COLLISIONAL EFFECTS IN ELECTRONIC RELAXATION

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CONTENTS

In the past few years some attention has been given to collisional effects on electronic relaxation of gas-phase molecules. By now, a substantial amount of experimental results and some theoretical studies are available.

The aim of this chapter is to give a brief summary of the existing experimental data concerning these effects. These data are treated on the basis of a simple model describing the time evolution of the molecular system collisionally coupled to the translational energy continua. From this point of view our approach is complementary to that adopted in the review article by Freed,[1] where attention is focused more on calculating the cross-section for a collisionally induced transition.

In Section I, we outline principal problems and give a phenomenological description and classification of the collisional effects in some typical molecular systems.

In Section II, we describe briefly the primary collisional effects, vibrational and rotational relaxation and dephasing processes, and discuss their influence on the time evolution of an electronically excited molecular system.

Section III is devoted to a review and analysis of experimental data. Special attention will be given to the problems of the reversibility of the electronic relaxation and to the dependence of the electronic relaxation rates on the intramolecular parameters and on the properties of the collision partner.

Finally, in Section IV we treat some specific problems such as the electronic relaxation in van der Waals complexes, magnetic-field effects, and some finer details of relaxation paths.

Among electronic relaxation processes, the collision-induced intersystem crossing (singlet–triplet transitions in closed shell molecules) have been the most extensively studied. In addition, the intramolecular and intermolecular coupling mechanisms may be more easily separated in this case than in the case of the collision-induced internal conversion. For this reason, our attention will be focused at the problems of collision-induced transitions between different spin manifolds.

I. ESSENTIAL FEATURES OF THE COLLISION-INDUCED ELECTRONIC RELAXATION

A. General Remarks

The efficient quenching of the atomic and molecular fluorescence by collisions has been observed in early studies of the luminescence of gaseous compounds (for a review of early works see Ref. 2). In a large number of cases these processes have been explained by the electronic-to-vibrational energy transfer, charge transfer or excited-complex (excimer or exciplex) formation. There remains, however, an important class of collisional processes corresponding to the essentially intramolecular relaxation induced (or assisted) by collisions with chemically inert partners. In such

cases, only a negligible part of the excited-system energy is transferred to the collision partner or transformed into the translational energy, its major part remains in the initially excited molecule but is redistributed in a different way between its internal degrees of freedom.

One can distinguish between two fundamental types of collision-induced processes:

1. Collisions that do not change the molecular electronic states. Such collisions only lead to relaxation and redistribution of the molecular vibrational and rotational energy.

2. Electronic relaxation: transition from a low (e.g., vibrationless) vibronic level of a higher electronic state to higher vibronic levels of the lower electronic state. Part of the electronic energy of the molecule is then transformed into vibrational energy. Such a transition from the initially excited singlet level to a quan-isoenergetic level of the triplet state is usually referred as the collision–induced intersystem crossing.

The first systematic investigations of collision-induced intersystem crossing have been carried out for a triatomic molecule with "anomalously" long decay time[3]—sulfur dioxide.[4-7] The fluorescence of SO_2, excited in the 260–335 nm spectral region, is efficiently quenched by collisions with ground-state SO_2 molecules and many other chemically inert quenchers with a simultaneous induction of the thermally equilibrated phosphorescence from low vibronic levels of the first excited triplet state. The rate of this transition is of the order of the gas-kinetic collision rate, indicating the high efficiency of such collisions. As a consequence of the high efficiency of the electronic relaxation, vibrational relaxation within the singlet manifold is practically absent.[5]

The collisional fluorescence quenching and phosphorescence induction processes have been later observed for a large number of small and medium-size molecules. The interpretation of these results was however rather confusing: collision-induced intersystem crossing considered as a transition from the pure singlet to the pure triplet state is in apparent contradiction with the Wigner rule of spin conservation,[8] at least in the case of light collision partners that cannot affect the intramolecular spin–orbit interaction.

The essential step in understanding collisionally induced intersystem crossing processes has been made by Gelbart and Freed.[9] In small molecules, the optical excitation does not prepare pure spin states but the quasistationary states resulting from the intramolecular singlet–triplet coupling. In a simple two-level model

$$|\sigma\rangle = \alpha|s\rangle + \beta|l\rangle \qquad \lambda = -\beta|s\rangle + \alpha|l\rangle \qquad (\alpha^2 + \beta^2 = 1)$$

where $|s\rangle$ and $|l\rangle$ are the pure singlet and triplet states, respectively and where (except for the accidental s–l resonance) $\alpha^2 \gg \beta^2$. This idea has been developed by Freed[10,11] who showed that in the limiting case of very weak perturbations (treated by first-order time-dependent perturbation theory) the probability of the collision-induced intersystem crossing (and the corresponding cross-section σ_{ISC}) is proportional to the mixing coefficient β^2 characterizing the initially prepared σ state and goes to zero when $\beta^2 \to 0$.

The last conclusion has been confirmed by the experimental study of collision induced transitions between singlet and triplet manifolds of the simplest atomic system—the helium atom. It has been shown[12,13] that collision may transfer helium atoms from singlet to triplet states but only by a very specific reaction path: collisional relaxation within the singlet manifold populates high n^1F states—nearly degenerate and significantly mixed with the corresponding n^3F states; the $n^1F \rightleftharpoons n^3F$ transitions are allowed ($\beta^2 \neq 0$) and further collisional relaxation within the triplet manifold transfers the atoms to pure triplet levels.

The experimental evidence indicating the absence of transitions between pure spin states must be kept in mind in each treatment of collision-induced transitions carried out in the basis of such states. We have to assume that collisions cannot directly induce transitions between $\{|s\rangle\}$ and $\{|l\rangle\}$ states but only the relaxation within the $\{|s\rangle\}$ and the $\{|l\rangle\}$ manifolds, which in turn affects the populations of the $|s\rangle$ and the $|l\rangle$ states.*

We propose in the following a simple model describing the time evolution of an electronically excited molecule perturbed by collisions, where the role of the latter is limited to "primary" collisional processes: vibrational and rotational relaxation within each spin manifold and collisional dephasing. We follow here the way indicated by Voltz[15] and Mukamel[16] in their studies of collision-induced intersystem crossing and by Derouard et al.,[17,18] who applied a similar treatment to the specific case of the singlet–triplet anticrossing in strong magnetic fields. This model can account for the apparent wide variety of collisional effects on the fluorescence decay and quantum yield in different classes of molecules. The actually available experimental material is rich enough and makes it possible to distinguish between several types of behavior of different molecules and to relate them to the character of the interstate coupling in these species.

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*This assumption is not strictly valid in the case of heavy collision partners, which may influence the intramolecular spin-orbit coupling by the heavy atom effect.[14] Collisions may also couple two electronic states belonging to the same spin manifold by the breakdown of orbital symmetry.

B. Phenomenological Description of Collisional Effects

The excited molecular systems may be roughly divided into a few groups characterized by the level-coupling schemes and the nature of the initially prepared state. Each of them shows a specific form of the fluorescence decay under collision-free conditions.[19, 20] The collisional effects in each group of molecules are also quite similar.

(a) "Large" molecules belonging to the "statistical limit" are well described in terms of a single radiative level $|s\rangle$ coupled to the $\{|l\rangle\}$ quasicontinuum. The fluorescence decay of the isolated molecule is exponential with decay time shorter than radiative lifetime (fluorescence yield smaller than unity). This decay is practically insensitive to collisional effects, when corrected for the vibrational and rotational relaxation within the $\{|s\rangle\}$ manifold. For benzene, the constant fluorescence yield in the wide pressure range has been first evidenced in the classical work of Kistiakovsky and Parmenter.[21] A similar behavior has been observed in the case of naphthalene, where the fluorescence decay time, as well as the triplet growth time and quantum yield do not depend on the pressure of the added inert gas.[22, 23]

(b) A group of medium-size molecules may be described in terms of a strong coupling between a single radiative $|s\rangle$ state and a number of discrete $|l\rangle$ states giving origin to a band of quasistationary states sharing the $|s\rangle$ oscillator strength. This is the strong-coupling sparse intermediate case of the theory of radiationless transitions. The excitation of individual quasistationary states results in a quasiexponential, anomalously long decay with lifetimes longer than the radiative lifetime. Collisions with inert partners induce a very efficient quenching in this case: the quenching constant k_q is equal to or higher than k_{coll}—the gas-kinetic collision rate in the hard sphere approximation. The decay remains exponential in a wide pressure range, the fluorescence decay time τ and fluorescence yield Q_f may be described by the Stern–Volmer law:

$$\frac{1}{\tau(p)} = \frac{1}{\tau(0)} + k_q P \qquad \frac{Q_f(0)}{Q_f(p)} = 1 + k_q \tau(0) P \qquad (1)$$

SO_2,[5-7] benzophenone,[24-26] and benzoquinone[27] belongs to this group.

