirable. So far none has been available, but also no proof has apparently been given that an exact analytical solution (in the sense of a simple functional expression for L and A in Eq. (1.16) or in the sense of a terminating algorithm) should be impossible.

Before proceeding we should also add a note concerning the actual evaluation of the exponential function of the various matrices needed for **U**. These matrices have been allowed (and required) to be complex (symmetric) in order to obtain finite problems even with decay into continuua. The easiest procedure for computing the exponential function (although not the only one) is the computation of a similarity transformation which diagonalizes the matrix, using standard algorithms.[45] Such a similarity transformation *cannot* always be found unless all elementary divisors are different. This statement is contrary to some statements in the literature of the problem, but it is easily proven by counterexamples. However, the difficulty arises only in rare

TABLE I. Densities of states $\langle\rho(E,J)\rangle$ for three size ranges of polyatomic molecules. $\langle\rho(E,J)\rangle$ is the average number of states in one wave number interval with given total angular momentum, averaged over 200 cm^{-1} (see Ref. 3; 1 cm^{-1} corresponds to a frequency of $2\pi\times 3\times 10^{10}$ Hz).

	O_3		CD_4		$C_2H_2Cl_2$(*cis*)	
E/cm^{-1}	$J=0$	$J=32$	$J=0$	$J=32$	$J=0$	$J=32$
1000	$5\cdot 10^{-3}$	0.03	$1.5\cdot 10^{-2}$	...	0.05	2.6
3000	$1.5\cdot 10^{-2}$	0.35	0.08	...	2.2	110
5000	$5\cdot 10^{-2}$	1.2	0.26	4.2	27.	$1.4\cdot 10^{3}$
8000	0.12	4.4	0.81	35.	454	$2.5\cdot 10^{4}$
10 000	0.19	8.1	2.5	93.	$2.1\cdot 10^{3}$	$1.2\cdot 10^{5}$
15 000	0.35	21.	50.	616.	$4.5\cdot 10^{4}$	$2.6\cdot 10^{6}$
20 000	0.46	29.	306.	$6.6\cdot 10^{3}$	$4.9\cdot 10^{5}$	$2.9\cdot 10^{7}$

exceptions in real physical situations and is easily recognized whenever it occurs.

III. STATISTICAL SIMPLIFICATIONS. MASTER EQUATIONS FOR MULTIPHOTON EXCITATION OF MULTILEVEL SYSTEMS

We have seen in Sec. II that for the limiting cases of weak and strong fields an approximate treatment requires the solution of linear systems with constant coefficients [Eqs. (2.27) and (2.32)]. This is equivalent to solving the Schrödinger equation with a *time independent* perturbation. This is readily done with conventional matrix techniques. For polyatomic molecules this is not a practical solution because of the large size of the matrices involved. We have collected the densities of states $\rho(E,J)$ (see Sec. V and Ref. 3) for some "typical" polyatomic molecules in Table I. The overall size of the matrix to be handled would be about $\sum_J \int_0^{E_0} \rho(E,J) \times dE$. Although of course the ΔJ and other selection rules create many zeroes, the block for *a priori* allowed transitions from $J=32$ to $J=33$ would contain about 10^4 elements for ozone, if we include only states below the rather low-lying dissociation threshold of this molecule. There are many connected blocks of this size which cannot be decoupled. With the most advanced computational techniques it appears to be out of the question to solve such a problem exactly, even for ozone, which would be one of the most favorable examples as far as the size of the problem is concerned.

For the larger molecules the situation is much worse and we are not aware of any molecule for which URIMIR has been observed and for which the matrix problem would be of an order less than 10^{10}. There are two ways to approach the problem. Firstly, one might reduce the effective dimensionality of the problem (by separating out the "ir-active vibration," which is coupled in some—often not so well specified—way to "the other degrees of freedom"). Such model treatments, which have been popular so far, have their merits in explaining some of the qualitative features of URIMIR, but we prefer a second, namely statistical-mechanical approach. Table I suggests, indeed, that even for weak fields, with coupling matrix elements in the GHz region, at each level of excitation a large number of states are coupled for the larger molecules. We are interested in the time evolution of the overall population of such groups of states or "*levels*" in some frequency range Δ, composed of $N=\hbar\rho\Delta$ states. At low field strength such *levels* are naturally introduced by the stepwise excitation, which at least at first sight leads to a problem of low order. More generally we may group all states of similar energy and the same relevant quantum numbers with respect to the dipole selection rules (J, M, parity etc., see Sec. V) into one "level."

If a linear rate law were valid for the individual *states* [Eq. (1.4)] we could sum (average) over final (initial) states in each level and obtain the simpler equation

$$\dot{\bar{\mathbf{p}}}=\bar{\mathbf{K}}\bar{\mathbf{p}}\ , \tag{3.1}$$

where $\bar{\mathbf{p}}$ is a smaller vector given by

$$p_K=\sum_{l=1}^{N_K} p_{l(K)} \tag{3.2}$$

and $\bar{\mathbf{K}}$ by

$$K_{IJ}=N_J^{-1}\sum_{i=1}^{N_I}\sum_{j=1}^{N_J}K_{ij(IJ)}\ . \tag{3.3}$$

Hereafter we shall drop the bar over the averaged $\bar{\mathbf{K}}$ and $\bar{\mathbf{p}}$ and we will use capital indices for *levels*. Equations (3.1)–(3.3) are known to be good approximations to Eq. (1.4) if the K_{ij} are "reasonably" distributed. For incoherent excitation with "white" light one may actually use Eqs. (3.1)–(3.3) directly, using the Einstein coefficients for stimulated absorption and emission. A similar averaging *cannot* be done so trivially for the amplitudes of Eqs. (2.27) and (2.32) because of the possibility of coherence and interference effects. Nevertheless, statistical simplifications are expected because of the large numbers of states involved at each level.

In real experiments[18] the molecules are characterized initially by some *temperature* (typically 200–300 K). If many of the thermally populated states effectively absorb the laser frequency it is unnecessary (and incorrect) to describe the time evolution of the molecular system with Eq. (1.12) and some initial state vector b(0). Rather we have an initially diagonal density matrix (we restrict the treatment of the present section to unitary time evolution matrices)[46]

$$\mathbf{P}(t)=\mathbf{U}(t,0)\mathbf{P}(0)\mathbf{U}^{+}(t,0)\ , \tag{3.4}$$

giving

$$p_k(t)=\sum_l |U_{kl}|^2 p_l(0)\ . \tag{3.5}$$

Equation (3.5) is still exact [for diagonal $\mathbf{P}(0)$] and depends upon a knowledge of $\mathbf{U}$. It is no simplification and allows for strongly oscillatory solutions as they have been observed in previous work (e.g., Ref. 24), which was based upon Eq. (1.12). The question arises as to whether from Eq. (3.5) and the coarse-grained Eq. (3.2) we can get Eq. (3.1) or another simple linear rate law [*not* Eq. (1.4)]. This is the problem of deducing the master equation from the Schrödinger equation—the "hard" problem of statistical mechanics.[46–51] We shall "do" this problem (in a simple way) for URIMIR. Some of the material uses standard results from statistical mechanics whereas other results are of a more conjectural nature with a few apparently new considerations. We shall pay proper attention to the fact that we are in-

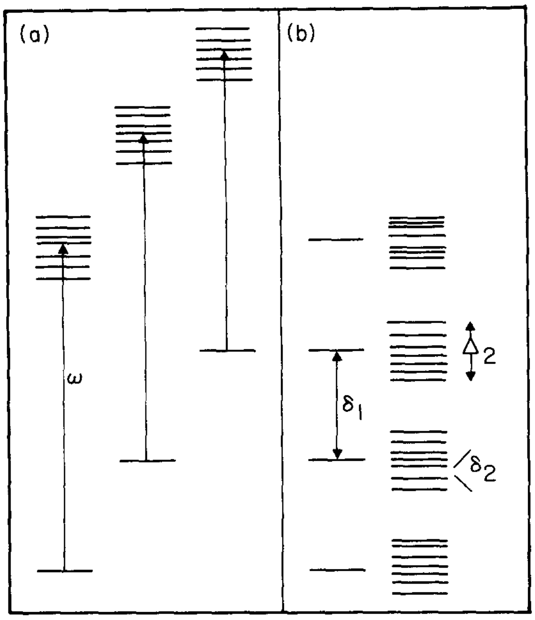


FIG. 3. Level scheme for Case A. (b) corresponds to the effectively time independent Hamiltonian of Eq. (2.27).

terested in relatively small molecular systems, relatively short times, and a coherent (nonstochastic) perturbation. We shall ask the following questions:

(i) Under which conditions are the solutions to Eq. (3.4), evaluated for the coarse-grained p_k of Eq. (3.2), approximately nonoscillatory of the relaxation type?

(ii) Is the rate law effectively linear? If yes, what are the effective rate constants as a function of molecular parameters?

(iii) What are the level populations at long times compared to the relaxation time but short compared to the recurrence time ("relaxed" populations)?

(iv) Is this relaxed distribution independent of the initial state?

Concerning question (ii) we shall allow for small oscillations superimposed on a linear overall rate law. Concerning (iii) we anticipate that for unitary **U** a constant diagonal **P** always satisfies the requirement of a stationary distribution. Derived from this is the coarse-grained microcanonical equilibrium distribution ($p_K \propto N_K$). However, this may not be the only stationary distribution and not the one actually obtained in a particular instance. This also concerns question (iv), the answer to which is *not* obvious, as we shall see.

Four cases in which statistical simplifications arise are presented. They have different ranges of validity characterized by the following parameters (for two levels): the average squared coupling matrix element $\langle |V_{IJ}|^2\rangle$, the frequency range over which the coupling is of this order (Δ_I and Δ_J, these are the level "widths"), and the average frequency distance between states in each level (δ_I and δ_J). All of these can, in principle, be obtained from high resolution molecular spectroscopy. $\langle |V_{IJ}|^2\rangle$ can be controlled to some extent by the experimentalist through the laser power.

A. Case A. Fermi's golden rule for the decay of an isolated state into a quasicontinuum

We consider Eq. (2.27) with a weak perturbation which couples one initially populated state to a manifold of quite densely spaced states. The physical situation for URIMIR is drawn in Fig. 3(a) together with the equivalent representation from Eq. (2.27) in Fig. 3(b). At the lower energy E_1 we assume $\delta_1 \gg |V_{kj}|$ where V_{kj} is the coupling of each state in Group 1 to the states of Group 2 (if $kT \gg \hbar\delta_1$ several states of Group 1 may initially be populated). We can then decouple the equations of motion by considering the coupling of each individual state in Group 1 to its own quasicontinuum in Group 2. At the energy of one laser quantum above Group 1 we require that $\delta_2 \ll |V_{kj}|$, which may not be unreasonable after a glance at the sharp rise in the densities of states of Table I. The states k in this quasicontinuum are supposed to have couplings of the same order

$$|V_{12}|^2 = N_2^{-1}\sum_{k=1}^{N_2} |V_{1k(12)}|^2 ,$$

over a range of at least Δ_2. By a well-known argument[29] one gets an exponential decay of the states of Group 1 into states of Group 2 known as Fermi's golden rule, with a rate constant

$$K_{21} = 2\pi |V_{12}|^2/\delta_2 . \tag{3.6}$$

Equation (3.6) is a valid representation of Eq. (2.27) if we have

$$\delta_1 \gg |V_{12}| , \tag{3.7}$$

$$\delta_2 \ll |V_{12}| , \tag{3.8}$$

$$\Delta_2 \gg 4\pi^2 |V_{12}|^2/\delta_2 . \tag{3.9}$$

Also, as always, the δ and the $|V|$ must be "reasonably" distributed. Furthermore there are two conditions concerning the time range under consideration

$$t > \pi\Delta_2^{-1} , \tag{3.10}$$

$$t \ll 2\pi\delta_2^{-1} . \tag{3.11}$$

Condition (3.10) is not serious, because not much decay occurs during this period. Condition (3.11) is of no practical importance if the Level 2 is sufficiently strongly coupled to the next higher level and so forth. It will then be depopulated long before the times of Eq. (3.11). We do not give any derivation for the Case A because it is so well known and it is very similar to the derivation for Case B, which we give in the Appendix. Figure 4 may illustrate that astronomical numbers of states N_2 in Level 2 are by no means required for such an exponential decay. The curve (a) for the decay of one state coupled to 61 states is practically indistinguishable from an exponential decay computed from Eq. (3.6) (we have, therefore, not drawn the exponential curve in addition). Curve (b) is for the decay of one state into a "quasicontinuum" of 13 states. For this model the conditions (3.7)–(3.9) are by no means fulfilled. Nevertheless we have some irreversible decay with a rate law at least qualitatively similar to the exponential [curve (a)]. Figure 5 shows the "recurrence" of state one for the model of one state decaying into 61 states at long times

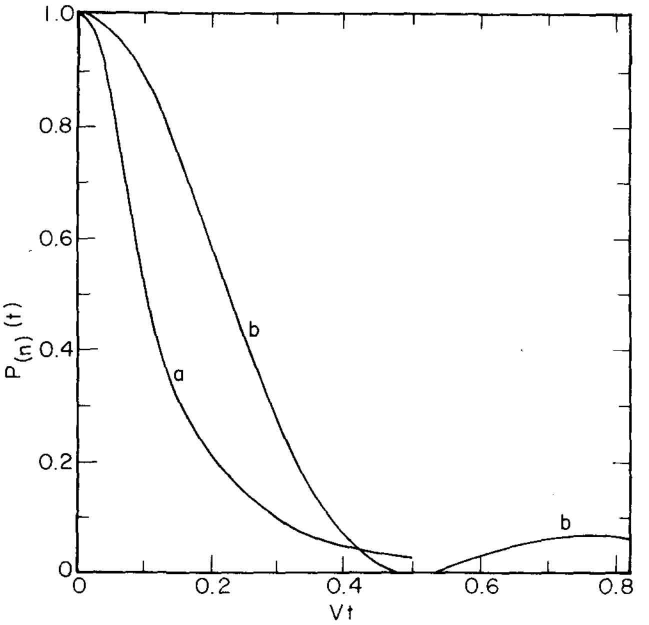


FIG. 4. Quasiexponential decay for Case A. The curve (a) is for one state coupled to 61 states. An exponential curve would be distinguishable from this only in the initial range. The curve (b) is for decay of one state into just 13 states—this decay is nonexponential and slower, but still "irreversible."

violating Eq. (3.11). As we noted above, these recurrences may or may not be important, depending on the time evolution of Level 2, etc.