(c) The coherent excitation of a band of quasistationary states resulting from the s-l coupling leads to a quasibiexponential fluorescence decay: its first component corresponds to the dephasing of the initially prepared coherent superposition of states, while the latter one is due to the indepen-

dent (incoherent) decay of individual states with anomalously long decay time as in the previous case. This is the coherently excited strong-coupling dense intermediate case of the theory of radiationless transitions. The first component of the decay is practically unaffected by collisions, while the second one is efficiently quenched, $k_q \gtrsim k_{coll}$. At sufficiently high gas pressures the first component prevails and the excited system shows an exponential decay as in the statistical case. Obviously, the pressure dependence of the fluorescence yield shows a strong deviation from the Stern–Volmer law.[28,29] Such a behavior has been observed in the case of pyrazine,[29] pyrimidine,[30] quinoxaline,[31,32] and biacetyl.[33]

(d) In a number of small polyatomic and diatomic molecules, the singlet–triplet (s-l) coupling may be treated in terms of the weak-coupling limit where efficient coupling exsists mostly between pairs of $|s\rangle$ and $|l\rangle$ states. The resulting $|\sigma\rangle$ and $|\lambda\rangle$ states have (except in the case if s-l quasiresonance) strongly predominant s- and l-character, respectively (see above). The optical excitation prepares essentially quasistationary states which, under collision-free conditions, decay exponentially with lifetime $\tau_\sigma \simeq \tau_s$. Collisions quench the fluorescence and the Stern–Volmer law may be applied, but the quenching constant is in general much lower than in previous cases (about 10% of k_{coll}) and depends strongly on the properties of the collision partner. Glyoxal[34,35] and propynal[36] as well as a number of diatomic molecules have to be classified in this group.

(e) In a few cases of diatomic molecules in excited states: the $A^1\pi$ state of CO[37,38] or the $B^3\pi_g$ state of N_2^{39}, the fluorescence decay which is quasiexponential under collision-free conditions is strongly modified by collisions. At sufficiently high gas pressures it may be approximated by a biexponential process with τ_1 shorter and τ_2 longer than the collision-free lifetime τ_σ. The pressure dependence of the decay and of the fluorescence quantum yield cannot be described by the Stern–Volmer law using a single quenching constant k_q.

We should keep in mind that the population of the $|l\rangle$ (triplet) levels isoenergetic with the initially excited $|s\rangle$ state may be also monitored, either by transient absorption or by resonant emmision. In the cases (a)–(c), the l-state population builds up due to the intramolecular processes at a pressure-independent rate.[22,23,32,40] Collisions lead to vibrational relaxation within the triplet manifold that populates the lower triplet levels and induces the (thermally equilibrated) phosphorescence emission. In the cases (d) and (e), the initial population of the $\{|l\rangle\}$ levels is close to zero and it grows with a pressure-dependent rate as shown by Slanger[41] in his study of the pressure dependence of the $d^3\Delta \rightarrow a^3\pi$ emission of CO under the optical excitation of the $A^1\pi$ state. One may conclude that in the first
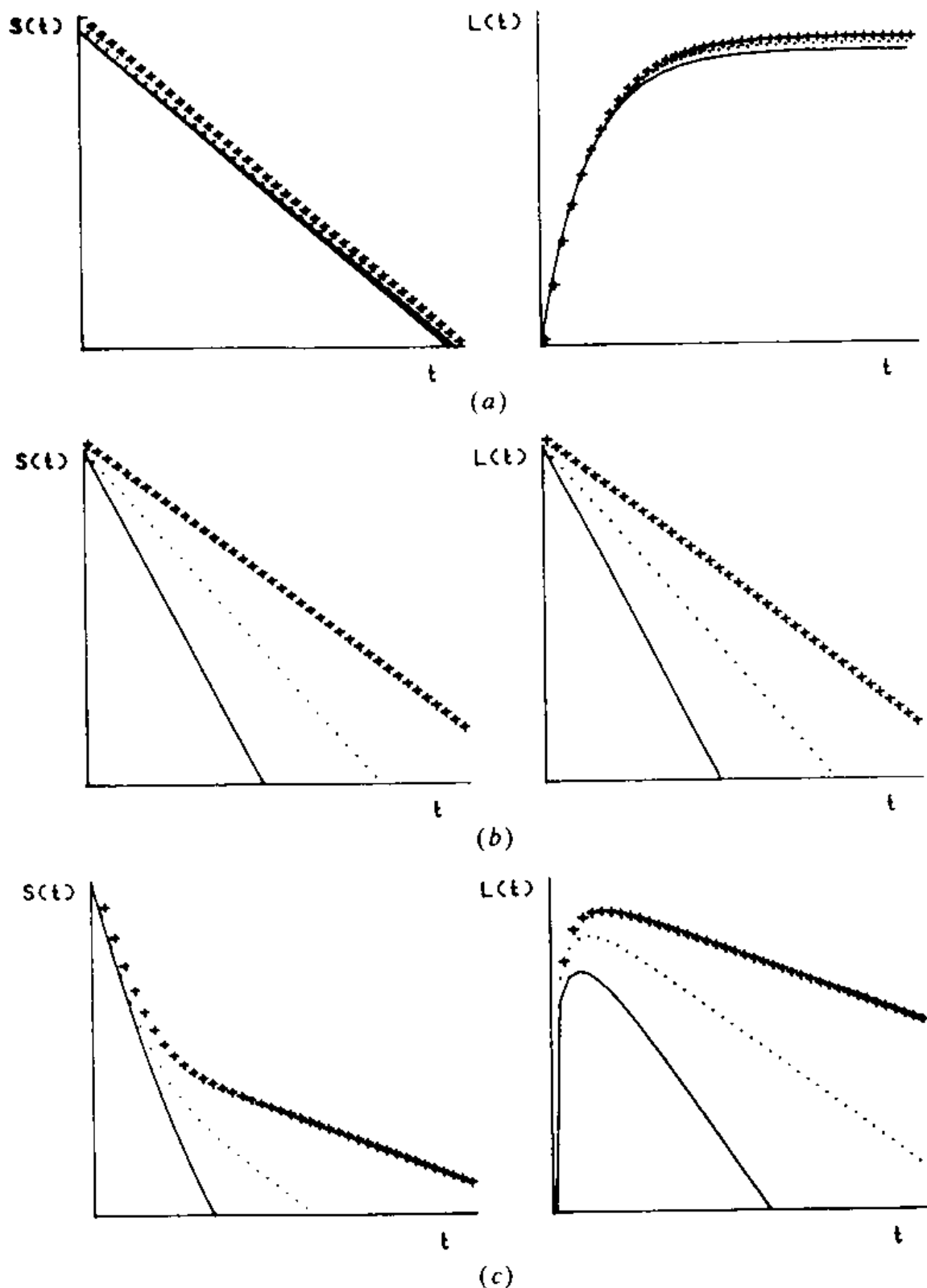
Fig. 1 Schematic representation of the pressure effect on the singlet ($S(t) = \log\langle s|\psi(t)\rangle^2$) and triplet ($L(t) = \log\langle 1|\psi(t)\rangle^2$) content of the excited molecular state. Crosses, collision-free conditions, points and solid line, increasing inert-gas pressure. (a) statistical-limit; (b) strong-coupling case (incoherent excitation); (c) strong coupling case (coherent excitation); (d) weak-coupling case (small polyatomics); (e) weak-coupling case (CO, N_2).

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(d)

(e)
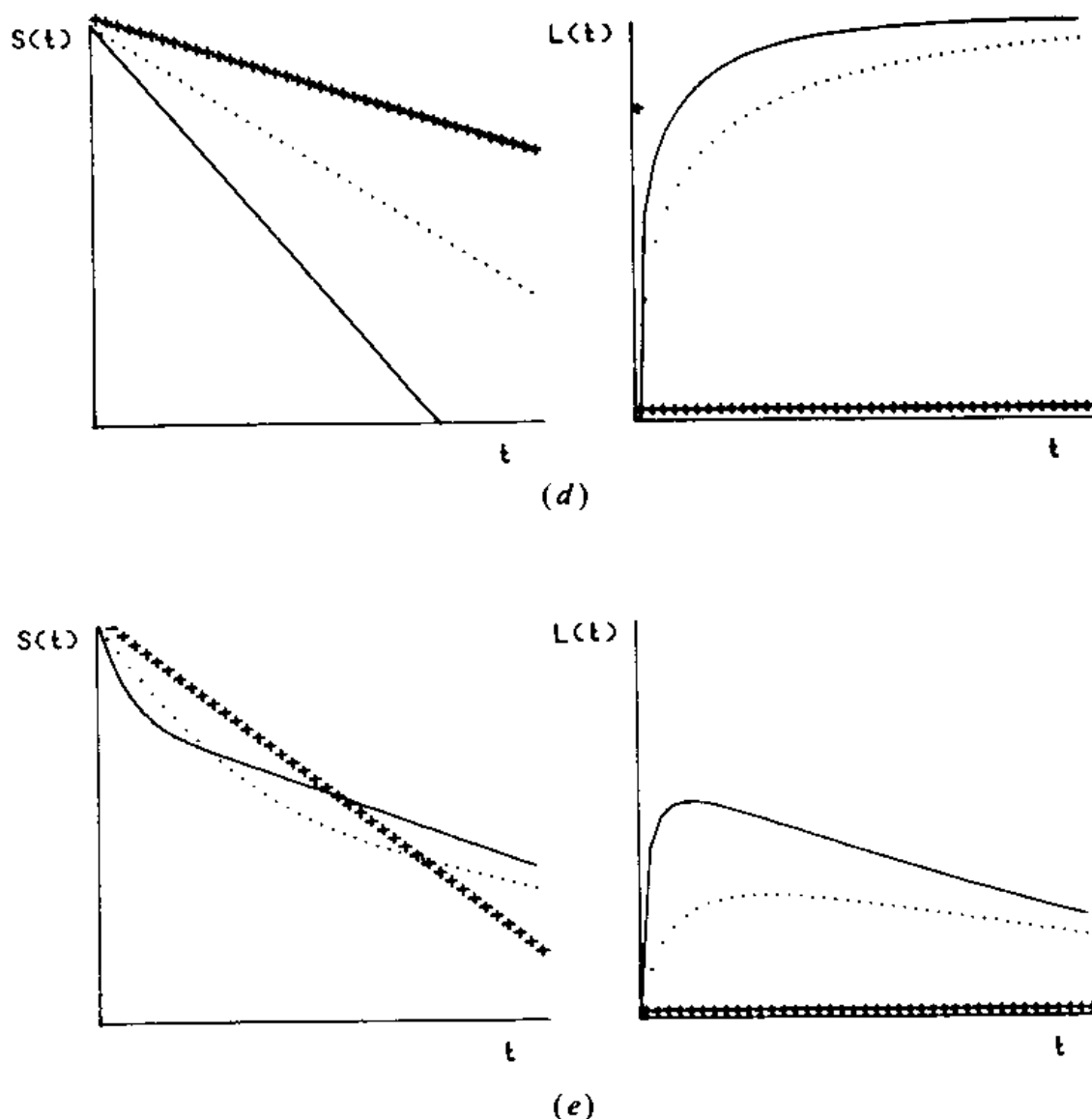
Fig. 1   (Continued)

case collisions maintain the inherent triplet character of the excited molecular state, while in the latter one they really induce the singlet–triplet transitions.