A glance at Table I might convince the reader that the conditions for Case A may be easily satisfied after the absorption of a few CO_2-laser quanta for most polyatomic molecules. However, this may be illusory, because strong optical selection rules may considerably reduce the effective density of states useful for Eqs. (3.7)–(3.9). Furthermore Δ_2 may not be sufficiently large in all cases. Therefore it is necessary to consider further possibilities. We may note, before proceeding, that in the work of Bloembergen and Larsen[21] Case A is implicitly assumed at the highest states of their "Region 1." They characterize these states by an effective decay width into the "quasicontinuum of Region 2" whereas they use Eq. (2.27) for the Region 1. As we see, this *may* be justified. Of course the treatment of the rate processes after the threshold of the quasicontinuum is left open. The "leakage" idea is also rather related.[52]

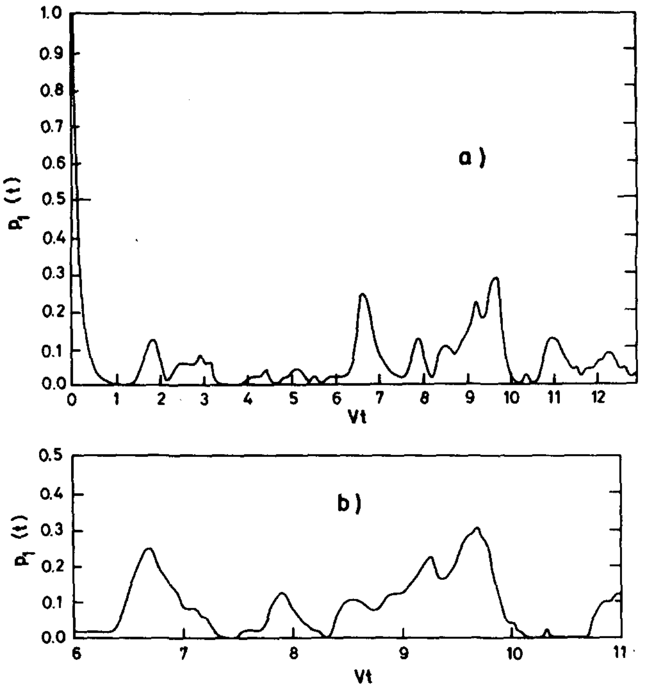


FIG. 5. Exponential decay and recurrence for one state coupled to 61 states in level 2. The system is the same as in Fig. 4, but for longer times. (b) gives a "high resolution" view of the time range near the recurrence time $2\pi\delta_2^{-1}$.

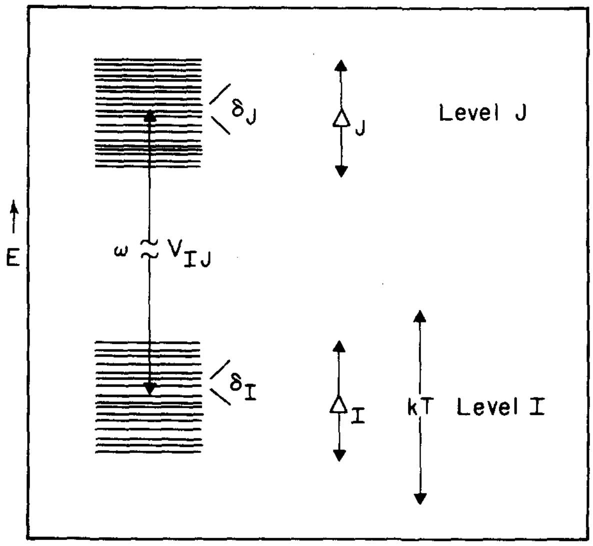


FIG. 6. Level scheme for Case B, see text for explanation of symbols.

We wish to stress that all the parameters of Eqs. (3.6)–(3.9) can be either measured by high resolution spectroscopy or obtained from *ab initio* calculations, although neither may be simple for polyatomic molecules. At the risk of being pedantic we also stress that Eq. (3.6) describes transitions from one state to a *group* of molecular states and not to states in this group individually—this is the statistical-mechanical aspect. In particular this transition rate *cannot* be obtained by summing over the Einstein coefficients for absorption, which govern the transitions between individual states at low power induced by "white" light.

B. Case B. Pauli master equation for transitions between groups of states with a weak global interaction

We now consider the case that we have for both levels *I and J*

$$\delta_{I,J} \ll |V_{IJ}| ,$$

and that a large number N_J of states of level J is initially randomly populated, say, from a thermal distribution with $kT \gg \hbar\delta_J$. For URIMIR this may apply if for very large molecules at higher temperatures the initial thermal population already covers the dense region of the spectrum. More generally Case B *may* apply at higher excitation energies for all larger molecules. The situation is shown in Fig. 6. The effective level widths again are given by the condition that the individual coupling matrix elements must be of the order of the average $|V_{IJ}|$ for *all* states in this range. The problem of deriving a master equation for such a situation is well known from statistical mechanics with the early derivation by Pauli[47] and much later work.[48–51] We give a simple derivation for the case of discrete molecular spectra in the Appendix. Here we state only the result, namely a rate equation for levels of the form (3.1) with rate constants

$$K_{IJ} = 2\pi |V_{IJ}|^2/\delta_I \ , \qquad (3.12)$$

$$|V_{JI}|^2 = |V_{IJ}|^2 = (N_I N_J)^{-1} \sum_{i=1}^{N_I} \sum_{j=1}^{N_J} |V_{ij(IJ)}|^2 \ . \qquad (3.13)$$

The following assumptions have to be made (see, however, below) in order to derive Eqs. (3.1) and (3.12)

$$P_{jk}(0) = \delta_{jk} p_J(0) N_J^{-1} \ , \qquad (3.14)$$

$$\Delta_J(\text{and } \Delta_I) \gg 4\pi^2 |V_{IJ}|^2 \delta_I^{-1}(\text{and } \delta_J^{-1}) \ , \qquad (3.15)$$

$$\delta_J(\text{and } \delta_I) \ll |V_{IJ}| \ . \qquad (3.16)$$

The frequency spacings and coupling matrix elements must furthermore be distributed reasonably (smoothly) around their average values δ_I and δ_J, and $|V_{IJ}|$. The times considered must satisfy (similar to Case A)

$$t > \pi \Delta_I^{-1}(\text{and } \Delta_J^{-1}) \ , \qquad (3.17)$$

$$t \ll 2\pi(\delta_I^{-1} + \delta_J^{-1}) \ . \qquad (3.18)$$

These conditions are probably fulfilled in a number of cases where URIMIR has been observed. We are faced, however, with an additional problem. For weak coupling [Eq. (2.27)], which is of interest here, URIMIR must be considered as a sequence of many excitation steps from Level 1 to Level 2, from Level 2 to Level 3, and so forth. If we are allowed (and required in the thermal case) to assume initially a diagonal density matrix, this need not be true any more for the density matrix of Level 2 (3, 4, etc.) at time t and therefore, the transitions from Level 2 to 3 and so on may perhaps *not* be described by the simple rate law Eqs. (3.1) and (3.12). We therefore either have to make a *repeated random phase assumption*[47] for the various levels, or we have to argue that Eq. (3.14) is too stringent a condition. The former may lead to contradictions. We shall show with a simple example that the latter is a proper assertion for all practical purposes. For the full details of the theory we refer to the extensive literature on the subject.[48–51, 53–56]

In Fig. 7 we have shown the time evolution for a three level system, each level comprising 19 states, as it follows from the solution of Eq. (2.27) using Eq. (3.5). Level 1 is assumed not to be coupled directly to level 3 (WF-QRA see Sec. II). Figure 7(a) shows the time evolution for an ensemble satisfying Eq. (3.14), being in level 1 at $t=0$. Figure 7(b) is the result of simple three level kinetics, Eqs. (3.1) and (3.12). We find that the differences are small and actually due to the fact that the conditions (3.15) and (3.16) could not be completely satisfied in the model. It is important to note that the kinetics for level 3 need not follow Eq. (3.1), in principle, but it does! This can be understood from looking at Fig. 7(c) which is a "quantum mechanical trajectory"

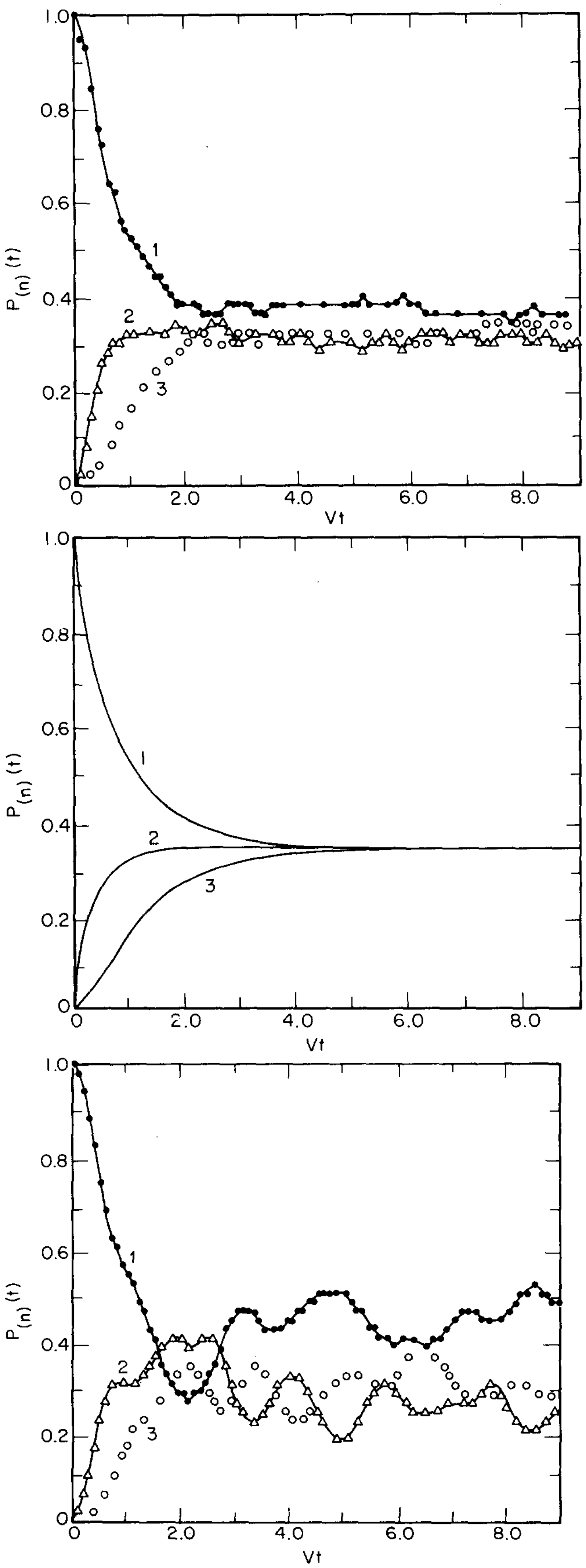


FIG. 7. (a) Three level kinetics computed from Eqs. (2.27) and (3.5). There are 19 states in each level. (b) Three level kinetics from Eq. (3.1) with rate constants from Eq. (3.12). (c) Three level kinetics from Eqs. (2.27) and (1.12) assuming an irregular choice of initial phases for the same spectrum as (a).

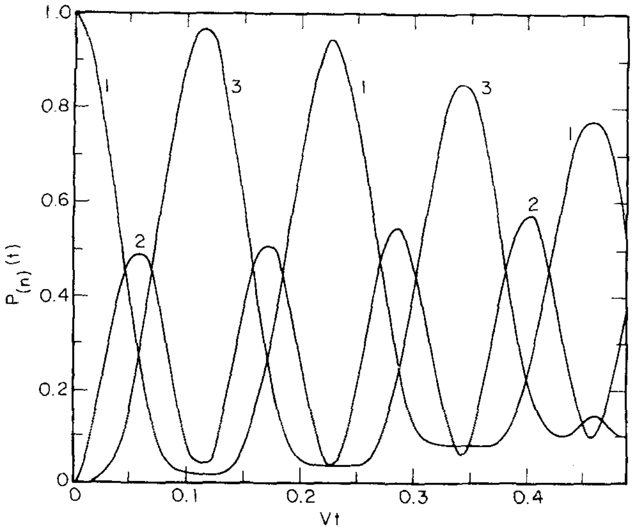


FIG. 8. Time evolution for the same system as in Fig. 7(c) but with equal initial phases for all states in Level 1.

from Eq. (1.12) but for the same system, being in Level 1 initially, now with some arbitrary irregular choice for the phases of the initial state vector. Although the fluctuations are now rather large (19 is *not* a very large number!) the overall time evolution is still similar to simple three level kinetics. We note that Fig. 7(a) corresponds to the average of (infinitely) many trajectories like the one shown in Fig. 7(c). Figure 7(c) illustrates that the random phase assumption is not really necessary. One must avoid, however, too specific a choice of phases. If we assume equal phases for the initial state vector (still for the same system) we obtain the result of Fig. 8 which is oscillatory and unrelated to simple three level kinetics. However, it is *extremely improbable* that such a situation would occur in URIMIR. The real state of any particular molecular system with all probability is characterized by some irregular combination of phases even if the *random* phases of the initial thermal distribution are lost at higher levels of excitation.

We think that the conditions of Case B are actually fulfilled at higher energies for many polyatomic molecules making some reasonable assumption about Δ (10^{11}–10^{13} Hz, related to anharmonic couplings known from Fermi Resonances of near degenerate states) and with the present day relatively weak laser fields leading to $|V|$ in the GHz region, rapidly decreasing at higher energies. However, these estimates may be too optimistic and with very low intensities Eq. (3.16) may be violated, whereas at very high intensities Eq. (3.15) may be violated. Therefore, we consider now two more unusual cases, which cover this range of possibilities.

C. Case C. Transitions between groups of states with specific pairwise interactions

The situation is similar to Case B, Fig. 6, but now we require

$$\omega \gg \delta_{I,J} \gg |V_{IJ}| \ . \tag{3.19}$$

The first inequality is not essential, but it enables us to use the quasi-resonance-approximation. Due to the second inequality we shall have mainly effective pairwise interactions between states closest to resonance. Even those states will on the average be quite far off resonance, so we may anticipate relatively weak excitation. Physically Case C can be obtained by irradiating large polyatomic molecules with relatively low laser intensities. We also can require pairwise interactions artificially, due to some selection rule, without restrictions upon the $\delta_{I,J}$.