Pressure effects on the time dependence of the $|s\rangle$ and $|l\rangle$ states populations are schematically represented in Fig. 1.

II. MODEL TREATMENT OF THE COLLISION-INDUCED ELECTRONIC RELAXATION

A. Outline

In the absence of external perturbations, the time evolution of an excited, collision-free molecule is described in terms of its density matrix ρ

by the following set of equations:

$$\dot{\rho}_{ss} = i \sum_l (v_{ls}\rho_{sl} - v_{sl}\rho_{ls})$$

$$\dot{\rho}_{ll} = i \sum_s (v_{sl}\rho_{ls} - v_{ls}\rho_{sl})$$

$$\dot{\rho}_{ss'} = -i\epsilon_{ss'}\rho_{ss'} + i \sum_l (v_{ls'}\rho_{sl} - v_{sl}\rho_{ls'})$$

$$\dot{\rho}_{ll'} = -i\epsilon_{ll'}\rho_{ll'} + i \sum_s (v_{sl}\rho_{ls} - v_{ls}\rho_{sl'})$$

$$\dot{\rho}_{sl} = -i\epsilon_{sl}P_{sl} + i \sum_{s'} v_{s'l}\rho_{ss'} - i \sum_{l'} v_{sl'}\rho_{l'l} \qquad (2)$$

This evolution will be modified in the presence of collisions by what was previously defined as "primary" processes: vibrational and rotational relaxation within the $|s\rangle$ and $\{|l\rangle\}$ manifolds, dephasing of initially prepared coherent states and (in principle) coherence-transfer effects. The basis of zero-order states (pure-spin states in the case of intersystem crossing) has been chosen for this discussion, because it provides clear separation of intramolecular and intermolecular effects: the $|s\rangle$ and $|l\rangle$ states are mutually coupled by the intramolecular (spin–orbit) coupling v_{sl}, while collisions may uniquely couple $|s\rangle$ and $|s'\rangle$ ($|l\rangle$ and $|l'\rangle$) states within each manifold.

Without attempting a general discussion of dephasing and of vibrational and rotational relaxation processes it seems useful to give here a short summary of the essential features of "primary" collision effects.

B. "Primary" Collision Effects

1. Rotational Relaxation

It is well known that rotational relaxation in the ground and excited electronic states is highly efficient, and its rate is of the same order (or higher) as the gas-kinetic collision rate in the hard-sphere approximation.[42] This means that collisions with large impact parameters b involving the attractive part of the intermolecular potential are at least as important as head-on collisions. This assumption has been directly confirmed in cross-beam experiments[43] by the angular distribution of rotationally relaxed (or excited) molecules. In addition, a good correlation between cross-sections of rotational relaxation σ_{rot} and the depth of the potential energy well for a large series of colliders confirms the role of attractive interactions.[44]

Satisfactory correlations have been equally obtained between σ_{rot} and the strength of van der Waals forces expressed by such parameters of the collider as its dipole moment, polarizibility and ionization potential.[45]

Rotational relaxation (at least for nonresonant interactions) does not show any general propensity rules.[42] Differential cross-sections for $J \rightarrow J'$ rotational relaxation show only a slight dependence on ΔJ and ΔE, as long as ΔE does not exceed kT. The efficient transition into a large number of rotational levels in a single collision has been observed in many molecules such as OH,[46] I_2,[47] NO,[48] glyoxal,[49, 50] and benzene.[54]

In most cases, the rotation-level spacing is small as compared to kT. Therefore, rotational relaxation may be considered as a reversible process leading to a rapid establishment of the Boltzmann equilibrium between populations of rotational levels within a given vibronic state. The equilibrium (Boltzmann) density matrix is diagonal, i.e., all phase information is lost during the rotational (collision-induced) relaxation. The effect may be described by the supplementary terms to (2)

$$\dot{\rho}_{ll} = \sum_{l \neq l} (k_{ll'}\rho_{l'l'} - k_{l'l}\rho_{ll})$$

$$\dot{\rho}_{ll'} = -\frac{1}{2} \left(\sum_{l'' \neq l} k_{l''l} + \sum_{l'' \neq l'} k_{l''l'} \right) \rho_{ll'} \tag{3}$$

$k_{ll'}$ and $k_{l'l}$ are related to each other by the detailed balance requirement:

$$\frac{k_{ll'}}{k_{l'l}} = \frac{g_l}{g_{l'}} exp\left(\frac{\epsilon_{l'l}}{kT}\right) \qquad (\epsilon_{l'l} = \epsilon_{l'} - \epsilon_l) \tag{4}$$

where g_l and $g_{l'}$ represent degeneracies of $|l\rangle$ and $|l'\rangle$ levels and $\epsilon_{l'l}$ —their energy spacing. Similar equations apply within the $\{|s\rangle\}$ manifold. We assume in the following that $k_{ll'}$, $k_{l'l}$, $k_{ss'}$ and $k_{s's}$ are proportional to the perturbing gas pressure.

2. Vibrational Relaxation

The rate of collisionally induced vibrational relaxation varies within extremely wide limits: for diatomic molecules with high vibrational frequencies, particularly in the ground electronic state, the vibrational relaxation rate constant k_{vib} is of the order of $1 \text{ s}^{-1} \text{ torr}^{-1}$ (e.g., $CO + He$)[52], while in the A state of the CF_2 radical k_{vib} varies between $1 \cdot 10^4$ and $6 \cdot 10^4$ for $v = 1$ level and between 2.10^5 and $1 \cdot 2 \cdot 10^6$ for $v = 6$ level for different collision partners.[53] k_{vib} attains the gas-kinetic collision rate for relatively large polyatomic molecules in excited electronic states ($k_{vib} \simeq 10^7 \text{ s}^{-1} \text{ torr}^{-1}$ for 6^1 level of the B_{2u} state of benzene with hexane or heptane as collision partners).[54]

It seems well established that the vibrational relaxation in small molecules is correctly described by the SSH model[55] assuming the dominant role of repulsive interactions. The mechanisms of the vibrational relaxation in medium-size molecules is certainly more complex and not completely elucidated. Recent studies carried out in the low-pressure range (one collision per lifetime) indicate that collisions may lead to highly selective transitions to some specific vibronic states; these "propensity rules" cannot be explained by simple consideration of ΔE (energy) and Δv (vibrational quantum number) changes (as in the SSH model) but are related to some dynamical properties of vibrational modes[54,56,57].

It should be noted that even if the attractive part of the intermolecular potential plays a nonnegligible role in the vibrational relaxation, there is no apparent correlation between rotational and vibrational relaxation rates. As may be seen from the foregoing discussion, k_{rot}/k_{vib} ratios may vary by many orders of magnitude.

In small molecules and also at the bottom of the vibrational manifold of larger molecules, the vibrational levels are sparsely spaced (vibrational energy spacing larger than kT), and vibrational relaxation is relatively slow and may be considered as irreversible. If we consider the interaction between the vibrationless level of the $\{|s\rangle\}$ manifold and between higher vibronic levels of the $\{|l\rangle\}$ manifold, the vibrational relaxation in the $\{|s\rangle\}$ manifold may be neglected. Thus the $|s\rangle$ level decays only radiatively with the rate constant $k_s = k_s^r$, while the decay rate of the $|l\rangle$ levels is given by the rate constant $k_l = k_l^r + k_l^{vr}$, k_l^{vr} (proportional to the gas pressure) being the rate of depopulation by vibrational relaxation within the $\{|l\rangle\}$ manifold. k_s^r and k_l^r are radiative relaxation rates (k_l^r is assumed to vanish when $|l\rangle$ belong to the lowest triplet state of the molecule). The radiative and vibrational irreversible decay may be accounted for by:

$$\dot{\rho}_{ss} = -k_s^r \rho_{ss} \qquad \dot{\rho}_{ll} = -k_l \rho_{ll}$$

$$\dot{\rho}_{ll'} = -\frac{1}{2}(k_l + k_{l'})\rho_{ll'} \simeq -k_l \rho_{ll'}$$

$$\dot{\rho}_{ss'} = -\frac{1}{2}(k_s^r + k_{s'}^r)\rho_{ss'} \simeq k_s^r \rho_{ss'}$$

$$\dot{\rho}_{sl} = -\frac{1}{2}(k_s^r + k_l)\rho_{sl} \qquad (5)$$

It should be noted that vibrational relaxation is taken here into account in a highly simplified way—a damping process that takes place in addition to radiative damping. This is sufficient for our purpose because, as stated above, vibrational relaxation is essentially irreversible and because we are interested in the population change only within the originally excited

energy regime. Different situations may require that we treat vibrational relaxation similarly to rotational relaxation as described above.