In either case the problem breaks up into many problems of order 2, which are easily solved within the WF-QRA, Eq. (2.28). Suppose we have N pairs between levels I and J, and at $t=0$

$$p_J(0) = \sum_{j=1}^{N} p_{j(J)}(0) = 1 \ ,$$

then we obtain for the population of Level I at time t [with $p_{j(J)}(0) = p_{k(J)}(0)$]

$$p_I(t) = N^{-1}\sum_{i=1}^{N}[V_i^2/(V_i^2+D_i^2)]\{\sin[(t/2)(V_i^2+D_i^2)^{1/2}]\}^2 \ . \tag{3.20}$$

D_i and V_i are the off-resonance shift and coupling matrix elements for pair i, respectively. If N is very large and D and V are distributed according to some smooth (independent) distribution functions $F(D)$ and $G(V)$, then we can replace the sum by an integral, neglecting terms of order $1/N$

$$p_I(t) = \int_{-\infty}^{+\infty} dD\, F(D) \int_{-\infty}^{+\infty} dV\, G(V) \frac{V^2}{V^2+D^2} \times \{\sin[(t/2)(V^2+D^2)^{1/2}]\}^2 \left\{ \int_{-\infty}^{+\infty} dD \int_{-\infty}^{+\infty} dV\, F(D)G(V) \right\}^{-1} . \tag{3.21}$$

The distribution functions $F(D)$ and $G(V)$ must be such that in spite of the formal integration limits our requirements on δ and V are satisfied [Eq. (3.19)].

We shall investigate some particular solutions of Eq. (3.21). First we choose $F(D) = \delta(D)$, i.e., all pairs are in exact resonance. This is not realistic but simple. Furthermore, we take $G(V) = \text{const.}$ for $-V_m \leq V \leq +V_m$ and zero outside this interval. This gives

$$p_I(t) = \tfrac{1}{2}\{1 - [\sin(V_m t)/V_m t]\} \ . \tag{3.22}$$

Although oscillatory in the beginning, this finally relaxes to $p_I(\infty) = \frac{1}{2}$. We can define a half relaxation time $t_{1/2}$ by $p_I(t_{1/2}) = \frac{1}{2} p_I(\infty)$ giving $(V_m t_{1/2}) \simeq 1.9$. If we assume $F(D) = \delta(D)$ and $G(V) = V_L[\pi(V^2+V_L^2)]^{-1}$ (Lorentzian), we obtain the interesting result

$$p_I(t) = \tfrac{1}{2}\{1 - \exp(-V_L t)\} \ , \tag{3.23}$$

with the truly exponential half relaxation time $(V_L t_{1/2}) = \ln 2$. We stress that the assumptions on $F(D)$ and $G(V)$ are not realistic and violate the ideas of Eq. (3.19). However, Eqs. (3.22) and (3.23) give an interesting, simple analytical insight into the statistical behavior of systems which are *not* characterized by strong global interactions but rather by very specific, pairwise ("nonergodic") couplings. Statistical behavior arises through the initial condition ($p_{k(J)} = p_{1(J)}$, which is satisfied if

$kT \gg \hbar\delta_J$) and through our low resolution look only at *level* populations.

We turn now to a physically more realistic description, with distribution functions $F(D) = \text{const.}$ in the interval $(-D_m \leqslant D \leqslant +D_m)$ and $G(V) = \text{const.}$ in the interval $(-V_m \leqslant V \leqslant +V_m)$ and zero outside these intervals. Equation (3.21) then becomes

$$p_I(t) = V_m^{-1} D_m^{-1} \int_0^{V_m} dV \int_0^{D_m} dD \frac{V^2}{V^2 + D^2} \left\{ \sin\left[\frac{t}{2}(V^2 + D^2)^{1/2}\right] \right\}^2 . \tag{3.24}$$

Since we consider only pairwise, close neighbor interactions, Eq. (3.19) becomes

$$\omega \gg D_m \gg V_m . \tag{3.25}$$

Equation (3.24) is difficult to evaluate analytically for general values of the parameters V_m, D_m and t. As $t \to 0$ we obtain the typical quadratic behavior

$$p_I(t) \propto V_m^2 t^2 . \tag{3.26}$$

The relaxed distribution at $t \to \infty$ is given by

$$p_I(\infty) = (\pi V_m / 8D_m) + \tfrac{1}{4}\{1 - [(V_m^2 + D_m^2)/V_m D_m] \arctan(V_m/D_m)\} . \tag{3.27}$$

Because we assume $D_m \gg V_m$, this is approximately equal to

$$p_I(\infty) \simeq \pi V_m / 8D_m . \tag{3.28}$$

The kinetically most interesting time range is given by $D_m^{-1} \ll t \ll V_m^{-1}$, and for this we obtain

$$p_I \propto 0.25 V_m^2 D_m^{-1} t , \tag{3.29}$$

i.e., an approximately constant "relaxation rate constant" (note that $p_I \ll p_J$ at all times).

Figure 9 gives the result of the numerical integration of Eq. (3.24) with $V_m = 0.1 D_m$ (full line). The damped oscillations remind one of Eq. (3.22). The points are from a solution of Eq. (2.27) for two levels containing 31 states each and satisfying Eq. (3.19), but retaining all interactions)i.e., *all* states in levels 1 and 2 are coupled—not just pairwise—but they are mostly far off resonance). We see that Eq. (3.21) gives indeed a good description of the physical case under investigation. The differences are the fluctuations for the finite spectrum [these are large, since $N = 31$ is a *small* number compared to $N = \infty$, Eq. (3.21)], and the higher relaxed p_I due to the next closest neighbor and higher interactions in the "real" case. We do not consider here an analytical inclusion of higher interactions and the treatment for two levels with very different δ_I and δ_J, but we note that we always can use the estimates for Case C ("real")

$$p_I(\infty)_{\text{Case B}} \geqslant p_I(\infty)_{\text{real}} \geqslant p_I(\infty)_{\text{ideal pairwise}} . \tag{3.30}$$

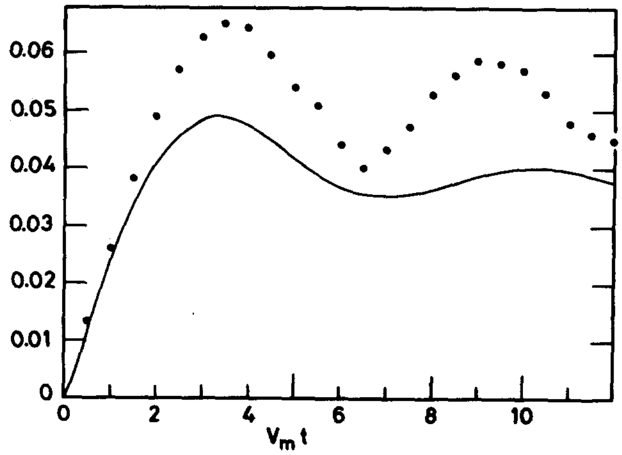


FIG. 9. Case C. The full line is from Eq. (3.24) with $V_m = 0.1 D_m$ (Level 1 is initially populated). The points are from the matrix problem Eq. (2.27) with 2×31 states and the same distribution functions for V and D ($V_m = 0.1\,D_m$) but unrestricted couplings (not just pairwise) between all states. An average over three spectra has been made to improve the statistics.

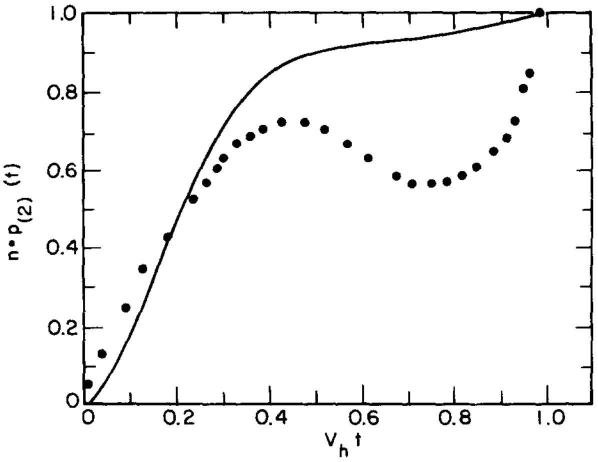


FIG. 10. Time evolution for Level 2 from Eq. (3.21) assuming Lorentzian distributions with half-widths $(V_h/D_h) = 0.1$ (solid line). The points give the time dependent relaxation rate coefficient.

Figure 10 illustrates that the oscillations disappear if one assumes "smoother" distribution functions $F(D)$ and $G(V)$, for example, two Lorentzians with half-widths $(V_h/D_h) = 0.1$, truncated at $10\,V_h$ and $10\,D_h$, respectively. in order to remain (roughly speaking) within the ideas of Eq. (3.19). The decay looks rather exponential with rate "constants" $k(V_h t)$ indicated by the points. Assuming untruncated Lorentzians for $F(D)$ and $G(V)$ one gets a clean exponential decay [see also Eq. (3.23)] but this is an unphysical assumption, violating Eq. (3.19). An interesting question is, of course, what the best $F(D)$ and $G(V)$ for polyatomic molecules might be (assuming that there is *one* best one).

Although Case C leads to nonoscillatory (or weakly oscillatory) behavior with ultimate relaxation, a rather interesting feature is the dependence of $\mathbf{p}(\infty)$ upon $\mathbf{p}(0)$. Indeed there is an infinity of $\mathbf{p}(\infty)$ as a function of $\mathbf{p}(0)$. Still, we may use for many practical purposes and to within some reasonable approximations (neglecting oscillations, etc.) an effectively linear rate law Eq. (3.1) with $\mathbf{K}$ being dependent on $\mathbf{p}(0)$ but roughly independent of time. This is

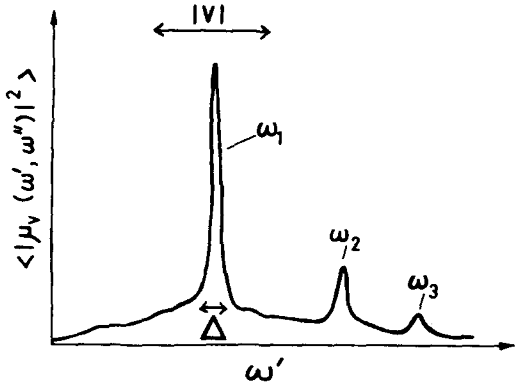


FIG. 11. Possible vibrational ir spectrum of a highly excited polyatomic molecule at ω'' [see text, Case D].

still a useful simplification. It is not necessary for Case C to require a diagonal initial density matrix, however, we must require the initial populations $p_{j(J)}(0)$ to be equal (or slowly varying with respect to the index j). If Case C applied at all levels of excitation one could rule out an appreciable excitation because of Eq. (3.28). However, Case C may sometimes apply at low energies, with Case B becoming relevant at higher energies. In such a situation the bottleneck for URIMIR would be at low energies with a steady-state distribution, which is strongly peaked at low levels of excitation [see also Sec. IV and Eqs. (3.28) and (3.30)]. We also note the relationship of the parameter D_m in Eq. (3.29) to the density of states, i.e., $D_m \propto \delta_I$. Therefore we have in all three Cases A, B, and C

$$K_{IJ} \propto |V_{IJ}|^2/\delta_I \,, \tag{3.31}$$

however, with the "asymmetric" dependence upon the initial state noted for Case C.

D. Case D. Transitions between groups of states with a strong global interaction

We consider a situation again similar to the one shown in Fig. 6, but now with a choice of parameters

$$\Delta_I \simeq \Delta_J \ll |V_{IJ}| \,. \tag{3.32}$$

The physical situation, which may correspond to such an assumption, it sketched in Fig. 11. There we have shown the possible coarse structure of an ir spectrum of a highly excited polyatomic molecule, disregarding rotation for the sake of a simple argument. Shown is the vibrational transition moment $\langle|\mu_v(\omega',\omega'')|^2\rangle$ averaged over a small interval Δ_J corresponding to the initial excitation or any other small interval containing many vibrational states (see Table I!). It may (although it need not) be that there are still a few very pronounced resonance frequencies $\omega_1, \omega_2, \ldots$ on a broader background. However, due to various rovibrational interactions it may be taken for granted that many different states contribute to the absorption in the range Δ. The spectrum will then have a complicated substructure and possibly a much more complicated coarse structure than shown in Fig. 11. However, with strong laser irradiation at ω_1, one may have average coupling matrix elements $|V_{IJ}| \gg \Delta$, the overall width of the coarse structure—this corresponds to the assumption (3.32). Although we do not believe that with the present experimental laser powers (in the GW/cm^2 range at most) such an assumption applies we shall consider this case for completeness. Degenerate oscillator model systems have been investigated previously.[24] Making rather special assumptions, typically oscillatory behavior in time has been found for the level populations. We shall see here that with the proper statistical assumptions (random or irregular initial phases!) even in Case D one gets relaxation as observed in the other cases, however, with some additional complications.

We start with an extreme case, which is easily treated analytically, namely $\Delta_I = \Delta_J = 0$ and a constant interaction C between states belonging to different levels

$$i\mathring{\mathbf{b}} = C\,\mathbf{B}\mathbf{b} \,. \tag{3.33}$$

The matrix B_{kj} has zero elements for k and j in the same level and $B_{kj} = 1$ if k and j belong to different levels. We assume the initial condition (3.14), with $p_J(0) = 1$, and we consider the time dependence of p_J

$$p_J(t) = N_J^{-1} \sum_{n=1}^{N_J} \sum_{m=1}^{N_J} |U_{nm}|^2 \,, \tag{3.34}$$

$$|U_{nm}|^2 = \left| \sum_{k=1}^{N} T_{mk} T_{nk} \exp(-iCe_k t) \right|^2 \,. \tag{3.35}$$

Note that we use no double indices here, i.e., $1 \leq n \leq N = N_I + N_J$, etc. $\mathbf{T}$ is the eigenvector matrix of $\mathbf{B}$

$$\mathbf{BT} = \mathbf{TE} \,. \tag{3.36}$$

$\mathbf{B}$ is a matrix of rank 2 with zero trace. Therefore we have only two eigenvalues e_k different from zero which we write $e_1 = +e$, $e_2 = -e$ with a positive e. Furthermore, $\mathbf{B}$ is invariant with respect to a permutation $\mathbf{Q}_{(ij)}$, if i and j are in the same level

$$\begin{aligned} \mathbf{Q}_{(ij)}\mathbf{B} &= \mathbf{B}\mathbf{Q}_{(ij)} \,, \\ \mathbf{Q}_{(ij)}\mathbf{BT} &= \mathbf{B}\mathbf{Q}_{(ij)}\mathbf{T} \,, \\ &= (\mathbf{Q}_{(ij)}\mathbf{T})\mathbf{E} \,. \end{aligned} \tag{3.37}$$

This immediately gives us the eigenvectors for the nonzero eigenvalues of $\mathbf{B}$

$$T_{k1} = T_{k2} = (2N_J)^{-1/2} \text{ for } k \leq N_J \,, \tag{3.38}$$

$$T_{k1} = -T_{k2} = (2N_I)^{-1/2} \text{ for } k > N_J \,, \tag{3.39}$$

and

$$e = \sqrt{N_I N_J} \,. \tag{3.40}$$

Therefore we have for n and $m \leq N_J$

$$|U_{nm}| = \delta_{nm} - (2/N_J)[\sin(Cet/2)]^2 \,. \tag{3.41}$$

We have used the fact that $\mathbf{T}\mathbf{T}^T = \mathbf{1}$. We finally obtain for the time dependent population

$$p_J(t) = 1 - N_J^{-1}[\sin(Ct\sqrt{N_I N_J})]^2 \,. \tag{3.42}$$

This is obviously a periodic solution which goes over into the resonant two state case, Eq. (2.28), for $N_I = N_J = 1$. However, if N_J is large ($\to \infty$) the amplitude of this motion goes to zero. Therefore, neglecting terms of the order $1/N_J$ there is *no* time evolution for the random phase, two level case. We can consider this as a special case of a master equation (3.1) with $K=0$. If we had assumed some definite, special phase relationship between the initial states, e.g., $b_m(0)=N_J^{-1/2}(1\le m \le N_J)$, then we would have obtained

$$p_J(t)=[\cos(Ct\sqrt{N_I N_J})]^2 \ . \qquad (3.43)$$

This is always a large amplitude periodic motion as in the two state case, with the period of motion decreased by the factor $\sqrt{N_I N_J}$. This is just another illustration of the tremendous difference in the behavior of random phase and specific phase systems. For the degenerate, random phase system with large N_J, a constant, possibly large off-diagonal coupling does not contribute to the time evolution at all.

We now turn to the more interesting general problem of quasidegenerate levels coupled by some arbitrary interaction matrix elements V, which are distributed according to some distribution function $G(V)$ (see Case C also). An analytical solution for $\mathbf{p}(t)$, given some $\mathbf{p}(0)$, as it is possible for the other three cases, presents a formidable, although probably soluble mathematical problem which we do not undertake the labor here to treat. We shall, instead, state the results of systematic numerical investigations of large matrices (2 and 3 level systems) satisfying the conditions for Case D.

(i) Assuming random (or "irregular") initial phases one obtains irreversible relaxation behavior (for times less than the recurrence time for finite systems).

(ii) Depending somewhat on the assumed $G(V)$ the relaxation is exponential or strongly damped oscillatory as in Case C. The relaxation rate constant $k_r=K_{IJ}+K_{JI}$, as obtained from the half-relaxation time if the decay is oscillatory, is given by

$$k_r \propto 2\pi\sqrt{\langle V^2\rangle-\langle V\rangle^2} \ . \qquad (3.44)$$

Assuming a "flat" distribution $G(V)$ the proportionality constant is close to 1. Unlike all the other cases k_r is *independent* of the initial and final density of states as long as we have

$$\Delta_I \text{ and } \Delta_J<\sqrt{\langle V^2\rangle-\langle V\rangle^2} \ . \qquad (3.45)$$

(iii) The relaxed distributions depend upon the initial distribution, as in Case C but unlike Case B. If we have $N_J=n$ and $N_I=n+m$ (positive m) then the relaxed distribution with the system being initially in Level I

$$p_I(\text{relaxed})=(m+n/2)(m+n)^{-1} \qquad (3.46)$$

and having only level J initially populated we get

$$p_I(\text{relaxed})=0.5 \ .$$

In the absence of analytical proofs we have to put these results forward as conjectures about the limiting behavior of very large matrices, which are nearly degenerate in the diagonal and have some arbitrary (not too different from "flat") distribution function $G(V)$ for the matrix elements V. Figure 12 shows a typical result for a two level system with 21 states in Level 1 and 43 states in Level 2. The curve a gives $p_1(t)$ with $p_1(0)=1$ and b gives $p_1(t)$ with $p_1(0)=0$. Again, in spite of the small numbers involved, the time evolution corresponds quite well to the stated limiting results with relatively small oscillations superimposed on a relaxation. Our "experimental" (i.e., numerical) results may help to suggest ways for more general analytical solutions for Case D, which is interesting in its own statistical mechanical context. However we think that for present day experiments on URIMIR, Case D is less relevant than the other cases and we do not go into more detail here. We note that for V being symmetrically distributed around zero we get the maximum possible relaxation rate constant $k_r \simeq 2\pi|V_{IJ}|$ from Eq. (3.44). Since in Case D by necessity δ_I and $\delta_J \ll |V_{IJ}|$ the excitation rate constant is much lower than the one obtained hypothetically with the Case B formula, Eq. (3.12). As one makes the transition from Case B to Case D (possibly!) by increasing the laser intensity, one will get an increase in the effective rate constant for excitation which is much *less* than proportional to $|V_{IJ}|^2$ (which itself is proportional to $|E_0|^2$, i.e., the intensity).

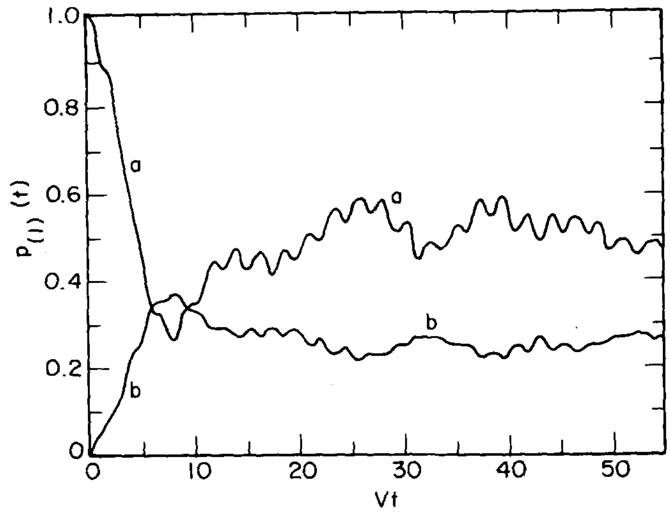


FIG. 12. Case D. Time evolution for Level 1 of a two level system with 21 and 43 quasidegenerate states in Levels 1 and 2, respectively. Curve (a) has $p_1(0)=1$ and curve (b) $p_1(0)=0$, leading to different relaxed distributions.

The cases investigated here, together with the possible intermediate cases, cover essentially all the situations where we can expect statistical simplifications leading to a rate Eq. (3.1) with approximately time independent rate constants, which may, however, depend upon the initial state. Table II summarizes the main features of these four cases. The results for Cases A and B depend upon the use of perturbation theory. For Cases C and D only the functional dependence of the rate constant and the relaxed distributions upon molecular parameters has been given. More detailed formulae for certain cases have been given in the appropriate subsections [see, e.g., Eqs. (3.46), (3.28) and (3.29), (3.44) with proportionality constants close to 1]. It must be noted that throughout Sec. III the coupling matrix elements $|V_{IJ}|$ correspond to some general effective off-diagonal matrix elements for linear systems with constant coefficients. In connection with Eq. (2.27) we have the correspondence $V_{ij}^{\text{eff}} \longleftrightarrow (V_{ij}/2)$ whereas in connection with Eq. (2.32) we have $V_{ij}^{\text{eff}} \longleftrightarrow V_{ij}$, with V_{ij}

TABLE II. Summary of cases with relaxation rate laws, see Sec. III.

Case	A	B	C	D
Irreversible relaxation?	yes	yes	yes	yes
Approximate relaxation rate constant $k_r = K_{IJ} + K_{JI}$	$2\pi \lvert V_{IJ} \rvert^2/\delta_I$	$2\pi \lvert V_{IJ} \rvert^2(\delta_I^{-1} + \delta_J^{-1})$	$f[V_m, G(V), F(D), (\delta_I, \delta_J)]$	$f[\sqrt{\langle V^2\rangle - \langle V\rangle^2}, G(V)]$ $\neq f[\delta_I, \delta_J]$
Nonlinear effects?	unimportant	unimportant	moderate	moderate
Relaxed distribution $(p_I/p_J)_r$	(∞)	δ_J/δ_I	$f[F(D), G(V), \delta_I, \delta_J]$	$f[N_I, N_J, \lvert x_I - x_J \rvert]$ $\neq f[\delta_I, \delta_J]$
Is $(p_I/p_J)_r = f[\mathbf{p}(0)]$?	no	no	yes	yes
Characteristic relationships for range of validity	$\delta_I \ll \lvert V_{IJ} \rvert$ $\delta_J \gg \lvert V_{IJ} \rvert$ $\Delta_I \gg 4\pi^2 \lvert V_{IJ} \rvert^2/\delta_I$	$\delta_I, \delta_J \ll \lvert V_{IJ} \rvert$ Δ_I and Δ_J $\gg 4\pi^2 \lvert V_{IJ} \rvert^2/\delta_I$(and δ_J)	$\delta_I, \delta_J \ll \omega$ $\delta_I, \delta_J \gg \lvert V_{IJ} \rvert$	$\Delta_I \simeq \Delta_J \ll \sqrt{\langle V^2\rangle - \langle V\rangle^2}$
Conditions for initial state	···	"Irregular phases" or density matrix diagonal—piecewise constant.	Piecewise constant populations—any phases	"Irregular phases," or density matrix diagonal—piecewise constant

being defined in Eq. (2.9). This multiple use of V_{ij} should not lead to confusion. A similar consideration applies to the diagonal elements. In principle, all the information required for the calculation of the relevant kinetic parameters in Table II, and for deciding which case applies, is contained in the hypothetically available complete ir spectrum of the molecule under consideration. This information may be obtained either from measurements or *ab initio* calculations or from simple models.

IV. DYNAMICAL LIMITING CASES WITH SIMPLE APPROXIMATIONS

In this section we shall investigate the form of the solutions of the differential equations derived in the previous sections, as a function of time and at steady state. Dynamical limiting cases are considered, in some of which very simple formulas are obtained. For each situation we shall discuss the total reaction rate, the possibility of isotopic selectivity and product ratios. For the specific dissociation rate constants we shall make use of the statistical theory of unimolecular reactions[2,3]

$$\langle k_i \rangle_{\Delta E} \equiv k(E) \lesssim W(E)/h\rho(E) \; . \tag{4.1}$$

$W(E)$ is the total number of dynamically accessible reaction channels[3] and $\rho(E)$ is the density of metastable molecular states. For the time being we shall also assume the equality in Eq. (4.1) (for simple, spin-allowed reactions) and suppress for convenience all diagonal indices except for the energy. A complete statistical theory for the general case, including all diagonal indices (J, M, Π etc.)[57] will be formulated in the next section. We shall mainly use the master equations derived in Sec. III as a starting point, but we shall also present a few model solutions based on the WF-QRA Eq. (2.27). This will further illustrate the validity of the master equation approach even for relatively few coupled levels. We shall mention it particularly, whenever there is a correspondence to *thermal* unimolecular reactions.

A. Strong field limit

In this limit we assume that all the up and down transitions in Fig. 1 are much faster than all the reaction rates $r_i(k)$. In thermal unimolecular reactions this corresponds to the "high pressure" limit. The monomolecular dissociation is the rate determining step. Since for example for simple bond fission reactions $k(E)$ levels off at a maximum value of typically 10^{13}–10^{14} s^{-1} (see Refs. 58, 59, e.g.), this implies effective coupling matrix elements $\lvert V_{IJ} \rvert \gg 10^4$–$10^5$ GHz. This is outside the present experimental possibilities. Typically we have $\lvert V_{IJ} \rvert \simeq 1$–$10$ GHz at most for the first few transitions, where the density of states is low. At higher levels of excitation the excitation rate constants may be as high as $2\pi \lvert V_{IJ} \rvert^2/\delta_I$, but $\lvert V_{IJ} \rvert$ may be assumed to decrease with increasing δ_I (see below). We treat this case nevertheless, for completeness. Also the situation may be more favorable for spin-forbidden reactions. Since in the strong field limit we have in general $V_{kj} \gg \omega$ we shall assume the validity of the short time approximation Eq. (2.32) with constant coefficients and assume the validity of a master equation Case B. It is well possible that sometimes Case D would be more appropriate, but no simple general results can be obtained then, so we discard this case at present.

In the strong field limit practically no dissociation occurs until steady-state (relaxed) distributions are established. We introduce the relaxed relative level populations

$$q_I = p_I \Big/ \sum_I p_I \; , \tag{4.2}$$

and obtain for the steady-state rate constant (formally)

$$k_{\mathrm{SFL}} = \sum_I q_I k_I \; . \tag{4.3}$$

Here, k_I is the specific average reaction rate constant for Level I. We introduce a continuous scale and note that for Case B we have for the relaxed distribution

$$q(E)dE = \rho(E)dE \bigg/ \int_0^{E_L} \rho(E)dE \ . \tag{4.4}$$

We have introduced an arbitrary upper integration limit E_L. Indeed, unlike the thermal case the "partition function" $\int_0^\infty \rho(E)dE$ would diverge. In this sense the strong field limit is not as well defined as the high pressure limit in thermal unimolecular reactions, where we have the partition function $\int_0^\infty \rho(E)\exp(-E/kT)dE$ which in general converges. However, the introduction of some E_L may appear to be justified on practical grounds, if the excitation rate decreases appreciably at some energy E_L such that *below* E_L we have $K_{E_L, E_L-\hbar\omega} \gg k(E_L)$ but $K_{E_{L+\hbar\omega}, E_L} \ll k(E_L)$. As we shall see below, such an assumption is not unreasonable qualitatively, although E_L will always remain rather fuzzy and, in addition, dependent upon the laser intensity. However, the strong field limit can *only* be defined to within such uncertainties and we wish to investigate the consequences in spite of this uncertainty.