3. Dephasing Effects

In addition to actual transitions between energy levels, collisions may result in a phase change in the molecular state without a change in the state itself. This occurs when an adiabatic energy change takes place during the collision, and leads to a phase relaxation in the molecular state. This dephasing effect may be accounted for by introducing damping of the off-diagonal elements in the density matrix with the corresponding rates γ_{sl}, $\gamma_{ll'}$, and $\gamma_{ss'}$ taken to be proportional to the gas pressure:

$$\dot{\rho}_{sl} = -\gamma_{sl}\rho_{sl} \qquad \dot{\rho}_{ll'} = -\gamma_{ll'}\rho_{ll}, \qquad \rho_{ss'} = -\gamma_{ss'}\rho_{ss'} \tag{6}$$

Dephasing plays a fundamental role in the homogeneous broadening of energy levels in the case of atoms where the population relaxation is relatively inefficient. Its importance for molecules has not been sufficiently elucidated: one can argue that with a high probability of rotational relaxation the importance of pure dephasing collisions will be smaller. Nevertheless, recent studies using the optical transient techniques suggest that the role of pure dephasing is nonnegligible: the cross-sections for dephasing collisions for iodine B^3O_u+ state are about twice as large as those for rotational relaxation[58] in this system.

C. Time Evolution of the Collisionally Perturbed Molecule

The time evolution of the molecule under the combined effect of collisions and of the intramolecular interactions is described by the set of equations[59,60]

$$\dot{\rho}_{ss} = i\sum_l (v_{ls}\rho_{sl} - v_{sl}\rho_{ls}) - k'_s\rho_{ss} + \sum_{s' \neq s} (k_{ss'}\rho_{s's} - k_{s's}\rho_{ss})$$

$$\dot{\rho}_{ll} = -i\sum_s (v_{sl}\rho_{ls} - v_{ls}\rho_{sl}) - k_l\rho_{ll} + \sum_{l'} (k_{ll'}\rho_{l'l'} - k_{l'l}\rho_{ll}) \tag{7a}$$

for the diagonal elements of the molecular density matrix and

$$\dot{\rho}_{ss'} = -i\epsilon_{ss'}\rho_{ss'} + i\sum_l (v_{ls'}\rho_{sl} - v_{sl}\rho_{ls'}) - \bar{\gamma}_{ss'}\rho_{ss'}$$

$$\dot{\rho}_{ll'} = -i\epsilon_{ll'}\rho_{ll'} + i\sum_s (v_{sl'}\rho_{ls} - v_{ls}\rho_{sl'}) - \bar{\gamma}_{ll'}\rho_{ll'}$$

$$\dot{\rho}_{sl} = -i\epsilon_{sl}\rho_{sl} + i\sum_{s'} v_{s'l}\rho_{ss'} - i\sum_{l'} v_{sl'}\rho_{l'l} - \gamma_{sl}\rho_{sl} \tag{7b}$$

for the nondiagonal density matrix elements.

In these equations, the rates $\bar{\gamma}$ include contributions from the rotational (reversible) relaxation, the vibrational and the radiative (irreversible) relaxations and from dephasing (proper T_2) processes:

$$\bar{\gamma}_{ss'} = \frac{1}{2}\left(\sum_{s'' \neq s} k_{s''s} + \sum_{s'' \neq s'} k_{s''s'} \right) + k_s^r + \gamma_{ss'}$$

$$\bar{\gamma}_{ll'} = \frac{1}{2}\left(\sum_{l'' \neq l} k_{l''l} + \sum_{l'' \neq l'} k_{l''l'} + k_l + k_{l'} \right) + \gamma_{ll'}$$

$$\bar{\gamma}_{sl} = \frac{1}{2}\left(\sum_{s' \neq s} k_{s's} + \sum_{l' \neq l} k_{l'l} + k_s^r + k_l \right) + \gamma_{sl} \tag{8}$$

In addition to relaxation and dephasing, the coupling to the thermal bath may shift the position of energy levels. In (7b) it is assumed that the energy differences ϵ_{sl} etc. already include this shift.

It should be noted that several approximations have to be introduced in order to get (7)–(8). The general expression for the time evolution of the molecular density matrix may be written in the form[61-63]

$$\dot{\rho} = -i[H_0 + V, \rho] + \int_0^t R(t-\tau)\rho(\tau)\, d\tau \tag{9}$$

where H_0 is the zero-order molecular hamiltonian, V is the intramolecular $(\{|s\rangle\} - \{|l\rangle\})$ coupling and where the tetradic operator R accounts for the thermal relaxation effects. Equation (7) involves first the Markoffian approximation, neglecting memory effects in (9). In the Markoffian limit, we have:

$$\dot{\rho}_{ij} = -i\epsilon_{ij}\rho_{ij} + i\sum_k (v_{kj}\rho_{ik} - v_{ik}\rho_{kj}) + \sum_{lm} R_{ijlm}\rho_{lm} \tag{10}$$

Equations (7) are of this form with explicit expressions for the elements of the tetradic R. Further approximations are involved at this point. It is common[59,60] to disregard elements r_{ijlm} for which $|\epsilon_{lm} - \epsilon_{ij}| > |R|$. In this spirit, elements of R that couple diagonal and off-diagonal elements of the density matrix are neglected in (7). So are R elements which couple coherence (off-diagonal) terms of ρ to other such terms. This approximation is valid as long as the pressure broadening is much smaller than the average level spacing. We shall use (7) also for higher pressure as a qualitative tool for estimating collisional effects. Note that in the high-pressure limit (pressure broadening much larger than the average level spacing) the pressure effect saturates, and the molecule behaves as a "large" (statistical-limit) molecule. Equation (7) correctly describes this

limit (see below), so that the approximation involved here is expected to affect only details of the relaxation behavior in the intermediate pressure range.

In what follows, we shall consider a few simple models based on (7).

D. Small-Molecule Weak-Coupling Case

As a prototype model for the decay of an excited molecule in presence of collisions we first consider the system schematically represented in Fig. 2: Two pure-spin states $|svj\rangle$ and $|lv'J\rangle$ (s and l now denote the electronic states while v, v' and J, J' stand for the vibrational and rotational quantum numbers, respectively below we often drop the specification of the vibrational levels) are intramolecularly coupled by the matrix element v_{sl} while the intramolecular coupling between all other levels belonging to the $\{|s\rangle\}$ and $\{|l\rangle\}$ manifolds is disregarded. This picture corresponds to a simplified description of a strongly localized intramolecular perturbation between two sets of rovibronic levels $\{|s, J\rangle\}$ and $\{|l, J'\rangle\}$, where a nonnegligible mixing occurs only between a single pair of levels $|s, J\rangle$ and $|l, J\rangle$ (with energies ϵ_{sJ} and ϵ_{lJ}) and gives rise to a pair of quasistationary states $|\sigma, J\rangle$ and $|\lambda, J\rangle$:

$$|\sigma, J\rangle = \alpha|s, J\rangle + \beta|l, J\rangle$$
$$|\lambda, J\rangle = -\beta|s, J\rangle + \alpha|l, J\rangle \tag{11}$$

where $\alpha = \cos(\phi/2), \beta = \sin(\phi/2), tg\phi = 2v_{sl}/(\epsilon_{sJ} - \epsilon_{lJ})$ (12)

For all other states with $J' \neq J$, we have:

$$|\sigma, J'\rangle \equiv |s, J'\rangle \qquad |\lambda, J'\rangle \equiv |l, J'\rangle \tag{13}$$

A further simplification consists in replacing the whole set of $\{|s, J'\rangle\}$ levels $(J' \neq J)$ by a single state $|u\rangle$, and the set of $\{|l, J'\rangle\}$ levels $(J \neq J)$
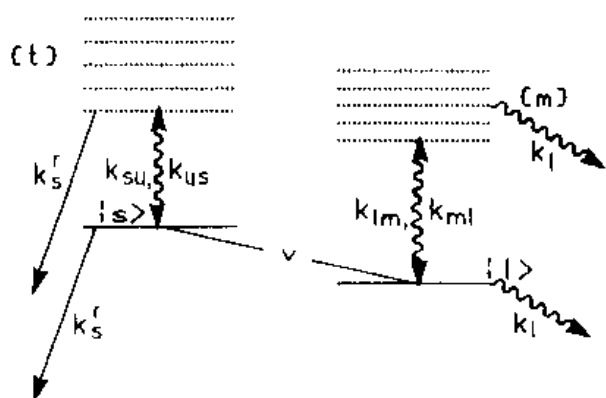

Fig. 2 Four-level model. Energy levels and transition rates.

by a single state $|m\rangle$. For this four-level model, (7) reduces to the form:

$$\dot{\rho}_{ss} = i(V_{ls}\rho_{sl} - V_{sl}\rho_{ls}) - k_s^r\rho_{ss}$$

$$\dot{\rho}_{ll} = i(V_{sl}\rho_{ls} - V_{ls}\rho_{sl}) - k_l\rho_{ll} + (k_{lm}\rho_{mm} - k_{ml}\rho_{ll})$$

$$\dot{\rho}_{mm} = -k_m\rho_{mm} + (k_{ml}\rho_{ll} - k_{lm}\rho_{mm})$$

$$\dot{\rho}_{uu} = -k_s^r\rho_{ss} + (k_{us}\rho_{ss} - k_{su}\rho_{uu})$$

$$\dot{\rho}_{sl} = -i\epsilon_{sl}\rho_{sl} + iV_{sl}(\rho_{ss} - \rho_{ll}) - \bar{\gamma}_{sl}\rho_{sl}$$

$$\dot{\rho}_{lm} = -i\epsilon_{lm}\rho_{lm} - \bar{\gamma}_{lm}\rho_{lm}$$

$$\dot{\rho} = -i\epsilon_{su}\rho_{su} - \bar{\gamma}_{su}\rho_{su} \tag{14}$$

where:

$$\bar{\gamma}_{sl} = \gamma_{sl} + \tfrac{1}{2}(k_{ml} + k_{us}) + \tfrac{1}{2}(k_s^r + k_l)$$

$$\bar{\gamma}_{lm} = \gamma_{lm} + \tfrac{1}{2}(k_{lm} + k_{ml}) + \tfrac{1}{2}(k_l + k_m)$$

$$\bar{\gamma}_{su} = \gamma_{su} + \tfrac{1}{2}(k_{us} + k_{su}) + k_s^r$$

Equation (14) describes the time evolution of the intramolecularly coupled pair of levels following optical excitation, where collisional coupling to other levels is accounted for by considering two additional representative levels. We expect that this picture may qualitatively account for the more important features of the collisionally induced electronic relaxation.