We obtain the rate constant

$$k_{\mathrm{SFL}} = \int_{E_T}^{E_L} \rho(E)k(E)\,dE \bigg/ \int_0^{E_L} \rho(E)\,dE \ , \tag{4.5}$$

$$k_{\mathrm{SFL}} = h^{-1}\int_{E_T}^{E_L} W(E)\,dE \bigg/ \int_0^{E_L} \rho(E)\,dE \ . \tag{4.6}$$

We have expressed explicitly the fact that $k(E<E_T)=0$ and have used Eq. (4.1). E_T is the threshold energy for reaction. Given E_L, Eq. (4.6) is easily evaluated with the usual methods of unimolecular reaction rate theory.[3] If E_L were independent of the laser power, k_{SFL} would also be independent of the laser power. We note that Eq. (4.6) is significantly different from the equation for the high pressure limit of *thermal* unimolecular reactions, namely,

$$k_\infty(T) = (Zh)^{-1}\int_{E_T}^{\infty} W(E)\exp(-E/kT)\,dE \tag{4.7}$$

$$= kT(Zh)^{-1}\sum_a \exp(-V_{a_{\max}}/kT) \ . \tag{4.8}$$

Z is the internal molecular partition function at temperature T $[Z=\int_0^\infty \rho(E)\exp(-E/kT)\,dE]$. Equation (4.8) contains a sum over maxima of adiabatic channel potentials $V_{a_{\max}}$ in the terminology of Ref. 3. If there are two chemically different reaction channels 1 and 2 we obtain for URIMIR the product ratio (in the SFL)

$$\frac{k_{\mathrm{SFL}}^{(1)}}{k_{\mathrm{SFL}}^{(2)}} = \frac{\int_{E_{T1}}^{E_L} W_1(E)\,dE}{\int_{E_{T2}}^{E_L} W_2(E)\,dE} \ . \tag{4.9}$$

Since E_L can probably be pushed to any desired limit, this shows that in URIMIR the chemical channel with the higher threshold (say E_{T2}) can always be pumped appreciably, although *not selectively*. In particular, if there is a low energy threshold E_{T1} for a complex elimination reaction or for an isomerization and a higher threshold E_{T2} for a simple bond fission reaction, then at sufficiently high laser power the bond fission reaction may become dominant, because of the faster increase of $W_2(E)$ compared to $W_1(E)$, even if $(E_{T2}-E_{T1})$ is quite large. Such an idea has already been used on a more intuitive level in experiments.[16] In *thermal* reactions there is an additional factor $\exp[-(E_{T2}-E_{T1})/kT]$ which usually suppresses the contributions from higher channels quite effectively

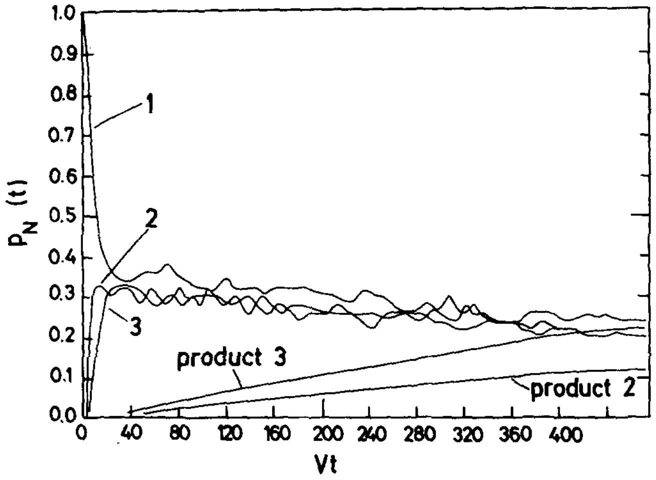


FIG. 13. Time evolution of a three level system in the strong field limit [from Eq. (3.5) with Level 1 populated initially, 21 states in each level, and $|V_{12}| \simeq |V_{23}| \gg \gamma_2 = 0.5\gamma_3$]. See also text.

$$\frac{k_\infty^{(1)}}{k_\infty^{(2)}} = \frac{\int_{E_{T1}}^{\infty} W_1(E)\exp(-E/kT)\,dE}{\int_{E_{T2}}^{\infty} W_2(E)\exp(-E/kT)\,dE} \ . \tag{4.10}$$

Thus, ir-laser photochemistry at very high intensities is quite different from thermal chemistry in the high pressure limit. These qualitative conclusions are independent of how precisely E_L can be defined.

In conclusion we show a model calculation in Fig. 13 for three levels, coupled successively, with Levels 2 and 3 having average decay widths $\gamma_2 = 0.5\,\gamma_3 \ll |V_{12}| \simeq |V_{23}|$, based upon Eq. (2.27) [or (2.32)]. Only 21 states are in each level. Nevertheless one has a simple three level kinetics with a rapid initial equilibration phase and slow subsequent decay with the rate constant given by Eq. (4.3) and the product ratio equal to (γ_2/γ_3) which is the equivalent to Eq. (4.9). Of course all this follows from our general considerations, once the master equation has been shown to be valid. The point we want to make is the very high degree of validity for relatively *small* numbers of coupled states at each level.

B. Weak field limit

In this limit we assume that the excitation rate near the reaction threshold is much smaller than all the specific reaction rates above threshold. The various excitation processes shown in Fig. 1 will then be the rate determining steps. With the typical laser intensities presently available and coupling matrix elements of a few GHz for the first few transitions it appears probable that URIMIR experiments so far correspond more closely to this limit. We note, however, that typical statistical threshold lifetimes for triatomics are of the order of nanoseconds and less, whereas for the larger polyatomic molecules investigated so far the threshold lifetimes are of the order of micro- and milliseconds.[3,58,59] It can be shown that real lifetimes are on the average then at least that long (see Eq. (4.1) and Refs. 3 and 60). Therefore, depending on the excitation rate at higher energies, which is not yet known with certainty, the experiments may also be somewhat *above* the weak field limit. But it is conceivable to select laser powers and molecules such that the weak field limit actually applies.

An assumption consistent with the weak field limit concerns the validity of a master equation Case B

$$\dot{\mathbf{p}} = \mathbf{K}\mathbf{p} \; . \tag{4.11}$$

K is now a tridiagonal matrix coupling only adjacent "levels" in the sense of Sec. III. We take here only the energy scale into account and treat the general case in Sec. V. By definition of the weak field limit equation (4.11) is of finite order L since the populations above threshold vanish. The explicit solution is most easily obtained by diagonalizing K [see Eq. (1.7)]

$$\mathbf{p}(t) = \mathbf{Y}(t)\mathbf{p}(0) \; , \tag{4.12}$$

$$\mathbf{Y}(t) = \mathbf{F}\mathbf{G}\exp(\mathbf{\Lambda} t)\mathbf{G}^T\mathbf{F}^{-1} \; . \tag{4.13}$$

Here G is *orthogonal* and F *diagonal*

$$F_{MM} = \left(\prod_{N=2}^{M} K_{N,N-1}\right)^{1/2}\left(\prod_{N=2}^{M} K_{N-1,N}\right)^{-1/2} \; , \tag{4.14}$$

$$F_{11} = 1 \; .$$

F transforms K into a tridiagonal *symmetric* matrix S, as is easily seen

$$\mathbf{F}^{-1}\mathbf{K}\mathbf{F} = \mathbf{S} \; . \tag{4.15}$$

G diagonalizes S by an orthogonal transformation

$$\mathbf{G}^T\mathbf{S}\mathbf{G} = \mathbf{\Lambda} \; . \tag{4.16}$$

In simple cases this can be done analytically, or else, powerful numerical methods are available for this type of matrix.[45] Equations (4.12)–(4.16) therefore provide an easy solution to Eq. (4.11). We have used the fact that K is real and that $K_{N,N-1}K_{N-1,N} > 0$, which is always true for our physical problem. Otherwise Eqs. (4.12)–(4.16) are general.

The eigenvalues of the matrix K with strictly positive $K_{N,N\pm1}$ and k_N and strictly negative

$$-K_{NN} = K_{N-1,N} + K_{N+1,N}(+k_N) \; , \tag{4.17}$$

are real, strictly negative, or zero if there is no loss.[61–63] If we assume that the largest eigenvalue λ_1 is the only one close to zero (or equal to zero), then after a sufficiently long time the contributions from all $\exp(\lambda_k t)$ but λ_1 are negligible. The populations for this "steady-state" situation are obtained from Eqs. (4.12) and (4.13)

$$p_N(t) = \exp(\lambda_1 t)F_{NN}G_{N1}\sum_{M=1}^{L} F_{MM}^{-1}G_{M1}p_M(0) \tag{4.18}$$

For the relative populations [cf. Eq. (4.2)] we get

$$q_N(\text{steady state}) = F_{NN}G_{N1}\left(\sum_{M=1} F_{MM}G_{M1}\right)^{-1} \; . \tag{4.19}$$

We note that, depending on the distribution of eigenvalues the "steady state" need not be physically meaningful, unless we have $\lambda_1 = 0$, where it corresponds to the equilibrium state. Summing up Eq. (4.18) over all N and differentiating with respect to time we find [cf. Eq. (1.3)]

$$-\frac{d\ln\sum_N p_N(t)}{dt} = k_{\text{uni}} = -\lambda_1 \; . \tag{4.20}$$

In order to proceed, one has to make assumptions about K. One extreme case which might arise is that the coupling K_{IJ} decreases drastically with energy, particularly near the reaction threshold. We shall call this the *reaction threshold bottleneck* (RTB) assumption. We can then put approximately for the last diagonal element

$$-K_{LL} = K_{L-1,L} + K_{L+1,L} \simeq K_{L-1,L} \; . \tag{4.21}$$

The loss term $K_{L+1,L}$ for excitation above threshold is only a small perturbation. Within this approximation the steady-state distribution using the rate constants from Case B becomes

$$q_I(\text{steady-state}) \simeq \rho_I\left(\sum_{N=1}^{L}\rho_N\right)^{-1} \; . \tag{4.22}$$

Note the similarity to Eqs. (4.2) and (4.4). Since the distribution (4.22) may be derived from a (microcanonical) equilibrium distribution, but truncated at some level L (the reaction threshold) we shall call such a distribution a *truncated equilibrium distribution* (TED). We shall discuss the physical meaning of the density of states ρ_I in Eq. (4.22) in more detail in Sec. V. With Eqs. (4.21) and (4.22) we obtain for the largest eigenvalue to first order

$$-\lambda_1 = k_{\text{RTB}} = K_{L+1,L}\,\rho_L\left(\sum_{N=1}^{L}\rho_N\right)^{-1} \; . \tag{4.23}$$

Using the Case B rate constant for $K_{L+1,L}$ we get (see Table II)

$$k_{\text{RTB}} = 2\pi\hbar\,|V_{L+1,L}|^2\rho_L\rho_{L+1}\left(\sum_{N=1}^{L}\rho_N\right)^{-1} \; . \tag{4.24}$$

If the order of the matrix L is sufficiently large and the variation of ρ over an interval N, $N+1$ is small, we can replace the sums by integrals

$$k_{\text{RTB}} = 2\pi\hbar^2\omega\,|V_{E_T+\hbar\omega/2,\,E_T-\hbar\omega/2}|^2\rho(E_T-\hbar\omega/2) \\ \times\rho(E_T+\hbar\omega/2)\left[\int_0^{E_T}\rho(E)\,dE\right]^{-1} \; . \tag{4.25}$$

We note that k_{RTB} is proportional to the laser intensity ($\propto |E_0|^2 \propto |V|^2$). Please also note that $|V|$ is the effective coupling matrix element, which is derived from ($V_{ij}/2$) defined in Eq. (2.9) in the WF-QRA [cf. Eq. (2.27)]. To the extent that the RTB-assumption holds true, we can obtain an average coupling matrix element from a measured value k_{RTB} at dissociation threshold, namely $|V_{E_T+\hbar\omega/2,\,E-\hbar\omega/2}|^2$, since the densities of states are relatively well known (see however Sec. V).

We can compare the RTB-assumption with the *strong collision assumption* for the low pressure limit of thermal unimolecular reactions.[26] There as well one has "equilibrium" populations up to the threshold energy E_T (however, Boltzmann!) and essentially zero populations above E_T. The unimolecular rate constant at steady state then becomes (considering only the energy scale)[2,3]

$$k_0^{sc}=k_c\int_{E_T}^{\infty}\rho(E)\exp(-E/kT)\,dE$$
$$\times\left\{\int_0^{\infty}\rho(E)\exp(-E/kT)\,dE\right\}^{-1}. \qquad (4.26)$$

This can be written in a slightly more suggestive form, assuming that $\rho(E)\simeq\rho(E_T)$ varies slightly compared to the exponential function above E_T

$$k_0^{sc}=k_c(kT)\rho(E_T)\left[\int_0^{E_T}\rho(E)\exp(-E/kT)\,dE\right]^{-1}. \qquad (4.27)$$

Equation (4.27) shows some formal similarities to Eqs. (4.23) and (4.25). The total rate constant for collisional deactivation of excited molecules, k_c, is introduced together with the integral $\int_{E_T}^{\infty}\rho(E)\exp(-E/kT)\,dE$ instead of the activation rate constant through a well-known argument using detailed balance.[2] The advantage is that k_c can be equated approximately to total collision numbers, e.g., the Lennard-Jones collision numbers. The *formal* argument in obtaining k_0^{sc} is otherwise similar to our derivation of k_{RTB}. However, the *results* are completely different, even the partition functions have different meanings. This is similar to our remarks in Sec. IV.A.

It is well known[2,3,64] that the strong collision assumption does not often pertain to thermal unimolecular reactions. Similarly, we may not expect our RTB-assumption to apply, as a rule, in URIMIR. A less drastic assumption would be that K_{IJ} decreases only rather smoothly with energy or even remains constant. Then the perturbation due to dissociation cannot be neglected and the steady-state populations from Eq. (4.19) may be quite different from their "equilibrium" value (4.22). We shall investigate solutions for such a case which we shall call *intermediate bottleneck* in more detail below (Sec. IV.D.).

The products in the true weak field limit always correspond to the lowest threshold, if the higher thresholds are separated by more than $\hbar\omega$ from the lowest threshold. It appears that so far this has been actually observed for most cases although there are quite a few controversial systems. This would place most present experiments rather close to the weak field limit as defined here. To conclude our discussion of the reaction threshold bottleneck we show in Fig. 14 the time evolution for a three level system similar to the one considered in Fig. 13 for the strong field limit [computed with Eqs. (3.4) and (2.27)]. This time we assume decay only from the third level but with $\gamma_3 \gg |V_{23}| \simeq 0.1|V_{12}|$. Correspondingly, Level 3 is not populated and Levels 1 and 2 decay with a common rate constant given in Eq. (4.23) after fast establishment of the steady-state population (4.22). Again the fluctuations even with just 21 states in each level are quite small. Therefore, the much simpler master equation treatment, and indeed the use of Eq. (4.23) would be quite appropriate for all practical purposes.

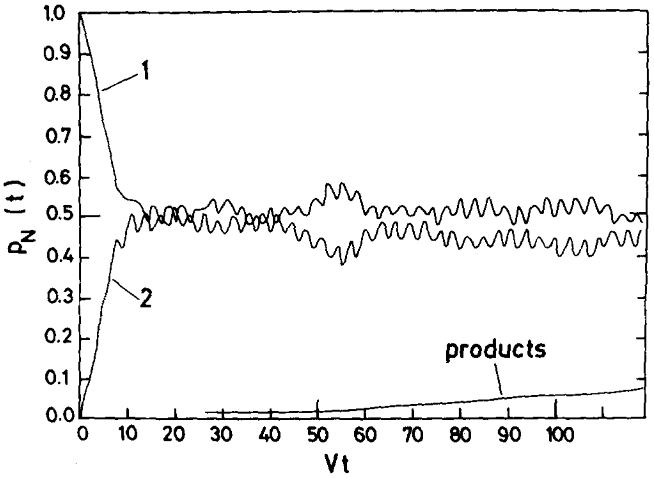


FIG. 14. Time evolution for a three level system in the weak field limit (RTB) [from Eq. (3.5) with 21 states in each level and $|V_{12}|=10|V_{23}|=\gamma_3/2$].

C. Early bottleneck assumption

With weak fields the rate determining step may sometimes be the first or the first few transitions at low energies (see Fig. 1) where the densities of states are still low and a master equation treatment *may* not be appropriate (however, still possibly Case C). We shall call this the *early bottleneck* assumption. This assumption is implicit in the work of Bloembergen, Cantrell and Larsen[20-22] who treat only the first few excitation steps explicitly and characterize the subsequent loss by a phenomenological decay term into the "quasicontinuum," which is assumed to begin after about 3-4 CO_2 laser quanta have been absorbed (for SF_6). The treatment of Mukamel and Jortner[23] is similarly valid for an early bottleneck only, since their representation of the higher excitation steps as coherent exact resonance transitions between nondegenerate levels is quite unrealistic (see Sec. III). However, the early bottleneck assumption may indeed be *appropriate* for many of the present experiments. In particular it allows for an easy explanation of the isotopic selectivity of URIMIR.[20-24]

Computing only the rate determining step indeed allows one to obtain good estimates of the total reaction rate (also relative rates for various isotopes). However this does not provide a quantitative understanding of the dynamics of the dissociation process and the product and product state distributions in the case of competing channels above reaction threshold. We therefore propose a combined Schrödinger/master-equation treatment as follows.

For a realistic level structure (from high resolution molecular spectroscopy) one solves Eqs. (2.27) and (3.4) up to energies where one of the Cases A-D applies. At the top one uses in the first round a phenomenological decay term, whose absolute magnitude can be estimated from the equations in Table II and Sec. III. Now already at energies below the truncation limit the rate law should be linear with a rate constant which can be obtained from the results of the first round. In the second round one can now truncate at a lower energy so

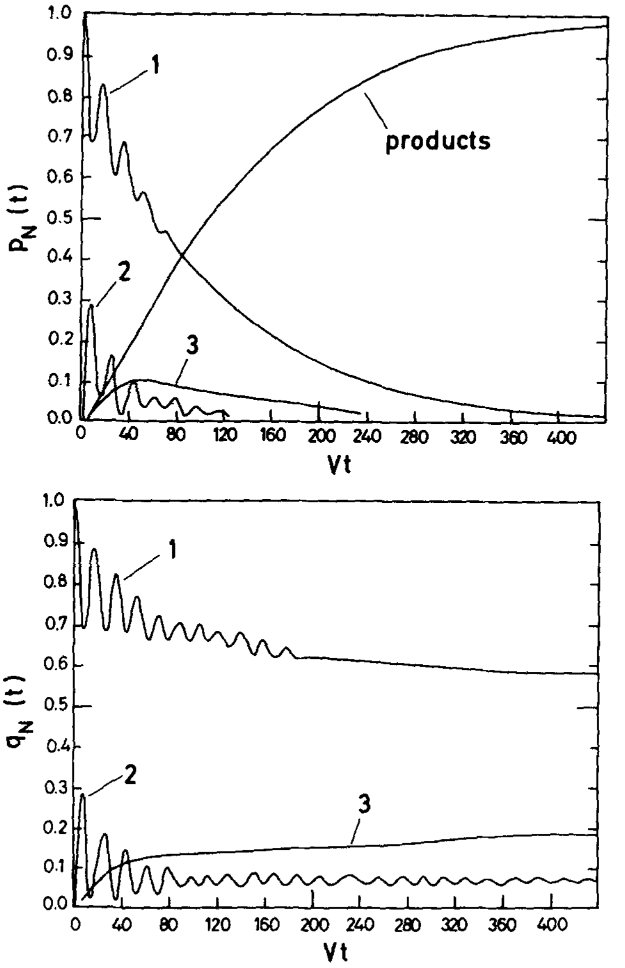


FIG. 15. (a) Time evolution for a five level system corresponding to the early bottleneck situation [from Eq. (2.27)]. The lowest two states are off resonance by 2.8 ($|V_{12}|/2$). The higher three levels contain 21 states each, with $\gamma_5 \simeq 10|V_{12}|$ and all other levels being stable. Curve 4 is close to 3 and therefore not drawn. (b) Gives the fractional populations Eq. (4.2) with the establishment of a steady-state. Small oscillations have not been drawn. See also text.

that above this truncation limit the rate law is linear, whereas below the truncation limit one may have oscillations. We can now compute the loss term for the oscillatory part and use it as a gain term in the first step of a master equation treatment. This breaks the problem in two parts, each of which is readily solved, without making arbitrary assumptions and using only valid approximations in each case. We shall present calculations for specific molecules along these lines in a later communication. Here we show only for a simple model how well such a treatment actually works. Figure 15 shows the result of a calculation [based on Eqs. (2.27) and (3.4)] for a five level system. The lowest two levels (1 and 2) contain just one state each, being slightly off resonance, whereas the upper three levels contain 21 states each. The level structures are chosen to satisfy approximately the conditions for Cases A and B. The highest level is assumed to decay at a fast rate $\gamma_5 \gg |V_{45}|$, it is therefore not populated appreciably. As one might expect, Levels 1 and 2 show a strongly oscillatory decay. However, Level 3 follows a smooth rate law and similarly Level 4, which is always very close to Level 3 and therefore not shown. Small oscillations have not been drawn, for clarity. In the second round of the calculation one solves the two level problem with a decay term added on Level 2, as obtained from the calculation, according to Eq. (2.27). This is very easy for the example treated here. For the upper three levels one uses a master equation (3.1) with a gain term at the lowest Level 3, taken from the decay of Level 2. Again such a master equation is very easy to solve and the results one gets are almost indistinguishable from the first computation which involves a matrix problem of order 65. Figure 15(b) shows the fractional populations $q_N(t)$ [cf. Eq. (4.2)]. One finds that due to the off-resonance shift Level 1 is always strongly populated relative to the others in spite of its low statistical weight (cf. Case C!). True steady-state is reached only after most of the dissociation is over, but the fractional population of Level 3 (which is almost equal to the one of Level 4) varies little after $(Vt)=40$, at which time only little product has been formed.

D. Model solutions for specific excitation matrices and intermediate cases

We shall now consider solutions for the master equations resulting from Case B with more general and more realistic assumptions. As we have discussed already, Case B applies probably to most polyatomic molecules after the absorption of the first few laser quanta [and with not too high laser intensities, see Case D]. The Cases A, C, and D can be dealt with on similar lines. We shall include the competition between excitation and dissociation both before and at steady-state. The general equation is again Eq. (4.11), which must be truncated at some level where dissociation is much faster than excitation. For the excitation of polyatomic molecules with a CO_2-laser this applies at much less than 100 steps on the energy scale, which is an easy problem to solve along the lines of Eqs. (4.12)–(4.19).

Within the general purpose of the present paper we present three models for the excitation matrix, none of which is believed to be very realistic by itself, but which we believe to "bracket" the total possible dynamical behavior. In *Model* 1 we require $K_{IJ} = 2\pi |V_{IJ}|^2 \delta_I^{-1}$ with constant $|V_{IJ}| \neq f(I, J)$ and $\delta_I^{-1} \propto \rho(E)$, the density of molecular states at energy E. This assumption will grossly *overestimate* the excitation rate at high energies.

Model 2 is based upon the idea that we start from some zero order basis in which only *one* pair of states for two levels is coupled with a large transition moment ($\propto v$), which is constant and independent of the level of excitation. This transition moment is now supposed to be redistributed among all states through some perturbation (as in Fermi and Coriolis resonances) over a range Δ, assumed to be constant. We then obtain from completeness at each level

$$K_{IJ} \propto \frac{v^2}{\Delta^2}\delta_J \ ,$$

$$K_{JI} \propto \frac{v^2}{\Delta^2}\delta_I \ .$$

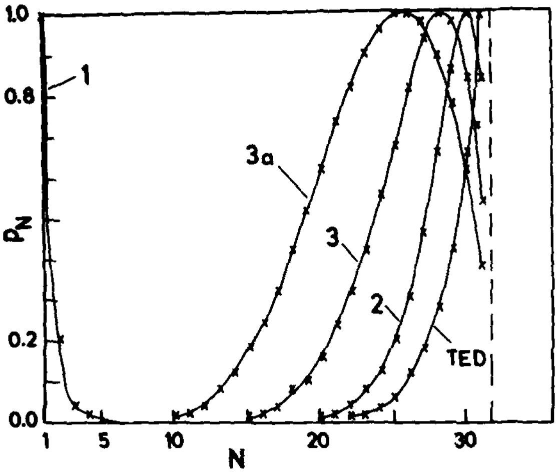


FIG. 16. Steady-state distributions for the levels (N) of a typical molecule, assuming coupling models 1, 2 and 3 (see text). TED is the truncated equilibrium distribution (RTB). 3*a* is before steady-state, with 25% of the molecules being dissociated. See discussion in text.

This model tends to *underestimate* the transition rates at high energies because one can easily show that there will be more contributions than from just one pair.

In *Model* 3 we shall assume that the total loss rate from each level (apart from reaction) is independent of the level, i.e., K_{II} = constant. Together with $K_{IJ}/K_{JI} = \delta_J/\delta_I$ this defines a coupling matrix. We shall allow for modification of this model later by assuming a functional behavior $K_{II} \propto E^{-n} \propto I^{-n}$, for which some physical reasons could be given.

We have solved the master equation with these model assumptions for a 32-level system with realistic densities of states for a "typical" polyatomic molecule. Level 32 was assumed to react at a very high rate, i.e., we consider at first the weak field limit. The results are shown in Fig. 16. The curve "TED" is the distribution from Eq. (4.22) truncated at level 31. This corresponds to the steady-state distribution of the reaction threshold bottleneck assumption. All distributions are normalized to their individual maxima for better visualization. The crosses correspond to the discrete level populations, the lines are drawn only to facilitate the distinction between the points of different distributions. For model 1 the rapid *increase* of the rate constant for excitation with N makes essentially the first step rate determining. This corresponds then to the early bottleneck assumption. Sec. IV.C. Indeed, from a master equation Case C one would get a similar distribution at low N. The total rate constant for dissociation $(-\lambda_1)$ equals about $-K_{11}$, the loss rate from the first level. The second eigenvalue is separated from this by about a factor of six, which leads to a meaningful steady-state distribution. By the time steady-state populations are reached, about one-third of the molecules have already reacted, the rest of the reaction takes place at steady-state. Model 2 gives a steady-state distribution peaked at high N, which is not too different from "TED." This is a consequence of the assumed rapid *decrease* of the excitation rate with N. The last transition is almost rate determining. We can compare the steady-state rate constant of model 2 with the RTB rate constant Eq. (4.23) which gives an upper limit, through

$$k_{\mathrm{real}} = F_d \cdot k_{\mathrm{RTB}} , \tag{4.28}$$

$$F_d = q_L(\mathrm{real})/q_L(\mathrm{TED}) . \tag{4.29}$$

The correction factor F_d has an obvious interpretation as a depletion factor for the last level. For model 2, $F_d = 0.512$, i.e., the steady-state rate constant is only a factor of 2 lower than k_{RTB}. Steady-state is reached for model 2 after about 30% of the molecules have reacted, similar to model 1. The two largest eigenvalues are separated by a factor of about 5. For the more realistic model 3 there is not such an obvious rate determining step. The largest eigenvalues are rather close together $(\lambda_1 : \lambda_2 : \lambda_3 = 1 : 1.7 : 2.5)$, and steady-state is reached only at long times (curve "3"). The depletion factor is nevertheless still $F_d = 0.194$, i.e., the steady-state rate constant is only lower than k_{RTB} by a factor of 5. Curve 3(a) shows the distribution after 25% of the reaction has taken place. This distribution is still quite far from steady state. The time dependent depletion factor is $F_d = 0.067$. We propose F_d as a very convenient way to characterize steady-state depletion and nonsteady-state effects, since k_{RTB} is easily computed for real molecules as well. This upper limit rate constant can be used as a first estimate, with corrections F_d computed from some models. Such a procedure is meaningless for the *early bottleneck* situation, however. For model 1, F_d would be 5×10^{-10}!