The existence of the intramolecular coupling between the levels $|s\rangle$ and $|l\rangle$ implies that under selective excitation the initially excited state of the molecule is the stationary state of the isolated molecule $|\sigma, J\rangle$. This corresponds to the initial form of the density matrix in the s, l, u, m basis:

$$\rho(t=0) = \begin{bmatrix} \alpha^2 & \alpha\beta & 0 & 0 \\ \alpha\beta & \beta^2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \tag{15}$$

Equation (7) implies that with this initial condition the off-diagonal elements of ρ involving the m and u levels will be zero for all times t:

$$\rho_{sm}(t) = \rho_{lm}(t) = \rho_{su}(t) = \rho_{lu}(t) = 0 \tag{16}$$

We will not try to solve (14) exactly but only to discuss approximate solution under different limiting conditions. We shall also present some

results of computer simulations for physically reasonable sets of rate constants k and γ. We first estimate separately the influence of collisional dephasing and of rotational and vibrational relaxation on the time evolution of the excited system.

Since in most real experiments the population of the radiative states is monitored by the intensity of the (spectrally unresolved) fluorescence (emitted from the $|s\rangle$ and $|u\rangle$ levels) we are essentially interested in the overall population $\rho_{ss} + \rho_{uu}$. Similarly the overall population of the optically nonactive levels $\rho_{ll} + \rho_{mm}$ (which may be monitored by transient absorption or by emission within the triplet manifold) is of interest.

1. Pure Dephasing Only

To consider the effect of pure dephasing we take $k_{lm} = k_{ml} = k_{sl} = k_{ls} = 0$, $k_s^r \neq 0$, $\gamma_{sl} \neq 0$. If we suppose that dephasing is fast relative to the intramolecular evolution: $\gamma_{sl} > v_{sl}$, we may approximate ρ_{sl} by its instantaneous stationary value taking $\dot{\rho}_{sl} = 0$ whereupon

$$\rho_{sl} = \frac{iv_{sl}(\rho_{ss} - \rho_{ll})}{i\epsilon_{sl} + \bar{\gamma}_{sl}} \tag{17}$$

This leads to a set of rate equations for ρ_{ss} and ρ_{ll} (obviously in this case $\rho_{mm}(t) = \rho_{uu}(t) = 0$ for all times t)

$$\dot{\rho}_{ss} = -K_{ls}\rho_{ss} - k_s^r\rho_{ss} + K_{sl}\rho_{ll}$$

$$\dot{\rho}_{ll} = K_{ls}\rho_{ss} - K_{sl}\rho_{ll} \tag{18}$$

where

$$K_{sl} = K_{ls} = \frac{2\bar{\gamma}_{sl}v_{sl}^2}{\epsilon_{sl}^2 + \bar{\gamma}_{sl}^2} \tag{19}$$

and where

$$\bar{\gamma}_{sl} = \frac{k_s^r}{2} + \gamma_{sl}$$

We see that in this case, following the initial dephasing, the subsequent evolution of the system may be correctly described by rate equations involving only the populations of the zero-order states and formally identical to usual equations of chemical kinetics. It is, however, interesting to note that the transition rate K_{sl} is *not* proportional to the perturber

pressure as it was assumed for the rates k_1^{vr}, k_{lm}, and k_{su}, but depends on the gas pressure in a more complex way. In the limiting case of weak intramolecular and intermolecular perturbations (weak relative to the level spacing, $\epsilon_{sl}^2 \gg v_{sl}^2$, $\bar{\gamma}_{sl}^2$) we have:

$$K_{sl} = K_{ls} = 2\beta^2 \bar{\gamma}_{sl}$$

K_{sl} is thus proportional to β^2, i.e., to the l-state content in the initially prepared quasistationary state. This conclusion, which readily follows from (15) and (19), is the same as deduced by Freed[11] from first-order perturbation treatment of collision-induced electronic transitions. In the other extreme limit, $\bar{\gamma}_{sl} \gg \epsilon_{sl}$, the rates $K_{sl} = K_{ls}$ become inversely proportional to $\bar{\gamma}_{sl}$. This results from the dilution of the coupling over the pressure-broadened l level (similar effects have been discussed with respect to line broadening[64,65]). However, in this limit the broadened levels may overlap and a model based on two levels only breaks down (see below).

2. Dephasing + Rotational Relaxation

In all real systems the effects of dephasing and of rotational relaxation are superimposed. The overall behavior is similar to that described in the previous case, except that now the populations of the $|m\rangle$ and $|u\rangle$ levels do not vanish. After the rapid decay of coherences, the evolution of the system is governed by the rate equations:

$$\dot{\rho}_{ss} = -(K_{ls} + k_s')\rho_{ss} + K_{sl}\rho_{ll} + k_{su}\rho_{uu}$$

$$\dot{\rho}_{ll} = K_{ls}\rho_{ss} - (K_{sl} + k_{ml})\rho_{ll} + k_{lm}\rho_{mm}$$

$$\dot{\rho}_{mm} = k_{ml}\rho_{ll} - k_{lm}\rho_{mm}$$

$$\dot{\rho}_{uu} = k_{us}\rho_{ss} - k_{su}\rho_{uu} \tag{20}$$

Here $K_{sl} = K_{ls}$ are again given by (19) with $\bar{\gamma}_{sl}$ defined by (11) (including the rotational relaxation contribution). Again these rate constants are proportional (in the very weak mixing limit) to the β^2 mixing coefficient of the initially excited state and show a linear dependence on $\bar{\gamma}_{sl}$ as long as $\bar{\gamma}_{sl} \ll \epsilon_{sl}$.

Collisions destroy the coherences associated with the initially prepared state and induce transitions between rotational levels. This results in redistribution of population between all interacting levels but the overall population (the trace of the density matrix) is not affected and decays only radiatively with the rate $k_s'(\rho_{ss} + \rho_{uu})$. Collisions, thus, modify the form of the excited-state decay but the overall fluorescence yield remains equal to one unless the levels s, u, and/or l, m are subjected to additional nonradiative decay processes (e.g., in the case of predissociation).

3. Effects of Vibrational Relaxation

Vibrational relaxation opens an additional decay channel due to irreversible transitions from the $|l\rangle$ and $|m\rangle$ levels to lower-lying vibronic states of the $\{|l\rangle\}$ manifold. The overall set of rate equation describing the system after the initial dephasing is

$$\dot{\rho}_{ss} = -(K_{ls}+k'_s)\rho_{ss}+K_{sl}\rho_{ll}+k_{su}\rho_{uu}$$

$$\dot{\rho}_{ll} = K_{ls}\rho_{ss}-(K_{sl}+k_{ml}+k_l)\rho_{ll}+k_{lm}\rho_{mm}$$

$$\dot{\rho}_{mm} = k_{ml}\rho_{ll}-(k_{lm}+k_m)\rho_{mm}$$

$$\dot{\rho}_{uu} = k_{us}\rho_{ss}-(k_{su}+k'_s)\rho_{uu} \tag{21}$$

The rates k_l and k_m correspond to any nonradiative decay channel, which couple to the levels $|l\rangle$ and $|m\rangle$. It should be kept in mind, however, that reverse collisionally induced electronic transitions may follow vibrational relaxation in the $\{|l\rangle\}$ manifold, thus leading to further emission. This effect must be taken into account when the $|s\rangle$ level is not the lowest one in the $\{|s\rangle\}$ manifold (see Section III.B).

4. Discussion

Equation (21) may be easily solved yielding a time evolution characterized by biexponential decay. The first (fast) component of the decay corresponds to the initial equilibration of populations between the optically active and the optically nonactive levels. The second (slow) component corresponds to the radiative decay of the thermally equilibrated system.

In addition to solving (21) we have performed a numerical integration of (14) with the initial condition given by (15), thus avoiding the fast dephasing approximation. Some results of this calculation for a reasonable choice of parameters are presented in Fig. 3. It is seen that the decay is indeed biexponential (except for very brief periods immediately following the exciting pulse).

These calculations were carried out for various sets of parameters $\epsilon_{sl}, V_{sl}, k_i, k_{ij}$ and γ_{sl}. In addition, the number of relevant levels in the $\{|s\rangle\}$ and $\{|l\rangle\}$ manifolds was accounted for by assigning to the levels $|m\rangle$ and $|u\rangle$ statistical weights N and N', respectively, thus considering them as sets of N (N') degenerated levels.