We turn now to the case where excitation and reaction effectively compete above threshold. For the same polyatomic molecule as considered above we have computed specific rate constants $k(E, J=0)$ Eq. (4.1) from the adiabatic channel model[3,58] (see Sec. V for other values of J) for a simple bond fission reaction. For the excitation process we use the modified model 3 with $K_{NN} \propto N^{-1}$ below threshold. At very low laser intensity ($K_{N,N-1} \propto$ intensity!) we again have the weak field limit with $k(E) \gg K_{N,N-1}$ for all $k(E) \neq 0$. This is shown in Fig. 17(a). At steady state ("S") no levels above threshold (dashed line) are populated. The weak field depletion factor for this model is 0.23, i.e., a factor of 4 correction compared to k_{RTB}. This is between the values for model 2 and for the unmodified model 3. In Fig. 17(b) we show the result of increasing the laser intensity by a factor of 10^7. The steady-state distribution for unreacted molecules is now to a large extent *above* the dissociation limit (the surface under the curve S to the right of the dashed line). If the laser were switched off after steady state is reached, all these molecules would still dissociate. The open points indicate the product energy distribution. In the weak field limit all the products are formed with essentially zero energy $(<\hbar\omega)$, see Fig. 17(a). By increasing the laser intensity, one favors the higher energy channels. Similar conclusions apply of course in the case of chemically different channels, as we have already seen in Sec. IV.A. Another interesting conclusion concerns the time dependence of the excitation process. Both in Figs. 17(a) and 17(b) we have shown the distributions at re-

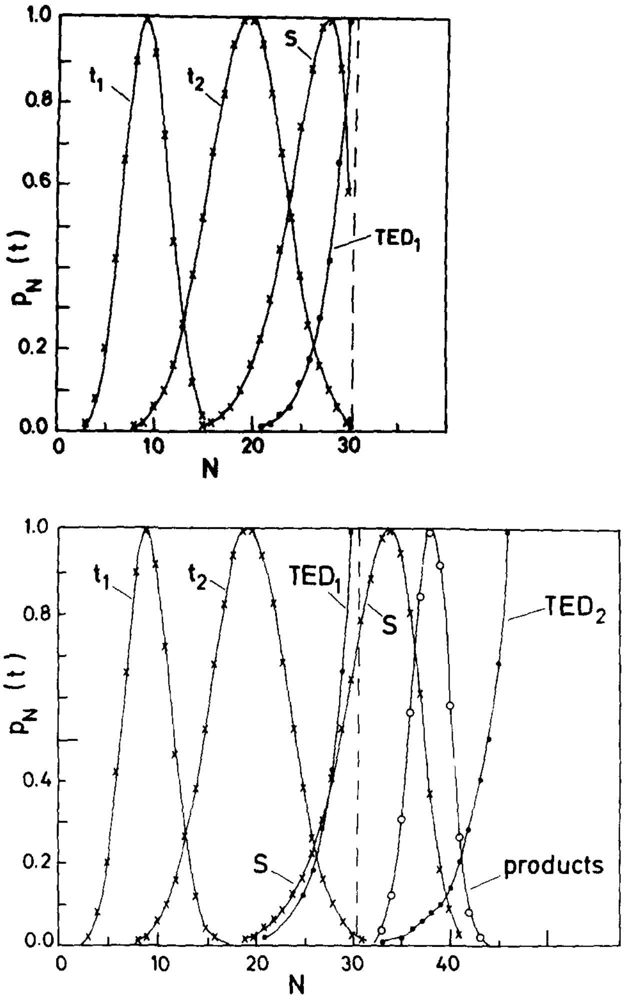


FIG. 17. Time dependent level (N) populations for a typical polyatomic molecule. (a) is for low laser intensity (weak field limit) as in Fig. 16, but for a modified model 3 (see text). (*S*) is the steady-state population. (b) is with 10^7-fold increased intensity and competition between excitation and decay. Note that most of the steady-state population (*S*) is above threshold (dashed line). The open circles give the product energy distribution at steady state (bond fission reaction). See also discussion in text.

duced times t_1 and t_2 such that the product $(Kt_{\text{real}}) = t_1$ (or t_2) is the same for both cases. K is a constant which is proportional to the laser intensity ($K_{N,N-1} \propto K \propto |V_{N,N-1}|^2 \propto$ intensity). As one would expect, the reduced time evolution is exactly the same, independent of the laser intensity, as long as no dissociation occurs. This is not true any more at long times. In particular the steady-state rate constants in Figs. 17(a) and 17(b) have the ratio

$$\left(\frac{k_b}{k_a}\right)_{\text{steady state}} = \frac{\lambda_1(b)}{\lambda_1(a)} = 6.19\times 10^6 ,$$

and *not* 1×10^7 which one would expect if one assumed the rate constant to be always proportional to the laser intensity. This is an example of *unimolecular fall-off* for laser excitation. We note that this provides an additional means (other than via k_{RTB}) to experimentally determine average coupling matrix elements for optical excitation of highly energized molecules. We have already discussed the maximum rate that can be obtained for strong fields in Sec. IV. A. We note that our theory allows us to compute complete "fall-off curves" for laser excitation, whenever experiments should become available. It has sometimes been claimed that only *energy fluence* (i.e., the product intensity ⊗ time for a laser pulse) is important for the rate of product formation. Our results show that this is only true for the weak field limit excluding also the early bottleneck, that is in practice for intermediate laser intensities. At low laser intensities the rate will be strongly intensity dependent due to *early bottleneck effects* (cf. Sec. IV.C. and Case C Sec. III). At high laser intensities the rate will be intensity dependent because of the "fall-off" effects. Still another conclusion can be obtained from Fig. 17. If one excites polyatomic molecules with a very short, powerful laser pulse (say in the picosecond range), then almost all of them may be above threshold at the end of the pulse. If they are in an energy range where $0 < k(E) < 10^{11}\ \text{s}^{-1}$, then all the reaction will go on *after* the pulse, eventually competing with collisional deactivation. This type of ir-laser photochemistry has considerable similarities to the conventional one step photochemistry and is quite different from the steady-state ir-laser photochemistry. Most present experiments with 100 ns pulses can be estimated to correspond more closely to the "steady-state" type photochemistry, where we do not wish to imply that steady state is actually reached during this period.

In this section we have obtained a considerable number of qualitative conclusions concerning the dynamics of URIMIR. We have implicitly assumed throughout this section that the internal energy is the only relevant parameter. For quantitative applications to real molecules it is necessary to consider further quantum numbers in some more detail.

V. CONCISE FORMULATION OF A COMPLETE STATISTICAL THEORY OF URIMIR

In the derivation of the master equations it was necessary to assume that the matrix elements $|V_{ij}|^2$ which are used for the computation of the average $|V_{IJ}|^2$ are "reasonably" distributed [see, e.g., Eq. (3.13)]. This means in particular that out of a large number of $|V_{ij}|$ not just one or a few are large and all the others are zero. (It does *not* mean that all the $|V_{ij}|$ are equal!) In principle we can see from the true spectrum whether this is true. In practice we want to find an approximate way to compute the $|V_{IJ}|^2$, without knowing the true spectrum. Similarly, in the use of the statistical rate constant Eq. (4.1) one has to assume that all the channels [$W(E)$] are effectively (not necessarily equally!) coupled to all the metastable states [$\rho(E)$].[3] When using approximate models for computing any of these quantities [$|V_{IJ}|$, δ_I, δ_J, $W(E)$, $\rho(E)$] it is therefore *primordial* to identify at first all strong selection rules and dynamical constraints.[57] If this has been done, we can then use the whole previous argument, using quantities like $|V_{E',J',\ldots\ E,J,\ldots}|^2$, $\delta(E,J,\ldots)$, $W(E,J,\ldots)$, $\rho(E,J,\ldots)$. We shall retain in our notation mainly the total angular momentum quantum number J as representative for all the others, since it turns out to be the most important "good quantum number."

We have three kinds of (almost) good quantum numbers. *Firstly,* those which are good quantum numbers for both the excitation process and the monomolecular reaction. The most prominent one of this kind characterizes the nuclear spin state. We can expect both nuclear spin species and motional species in the molecular symmetry group[57,65] to be *approximately* (!) conserved during an electric dipole transition and reaction. This type of selection rule has been discussed in much detail elsewhere[57] and we shall assume that it has been dealt with. Related constants of motion arise, when the problem consists of dynamically uncoupled parts. For instance an isomer (or some particular states) of the molecule may be energetically accessible but nevertheless dynamically decoupled, say, due to a high barrier, etc. This first kind of decoupling breaks the whole problem into various disconnected parts, and we shall assume that this has been done.

The *second* kind of good quantum number is conserved during the monomolecular step, but *not* in the excitation process. The total angular momentum quantum number J is of this kind, since we have the electric dipole selection rule $\Delta J = 0, \pm 1$. We have to keep track of the time-dependent populations, for various J, because of the strong dependence of the monomolecular rate constant $k(E,J)$ upon J.[3,58-60] Parity, which also belongs to this kind of good quantum number has much less importance in practice and we shall not discuss details.

Thirdly, we may have selection rules which are important for electric dipole transitions but unimportant for the monomolecular reaction. We think that these are always molecule specific and have to be identified in each particular case (e.g., the ΔK selection rule for symmetric tops).

If we have identified all strong selection rules, the rather irregular remaining couplings allow us to make statistical assumptions for suitably averaged quantities. We give an explicit treatment regarding J. The master equation becomes a doubly tridiagonal form in both energy *and* angular momentum

$$\mathbf{K} = \{K_{E\pm\hbar\omega;\,J\pm 0,1\,|\,E;\,J}\ ,\quad K_{E;\,J\,|\,E;\,J}\}\ , \tag{5.1}$$

$$-K_{E,\,J\,|\,E,\,J} = k(E,J) + \sum_{J'=J-1}^{J'=J+1} (K_{E+\hbar\omega,\,J'\,|\,E,\,J} + K_{E-\hbar\omega,\,J'\,|\,E,\,J})\ . \tag{5.2}$$

The statistical decay rate constant is given by

$$k(E,J) \lesssim W(E,J)/h\rho(E,J)\ . \tag{5.3}$$

The densities of metastable states $\rho(E,J)$ have to be interpreted as *averaged* densities of states given a total J in an interval ΔE around E.[3,58,59] They can be computed within the usual approximations of unimolecular rate theory. The number of dynamically accessible channels can be computed from the adiabatic channel model, for example

$$W(E,J) = \sum_{a(J)} h(E - V_{a_{\max}})\ . \tag{5.4}$$

Here $V_{a_{\max}}$ is the maximum of the ath adiabatic channel with total angular momentum J[58] and $h(x) = 1(0)$ for $x > 0(< 0)$ is the unit step function.

In practice one wants to compute $\rho(E,J)$, and $|V_{KL}|^2$ from a zero order model Hamiltonian, with $\hat{H} = \hat{H}_0 + \hat{H}_1$ such that we have for *averaged quantities*

$$\langle \rho^0(E,J)\rangle_{\Delta E} \simeq \langle \rho(E,J)\rangle_{\Delta E}\ , \tag{5.5}$$

and

$$|V^0_{KL}|^2 \simeq |V_{KL}|^2\ ,$$

or explicitly (see Sec. III)

$$\sum_{l=1}^{N_L}\sum_{k=1}^{N_K} |V^0_{kl}|^2 \simeq \sum_{l=1}^{N_L}\sum_{k=1}^{N_K} |V_{kl}|^2\ . \tag{5.6}$$

The zero order Hamiltonian may be chosen such that the individual $|V^0_{ij}|^2$ are quite unrealistic, if only the averaged quantities are good approximations. We note that $\hat{H}_0$ is model dependent and not a basic feature of the theory.

The master equation (3.1) is obviously more difficult to solve with the matrix in Eq. (5.1) than with the matrices in Sec. IV. We give here only the simple analytical results for the *strong field limit* (cf. Sec. IV.A) and the weak field limit reaction threshold bottleneck (cf. Sec. IV.B). In the *strong field limit* we obtain

$$k_{\mathrm{SFL}} = (hZ_L)^{-1} \sum_{J=0}^{\infty} \int_{E_T(J)}^{E_L(J)} W(E,J)\, dE\ , \tag{5.7}$$

$$Z_L = \sum_{J=0}^{\infty} \int_0^{E_L(J)} \rho(E,J)\, dE\ . \tag{5.8}$$

In the *weak field limit* we get

$$k_{\mathrm{WFL}} = \sum_{J=0}^{\infty} q(E_T(J),J) \sum_{J'=J-1}^{J+1} K_{E_T(J)+\hbar\omega,\,J'\,|\,E_T(J),\,J} \times h[E_T(J) + \hbar\omega - E_T(J')]\ . \tag{5.9}$$

$h[x]$ is again the unit step function. We introduce the reaction threshold bottleneck assumption

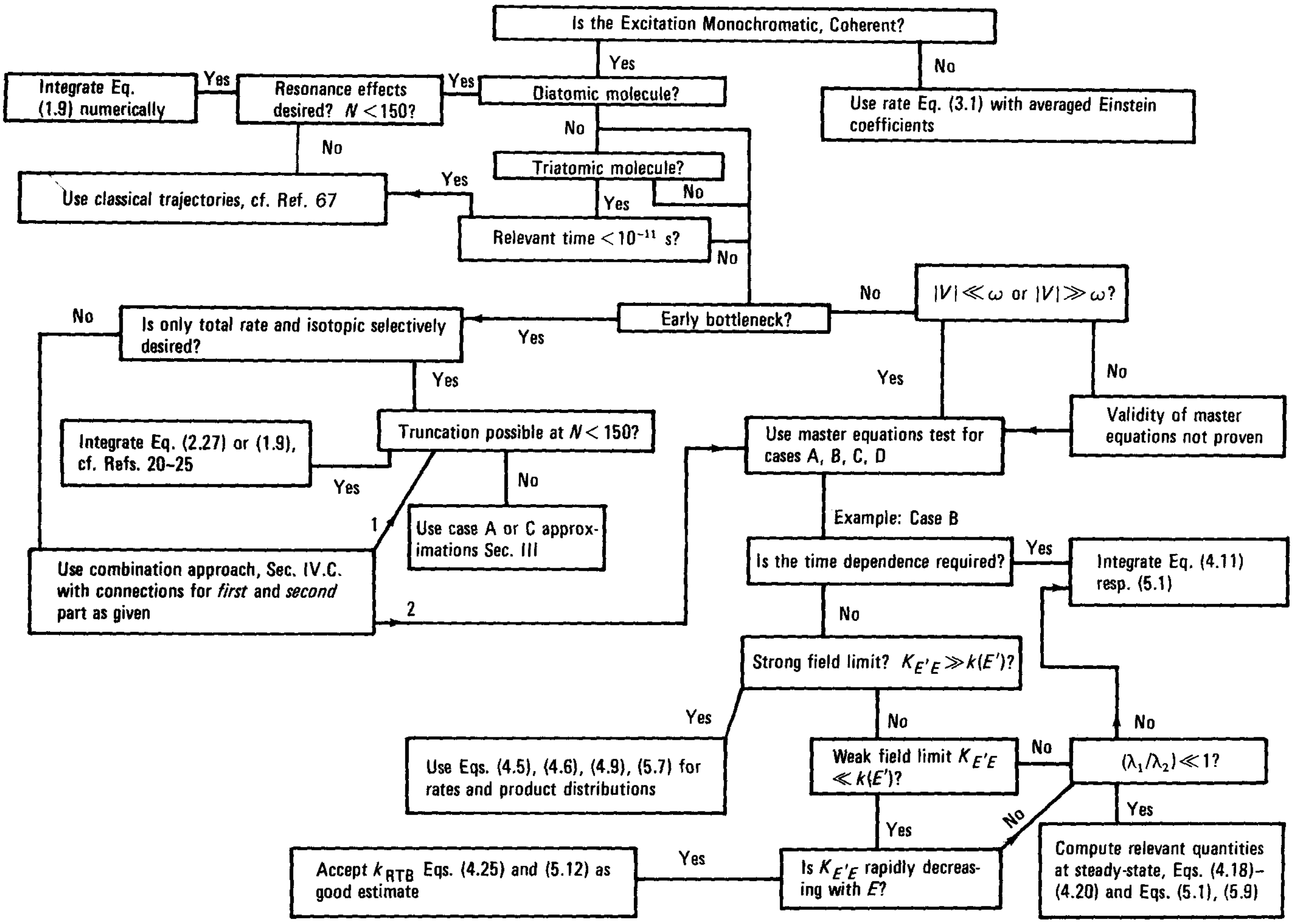
$$q(E_T(J),J) = \hbar\omega\rho(E_T(J),J) Z_T^{-1}\ , \tag{5.10}$$

$$Z_T = \sum_{J=0}^{\infty} \int_0^{E_T(J)} \rho(E,J)\, dE\ , \tag{5.11}$$

$$k_{\mathrm{RTB}} = Z_T^{-1} 2\pi\hbar^2\omega \sum_{J=0}^{\infty} \rho(E_T(J),J) \times \sum_{J'=J-1}^{J+1} |V_{E_T(J)+\hbar\omega,\,J'\,|\,E_T(J),\,J}|^2 \times \rho(E_T(J)+\hbar\omega, J') h[E_T(J) + \hbar\omega - E_T(J')]\ . \tag{5.12}$$

Most of the considerations of Sec. IV can be taken over with few changes. However, the depletion factor F_d is now a weighted average over all J and it is not possible to obtain all the $|V|^2$ from one measured rate constant any more. Still, we can compare the experimental results with k_{RTB} and a theoretical depletion factor computed from the first eigenvalue and eigenvector of the matrix (5.1). The particular importance of k_{RTB} arises from the fact that is always provides a strict upper limit

TABLE III. Flow chart for the computational approach to collisionless URIMIR.



for the rate constant, before and at steady state, at weak and at strong fields. For the product and product state distributions the equations of Sec. IV apply as well, combined with the equations of this section.

VI. SUMMARY AND CONCLUSIONS

The most important single result of the present paper is the proof, in Sec. III, that linear or approximately linear relaxation or master equations under certain conditions properly describe the time dependent behavior of polyatomic molecules subjected to *coherent monochromatic* radiation. We have been able to identify several cases, in which relaxation rate laws pertain and have given quantitative expressions for the effective rate coefficients as a function of molecular (spectroscopic) parameters. This gives a solid foundation for the use of linear rate equations in URIMIR, which has been introduced recently on a more phenomenological basis.[27,66] We believe, indeed, that a use of master equations will be *necessary* in a model independent theoretical treatment of URIMIR of truly polyatomic molecules. Master equations will also provide a most convenient basis for model calculations as noted in Sec. V. Any nonstatistical-mechanical approach will meet severe difficulties for molecules with more than two atoms. We show in Table III the possible theoretical approach to URIMIR, in the convenient form of a flow chart. For diatomic molecules the statistical considerations of Sec. III do not apply. In this case one can either integrate Eq. (1.9) numerically as discussed in Sec. II (see also Refs. 67 and 68) or use classical mechanics, as has been proposed recently.[67] N is the number of effectively coupled states in a quantum-mechanical calculation which may be considered to be feasible as long as $N<150$. For triatomic molecules we always have $N\gg150$, but classical trajectories can be calculated for short times. For large polyatomic molecules the zero point energy is a considerable fraction of the dissociation energy and the use of classical mechanics becomes questionable. At this point the use of semiclassical methods would appear to be more appropriate.[69]

The rest of Table III is a largely self-explanatory summary of the statistical mechanical and combination methods discussed in the present paper, including the quantum mechanical treatment of previous authors for the "early bottleneck" case.[20–25] The table is of course not meant to be complete, in particular we have omitted all methods which require the *explicit* introduction of the "rate of intramolecular energy transfer." To the extent that this terminology corresponds to a physical phenomenon, it is *implicitly* contained in the spectral properties of the Hamiltonian in our treatment. It may be noted that there is still a lacuna in the treatment for coupling matrix elements $|V|$ being of the order of the field frequency ω. It remains to be shown whether master equations are valid in this case as well. With present experiments mostly the case $|V| \ll \omega$ applies.

The fundamental validity of a master equation treatment being justified, it is possible to obtain some general theoretical *predictions*, which are rather independent of particular molecular properties. Some of these concern the dependence of the unimolecular rate coefficient upon laser intensity. *An absolute upper limit at all intensities is given by* k_{RTB} *Eqs.* (4.25) *and* (5.12). Deviations from this value arise:

(a) at very low intensities due to "early bottleneck" effects. These come from the fact that the intensity independent *diagonal* terms in Eqs. (2.27) or (1.9) play a dominant role compared to the intensity proportional off-diagonal couplings $|V|^2$. This leads to a strong, more than proportional intensity dependence of URIMIR which has been discussed previously (Refs. 20–25 and many experimental papers).

(b) At moderate intensities we may be close to the weak field limit of Sec. IV.B. In this limit the rate constant may be rather close to k_{RTB}, with deviations given by the parameter F_d as discussed in Sec. IV.B. k_{RTB}, and therefore the rate constants in the weak field limit are *proportional* to the laser intensity.

(c) At even higher intensities the rate constant will drop considerably below k_{RTB} for two reasons. Firstly we may make a transition from a master equation Case B to Case D (Sec. III), where the off-diagonal rate coefficients increase only with the square root of the intensity at most. This may or may not happen depending on molecular properties. Secondly, we *always* shall have *unimolecular "fall off."* This arises through the fact that at very high intensities the intensity independent terms in the *diagonal* of the rate coefficient matrix **K** play a dominant role compared to the intensity proportional off-diagonal terms, i.e., the monomolecular reaction step becomes rate determining. Therefore it is not quite true that the *"energy fluence"* of a laser pulse is the only relevant parameter in URIMIR at high intensities.[70] So far no experiments concerning this effect have been reported. We predict, however, that with sufficiently precise measurements the effect could be seen with present laser powers. The best candidates would be large polyatomic molecules or spin-forbidden reactions. Such experiments would provide an interesting check on the theory and also a way to learn more about the dynamics of URIMIR.

(d) Finally, in many experiments with high intensities and short pulses much of the actual reaction may go on far from steady-state. Again, in these cases the time dependent rate coefficient $k(t)$ is always below the steady-state rate coefficient (which is itself below k_{RTB}). In extreme situations with picosecond excitation and large polyatomic molecules the excitation and reaction steps may be completely separated in time as we have noted in Sec. IV.D.

A second set of predictions concerns the product (chemical channels) and product state (physical channels) distributions. In the weak field limit (in the sense of Sec. IV.B.) only the channel with the lowest reaction threshold E_{T1} should be populated if the next threshold E_{T2} is more than $\hbar\omega$ above E_{T1}. At intermediate and high intensities the product ratio changes to become the strong field limit ratio Eq. (4.9) at most (with appropriate changes in the nonsteady-state case). This ratio is quite different from a "thermal" product ratio. It is possible to pump a reaction with a higher threshold more strongly than one with a lower threshold [depending on $W_1(E)$ and $W_2(E)$], however, it is *not* possible to pump the reaction with a higher threshold *selectively*. This is perhaps the most easily tested prediction, using present day experimental techniques. It is not the aim of the present paper to discuss particular experiments, but we do not think that there is any experimental evidence against this prediction so far. The isotopic selectivity arises through the early bottleneck effects and has already been dealt with by other authors.[20–25]

Another aim of the present paper was to clarify[27,70] the relationship between collision-induced *thermal* unimolecular reactions and collisionless unimolecular reactions induced by monochromatic infrared radiation. The fundamental difference between the two types of reaction is the underlying distribution function. For *thermal* reactions this is the Boltzmann distribution characterized by the heat bath temperature T. For URIMIR this is the truncated "microcanonical" equilibrium distribution Eqs. (4.4) and (4.22). We note that actual steady-state (and nonsteady-state) distributions show further deviations from these *underlying* distributions both in thermal reactions and in URIMIR [e.g., Eq. (4.19)]. The point we want to make is that there is *no* theoretical justification for using a Boltzmann distribution for molecular states in collisionless URIMIR nor for using an Arrhenius equation for the rate constant.

Three important omissions of the present paper must be noted at the end. We have not included the possible influence of matter *on* radiation, i.e., our treatment assumes that the field remains unaffected by URIMIR. All sorts of interesting effects may arise if this is not justified at higher gas densities. However, in order to properly separate various effects one should choose the experimental conditions such that our assumption is correct, as is certainly true for some experiments.[18,19] We secondly have disregarded the influence of collisions important at higher gas densities. In the range where master equations are valid for URIMIR one may think of simply adding collisional terms [Eq. (1.5)] to the master equation, using results on collisional energy transfer from the theory of thermal unimolecular reactions.[2,3,64] However such a procedure remains to be justified theoretically. Some aspects of the problem have been discussed in Refs. 68 and 71. Thirdly, we have not made any quantitative calculations for specific experiments. The major reason for this is theoretical. We think it is best to separate the fundamental theory from the experiment specific applications, which mostly depend on additional model assumptions. A fit to an experimental result using some model parameters does not necessarily justify a theory or the underlying physical assumptions. In order to minimize the number of unknown parameters, a theoretical calculation would best be done for a molecule which satisfies the following criteria: (1) The high resolution spectroscopy and at least all harmonic force constants and large amplitude motions (internal rotations, etc.) should be well known. (2) The various reaction thresholds should be known beyond doubt. For this point simple bond fission reactions with known thermochemistry are ideal. (3) The thermal unimolecular reaction in both low and high pressure limits should be investigated quantitatively over a large temperature range. These three criteria may be useful in selecting an ideal test case for quantitative comparison of experiment and theory.

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APPENDIX: DERIVATION OF THE RATE COEFFICIENT FOR CASE B (EQ. 3.12)

We sum Eq. (3.5) over one level index

$$p_I(t) = \sum_{i=1}^{N_I} p_i(t) = \sum_{i=1}^{N_I} \sum_{j=1}^{N_J} |U_{ij(IJ)}|^2 p_{j(J)}(0) . \qquad \text{(A1)}$$

We assume the initial condition $p_J(0) = 1$, $p_j(0) = N_J^{-1}$

$$p_I(t) = N_J^{-1} \sum_{i=1}^{N_I} \sum_{j=1}^{N_J} |U_{ij(IJ)}|^2 . \qquad \text{(A2)}$$

From first order perturbation theory we obtain[29]

$$|U_{ij(IJ)}|^2 = 4 |V_{ij}|^2 \omega_{ij}^{-2} [\sin(\omega_{ij} t/2)]^2 , \qquad \text{(A3)}$$

$$p_I(t) = 4N_J^{-1} \sum_{i=1}^{N_I} \sum_{j=1}^{N_J} |V_{ij(IJ)}|^2 \omega_{ij(IJ)}^{-2} [\sin(\omega_{ij(IJ)} t/2)]^2 . \qquad \text{(A4)}$$

The $|V_{ij}|$ are general *off-diagonal* matrix elements [Eq. (2.27) or (2.32)], the ω_i are general *diagonal* elements and $\omega_{ij} = \omega_i - \omega_j$. We assume that the ω_i and ω_j are independently distributed according to $F(\omega_i) = \delta_I^{-1}$, $F(\omega_j) = \delta_J^{-1}$ and that $|V_{ij}|^2$ are independently distributed over the frequency range Δ at least, such that we can take the *average value* $|V_{IJ}|^2$ out of the sums. (A constant $|V_{ij}|^2$ would do, but is *not necessary.*) Δ is the effective level width, $N_J \delta_J \simeq N_I \delta_I = \Delta$. We can replace the sums by integrals, if N_I and N_J are large

$$p_I = 4 \delta_I^{-1} \Delta^{-1} |V_{IJ}|^2 \iint_{-\Delta/2}^{+\Delta/2} \omega_{IJ}^{-2} \left[\sin\left(\frac{\omega_{IJ} t}{2} \right) \right]^2 d\omega_I \, d\omega_J . \qquad \text{(A5)}$$

The integral can be evaluated approximately by noting that $\int_{-\infty}^{\infty} y^{-2} (\sin y)^2 \, dy = \pi$, with contributions mainly from the range $-\pi < y < +\pi$. This restricts us to times $\Delta \times t > \pi$. We obtain for the value of the double integral $\pi \times \Delta \times t/2$, and for the level population

$$p_I = 2\pi |V_{IJ}|^2 \delta_I^{-1} t . \qquad \text{(A6)}$$

We consider a time t_1 such that $p_I \gg 0$ but $p_J \simeq 1$, therefore we obtain in this time range

$$\mathring{p}_I = 2\pi |V_{IJ}|^2 \delta_I^{-1} = K_{IJ} . \qquad \text{(A7)}$$

We can repeat now the argument starting with a new initial population in (A1). We note that (A1) is valid either for *random* phases or irregular phases in contrast to Eq. (3.5), which is valid for random phase ensembles. Going through this in convenient time steps we get

$$\mathring{p}_I = K_{IJ} p_J - K_{JI} p_I , \qquad \text{(A8)}$$

which is valid for times short compared to the recurrence time. This derivation is not really different from the original one.[47] We have given it in order to make the connection with our coupling matrix elements and frequency spacings. More general master equations can be obtained with much less stringent assumptions,[48–51] however, less simple relationships to molecular parameters.

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