As may be expected the rate associated with the fast decay component increases with β^2 (i.e., with v_{sl} for constant ϵ_{sl} values) and with $\bar{\gamma}_{sl}$ (provided that $\bar{\gamma}_{sl} \ll \epsilon_{sl}$). The rate associated with the slow (equilibrated)
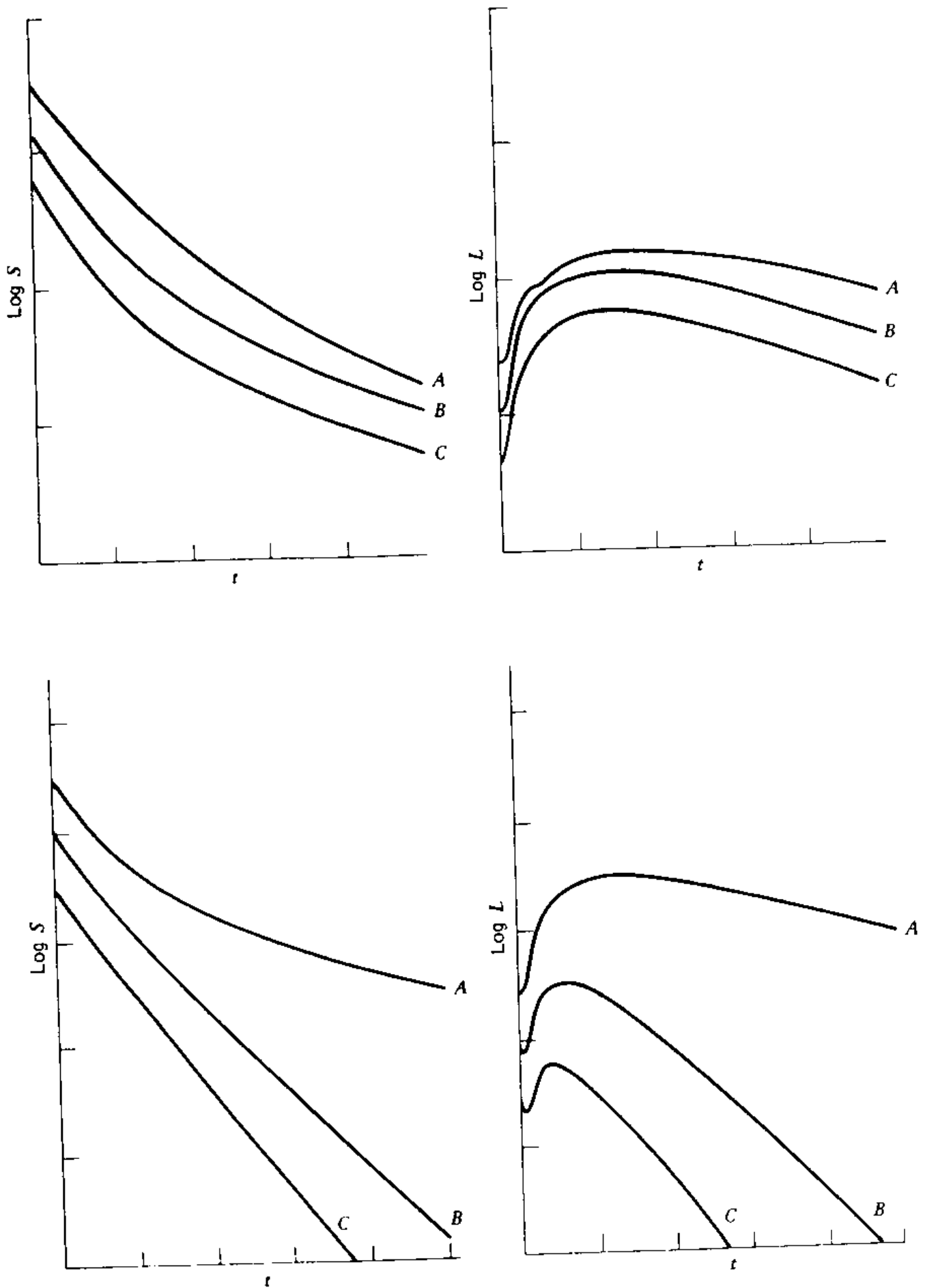
Fig. 3. Computer simulations of the time dependence of $S = \rho_{ss} + \rho_{uu}$ and $L = \rho_{ll} + \rho_{mm}$ for the four-level model. $\epsilon_{sl} = 10$, $v_{sl} = 3$, $k_s^r = 0.5$, $N = N' = 1$ and (top) $k_l = 0$, $\bar{\gamma}_{sl} = 3$ (A), 6 (B), 9 (C) (center) $\bar{\gamma}_{sl} = 6$, $k_l = 0$ (A), 1 (B) and 2 (C) (bottom $k_l = 0$, $\bar{\gamma}_{sl} = 6$. Initial excitation of the σ state (A) and of the λ state (B).
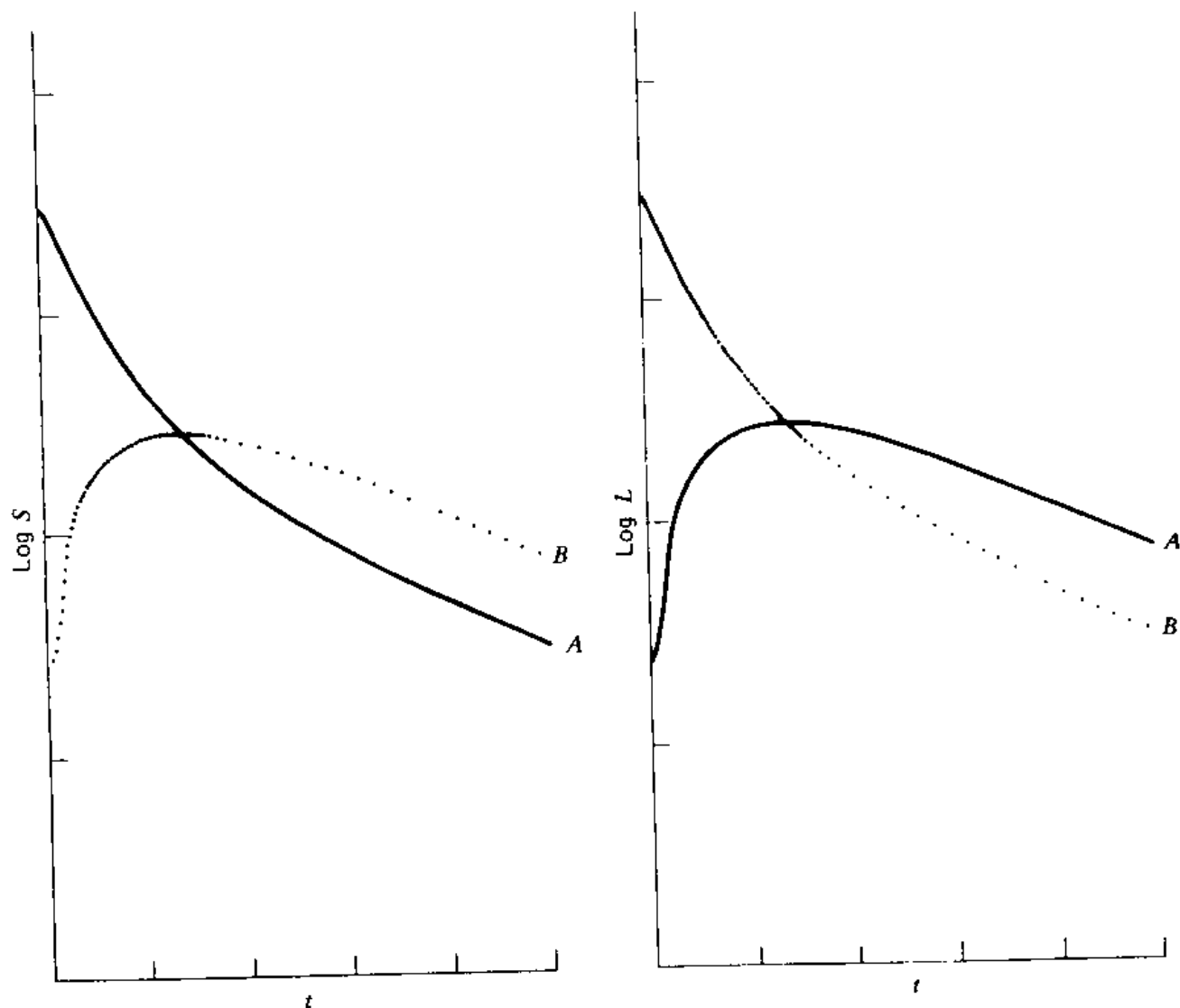
355

Fig. 3   (*Continued*)

decay component is given by

$$k_{eq} = \frac{k_s^r(\rho_{ss}^{eq} + \rho_{uu}^{eq}) + k_l(\rho_{ll}^{eq} + \rho_{mm}^{eq})}{Tr(\rho)}$$

where ρ^{eq} is the equilibrium (Boltzmann) density matrix. This is the total decay rate. The corresponding radiative decay rate (photon emission rate) k_{eq}^r is given by a similar expression with k_l replaced by k_l^r. Note that if (as is usually the case) $k_l = 0$, and since $(\rho_{ll}^{eq} + \rho_{mm}^{eq})/(\rho_{ss}^{eq} + \rho_{uu}^{eq}) \simeq (N+1)/(N' + 1) \gg 1$, the long time component may be very slow, even undetectable, in the absence of vibrational relaxation. However, since vibrational relaxation rates vary within very wide limits we may expect to encounter both extreme limits corresponding to $K_{sl} \gg k_l$ and $K_{sl} \ll k_l$, as well as intermediate situations. In the first case the decay will be biexponential; in the latter one the equilibrium between the s, u and l, m level populations

cannot be established because of the rapid nonradiative decay of the l and m levels. $\rho_{ss} + \rho_{uu}$ will thus decay exponentially with the rate $k_s^r + K_{ls}$. In the language of the chemical kinetics the first case corresponds to reversible and the latter one to irreversible $\{|s\rangle\} \rightarrow \{|l\rangle\}$ electronic relaxation.

Finally we note that if the initially excited state is the state $|\lambda\rangle$ with the predominant l-character, and if the vibrational relaxation within the l manifold is inefficient, the time dependence of ρ_{ss} and ρ_{ll} will be reversed relative to the former case: ρ_{ss} (and the fluorescence intensity) initially increases until the extablishment of the thermal equilibrium and then decays with the previously defined rate k_{eq}.

E. Intermediate-Size Molecules

The simple models discussed so far are appropriate for the small-molecule case. In larger molecules corresponding to the intermediate level structure cases many levels in the $\{|l\rangle\}$ manifold couple to the initial $|s\rangle$ level. The main new feature arising in this case can be seen by considering single $|s\rangle$ level coupled by the intramolecular interaction to a group of $|l\rangle$ levels. The relevant equations from the set (7) are:

$$\dot{\rho}_{ss} = i \sum_l (v_{ls}\rho_{sl} - v_{sl}\rho_{ls}) - k_s^r \rho_{ss}$$

$$\dot{\rho}_{sl} = i\epsilon_{sl}\rho_{sl} + iv_{sl}\rho_{ss} - i \sum_{l'} v_{sl'}\rho_{l'l} - \bar{\gamma}_{sl}\rho_{sl} \tag{22}$$

with the corresponding equation for ρ_{ls}. To simplify the calculation, we again assume that on the time scale of interest $\dot{\rho}_{sl} = \dot{\rho}_{ls} = 0$. We also disregard all terms of the form $\sum_{l'} v_{sl'}\rho_{l'l}$ in the equation for ρ_{sl} and for ρ_{ls}. This approximation is justified because when many levels l participate, $\rho_{l'l}$ is expected to be small at all times; also $v_{sl'}$ is expected to be an irregularly varying function of the index l', therefore we expect that:

$$\left| \sum_{l'} v_{sl'}\rho_{l'l} \right| \sim |v_{sl'}\rho_{l'l}| \ll |v_{sl}\rho_{ss}|$$

with this approximation we obtain (following the initial dephasing):

$$\dot{\rho}_{ss} = -\left(2 \sum_l \frac{v_{sl}^2 \bar{\gamma}_{sl}}{\epsilon_{sl}^2 + \bar{\gamma}_{sl}^2} + k_s^r \right) \rho_{ss} \tag{23}$$

so that the level s decays exponentially with a nonradiative component given by K_{sl}. If $\langle \epsilon_{sl}^2 \rangle \gg \langle \bar{\gamma}_{sl}^2 \rangle$ only one term in this sum is important and

we regain the small-molecule limit. When $\bar{\gamma}_{sl}$ (which is essentially proportional to the pressure) becomes of the same order of magnitude as ϵ_{sl} the pressure dependence saturates and for higher pressures the relaxation will be pressure independent.

Equation (23) describes the relaxation of fluorescence only after the initial dephasing. It is useful at this point to recall the corresponding isolated molecule case. In that case, when many $|l\rangle$ levels lie close enough to the level $|s\rangle$ (strong-coupling case of the isolated intermediate case molecule) so that the initial excitation results in a coherent superposition of exact molecular levels, the initial decay corresponds to the rapid intramolecular dephasing. In the isolated molecule, this initial prompt decay is followed by a long tail characterized by the diluted radiative lifetime of exact molecular levels. Equation (23) describes the finite pressure case corresponding to this long tail. The slow component is represented by the term $k_s^r \rho_{ss}$, which is small because of the population distribution over all strongly coupled $|s\rangle$ and $\{|l\rangle\}$ levels. In addition there exists a nonradiative decay component proportional to the pressure (because γ_{sl} is proportional to the pressure). As the pressure is increased, the initial dephasing time (dependent on the total width of the band of $\{|l\rangle\}$ levels effectively coupled to $|s\rangle$ and not on their widths) is practically unaffected. In contrast to this, the long time decay rate is enhanced by the pressure-induced component in (23) until, when the broadened levels overlap, the two decay components coalesce and the fluorescence decays according to a simple exponential law with a rate given by the golden rule:

$$2\sum_l \frac{|v_{sl}|^2 \bar{\gamma}_{sl}}{\epsilon_{sl}^2 + \bar{\gamma}_{sl}^2} \simeq 2\rho_l \int dx \frac{|v_{sl}|^2 \bar{\gamma}_{sl}}{x^2 + \bar{\gamma}_{sl}^2} = 2\pi |v_{sl}|^2 \rho_l$$

where ρ_l is the l-level density and we assume: $\bar{\gamma}_{sl}^2 \gtrsim \epsilon_{sl}^2$. As stated above, the pressure dependence disappears and the molecule behaves as a "large" (statistical-limit) molecule.

This discussion also indicates the expected behavior of larger molecules. Obviously, when the isolated molecule shows the statistical-limit behavior we do not expect any important modification of its decay character in presence of collisions with chemically inert molecules.

F. Some Specific Comments

(a) It has been assumed so far that collisions do not modify any intramolecular parameters. In the specific case of singlet–triplet transition this is essentially equivalent to the assumption that the spin–orbit coupling is the same in the collisional complex as in the isolated molecule. This

approximation is reasonable as long as the collision partners do not contain heavy atoms. In experiments involving heavy collision partners such as Kr or Xe, the "external heavy-atom effect" may play a nonnegligible role. Similarly, when the $s-l$ coupling is forbidden in an isolated molecule by orbital symmetry, collision perturbation (lower symmetry of the collisional complex) may induce coupling between the two electronic states. This seems to be the case of the $B\,^2\pi_g$ and $W\,^3\Delta_u$ isoenergetic states, of N_2 where the coupling is strictly forbidden by the $g \nleftrightarrow u$ Kronig rule. Collision-induced transitions between those states have been observed[39] and must be due to the breakdown of the $g \nleftrightarrow u$ rule in the collisional complex.

(b)   The treatment presented here is based on the assumption that the duration of a collision is much shorter than all other time scales of interest, i.e., $t_{coll}\, V_{sl} \ll 1$ and $t_{coll}\Gamma \ll 1$ where Γ represents any of the k and γ parameters appearing in (7). If this conditions are not satisfied (e.g., if collision result in the formation of a long-time collisional complex) we may expect substantial deviations from the predicted time behavior.

As a matter of fact, recent observations of the vibrational, rotational, and electronic relaxation induced by low-energy collisions in supersonic jets involving a long interaction times between collision partners show a drastic increase of the cross-sections with respect to the room temperature values.[65a-c]

(c)   As mentioned above, the $s-l$ transitions (in absence of the vibrational relaxation) will affect the fluorescence yield only in the case when the $\{|l\rangle\}$ manifold is subjected to nonradiative decay. When the $\{|l\rangle\}$ manifold corresponds to a dissociative electronic state, we are in the specific case of the collision-induced (or enhanced) predissociation. Such a behavior has been observed for the BO_u^+ state of I_2, where collisions induce transitions to the isoenergetic $A\,1u$ dissociative state (see below).

III.   REVIEW AND ANALYSIS OF EXPERIMENTAL DATA

We will apply the model treatment defined in the preceding section to the analysis of experimental data and to the discussion of particular problems concerning the mechanism of collision-induced electronic relaxation processes. We will try to find in the actually available experimental material the answers to some—practically important—questions:

1.   In what kind of molecular system the electronic relaxation may be considered as reversible? What is the influence of the reversible relaxation on the deactivation paths?

2. Is it possible to correlate the cross-sections for collision-induced s–l transitions with the intramolecular s–l coupling strength? Do the strongly mixed states play a specific role of "gates" between s and l manifolds?

3. What is dependence of $s \rightarrow l$ cross-sections on the properties of the collision partner?

We will center our attention at the most interesting case of small molecules and at the most extensively studied process of collision-induced intersystem crossing.

A. Reversibility of Collision-Induced Electronic Relaxation

As shown before (Section II. D.4) the electronic relaxation becomes irreversible when the l-level density is sufficiently large and/or when the vibrational relaxation within the $\{l\}$ manifold is much more rapid than the electronic relaxation:

$$\frac{\rho_l}{\rho_s} \gg 1 \quad \text{and/or} \quad k_l > K_{ls}$$

This means that even in relatively small polyatomic molecules the electronic relaxation is practically irreversible (the fluorescence of collisionally perturbed molecules exhibits a purely exponential decay with the pressure dependence of the lifetime and yield given by Stern–Volmer law [cf. (1)]. Such a behavior has been observed in the well-known case of intersystem crossing in glyoxal[34,35] and may be easily explained by the properties of the molecule. The ratio of triplet and singlet level densities in the vicinity of the ^1A_u 0° level may be roughly estimated as being of the order of: $\rho_l/\rho_s \approx 100.$[66] The rate of collision-induced $s \rightarrow l$ crossing for ground-state glyoxal as collision partner is $K_{ls} = 2.10^6$ sec^{-1} torr^{-1}. The vibrational relaxation rate within the triplet manifold is not known but is certainly not very different from that of relaxation in the singlet manifold: $k_s \approx 10^7$ sec^{-1} torr^{-1}.[35] Hence, the probability of the reverse crossing for the molecule transferred to the triplet level isoenergetic with the singlet 0° state is of the order 10^{-3}; the transition must be thus considered as practically irreversible.

Reversible electronic relaxation has been found in smaller molecules. In methylene (for which collision-induced intersystem crossing has been extensively studied for many years[67,68]) the reversible character of singlet–triplet transitions has been evidenced in a study of pressure effect on the CH_2 radical prepared either in the singlet state (by photochemical decomposition of diazirine) or in the triplet state (by photofragmentation of

diazirine due to the triplet–triplet energy transfer). It has been shown that for a sufficiently high pressure of inert gas (N_2, SF_6) one attains an equilibrium $^1CH_2 / ^3CH_2$ concentration ratio, independent of the initially prepared state.[69] The nonexponential (quasibiexponential) decay of the $B^3\pi_g$ state of N_2 in presence of collisions with Ar has been equally explained by reversible, collision-induced transitions between closely spaced $B^3\pi_g$ and $w^3\Delta_u$ states.[39]

A direct proof of the reversibility of singlet–triplet transition has been deduced from time-resolved studies of the fluorescence observed under a selective excitation of $\{\sigma\}$ and $\{\lambda\}$ rovibronic states resulting from the perturbation between $A^1\pi$ $(v=0)$ and $e^3\Sigma^-$ $(v=1)$ vibronic states in CO. In the former case, the fluorescence shows a biexponential decay, while in the latter one it exhibits an initial induction followed by the decay (Fig. 4; see also Fig. 3 bottom). The ratio of rate constants for the $s{\rightarrow}l$ and $l{\rightarrow}s$ processes (determined by a simple kinetic treatment) is in a good agreement with the expected thermal distribution after a complete equilibration of the $(\{s\} + \{l\})$ system.[37,70]

Similar nonexponential decays induced by collisions with inert partners have been observed by Erman et al.[71-73] for CO, CN, and CS excited by the electron impact. For CN (prepared by electron-impact fragmentation of the parent compound with a high yield of vibrationnally "hot" ground-state molecules) the authors observe an increase of the fluorescence ($A^2\pi \rightarrow X^2\Sigma^+$) in presence of collisions. Such an unusual effect may be explained by collisionally induced inverse relaxation from strongly populated and long-lived high vibrational levels of the ground state to quasiresonant low levels of the $A^2\pi$ radiative state.[72] This explanation was confirmed by a time-resolved study of the CN fluorescence from selectively excited levels of the A state: the biexponential decay with a long component longer than the radiative lifetime of the A state is clearly due to reversible A X collision-induced transitions.[73a]

LnI

Ar, p = 37 Torr
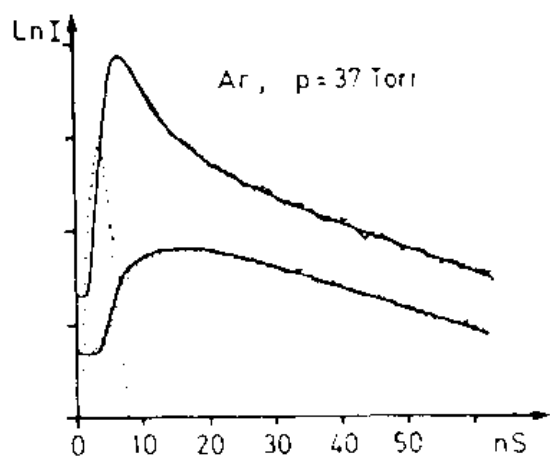
0 10 20 30 40 50   nS

Fig. 4. Fluorescence decay from the CO $A^1\Pi$ $(v=0)$ level. Selective excitation of $\{\delta\}$ (top) and $\{\lambda\}$ (bottom) rovibronic levels.

Complex and not entirely elucidated effects of the inert-gas pressure have been equally observed in the case of fluorescence from the second excited state $(B^2\Sigma^+)$ of the CN radical in an early work by Luk and Bersohn.[74]
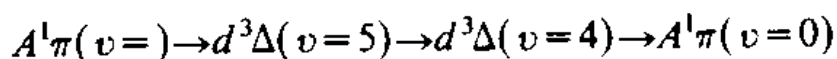
B. Vibrational Relaxation by Reversible Electronic Relaxation

As shown above, the electronic relaxation in small molecules may be more efficient than the vibrational relaxation within the same electronic state. If, moreover, one of interacting electronic states is nonradiative, that is, if the lifetime of molecules transferred to the $|l\rangle$ state is much longer than that of the $|s\rangle$ state, new specific deactivation channels may play an important role. The usual path of vibrational relaxation within the $\{s\}$ manifold: collision-induced transitions from initially excited vth to $(v-1)$th vibronic level may be less efficient than a many-step process involving

1. Electronic relaxation from the $|s, v\rangle$ state to resonant $\{l\}$ levels,
2. Vibrational relaxation within the $\{l\}$ manifold favored by the long lifetime of excited species.
3. The inverse electronic relaxation from the l manifold to lower lying $|s, v-1\rangle, \ldots, |s, v-n\rangle$ states.

Such a mechanism has been proposed by Slanger[41] and observed for the first time by Bondybey et al.[75,76] in the case of diatomic molecules inbedded in rare-gas matrices. In their subsequent work,[77] similar effects have been found for collisional processes in the gas phase. The vibrational relaxation of CO^+ excited to the $v=3$ and $v=2$ levels of the $A^2\pi$ state induced by collisions with He is more efficient by 4–5 orders of magnitude than in the ground-state $CO + He$ system.[52] Moreover, the form of the fluorescence decay from the $v=1$ level observed under $v=2$ excitation cannot be fitted if a direct $v=2 \rightarrow v=1$ relaxation path is assumed: the induction time of the relaxed emission being much longer than the decay of the resonance fluorescence.

A similar behavior has been observed under the optical excitation of the $v=1$ level of the CO $A^1\pi$ state perturbed by the isoenergetic level of the triplet $d^3\Delta$ state. Again, a large delay of the emission from the $v=0$ level with respect to the $v=1$ level decay must be considered as due to the transit through long-lived triplet states. Since this delay may be fitted by the vibrational relaxation rate within the triplet manifold (directly measured in independent experiments), a three-step relaxation path:

$$A^1\pi(v=) \rightarrow d^3\Delta(v=5) \rightarrow d^3\Delta(v=4) \rightarrow A^1\pi(v=0)$$

has been proposed in this case.[70]

The vibrational relaxation occurring apparently in a single electronic state but due in fact to the reversible internal conversion (or intersystem crossing) may play an important role in diatomic molecules exhibiting a strong collisional coupling between radiative and nonradiative (long-lived) states. It may be responsible in part for surpisingly high rates of the (apparent) vibrational relaxation in excited states of diatomics: for the CO $A^1\pi$ state + Ar, the apparent rate constant for the vibrational relaxation in the singlet manifold amounts to 3.10^6 s^{-1} torr^{-1} when a direct mechanism is assumed,[78] while in fact the process occurs in the triplet manifold with much lower rate of 2.10^5 s^{-1} torr^{-1}.[70]

The importance of this mechanism is certainly reduced in polyatomic molecules, where direct vibrational relaxation is efficient and the inverse electronic relaxation is less probable.

C. Dependence of Collisional Relaxation Rates on Intramolecular Parameters

As shown in Section II, the rate constant of the collision-induced electronic relaxation (K_{ls} or K_{sl}) depends on intramolecular parameters ($s-l$ coupling constant—v_{sl} and $s-l$ level spacing ϵ_{sl}) as well, as on the strength of the external, collisional perturbation (expressed in (19) by the overall dephasing rate $-\bar{\gamma}_{sl}$). The separation of both factors is not always self-evident. Nevertheless, for the simplicity sake we will first discuss the relation between the amount of the intramolecular $s-l$ coupling (mixing) by assuming constant value of the intermolecular interaction.

The experimental material being still very limited, it seems preferable to start by a concise review of proposed theoretical models and consider the sparse experimental data as a mean to check their validity in a few specific cases.

1. Theory

As already mentioned, the first and essential step has been made by Gelbart and Freed,[9] who showed that a nonzero mixing between $|s\rangle$ and $|l\rangle$ states in isolated molecules is a necessary condition for collisional $|s\rangle \to |l\rangle$ transitions. Therefrom, the linear dependence of collisional cross-sections on the mixing coefficient β^2 has been deduced from the theory involving the first-order time-dependent perturbation method.[10,11] This approximation is valid for very weak external perturbations and/or very high kinetic energies of colliding particles (very short duration of the collisional perturbation, τ_{coll}). For a number of molecular systems these conditions are obviously not fulfilled and a more general treatment must be applied.

The case of the intersystem crossing in methylene[67,68] has been extensively discussed. The absence of detectable singlet–triplet radiative transitions may be considered as a direct proof of the weakness of the s–l mixing, while the nonradiative transitions are easily induced by collisions. Dahler et al.[79-81] adopted in the theoretical study of the methylene case an approach different from that of Freed and Gelbart. They consider as the essential mechanism of transitions the s–l level crossing due to different shifts of $|s\rangle$ and $|l\rangle$ levels in the collisional complex. In the vicinity of the crossing point, the s–l mixing is obviously much stronger than in the isolated molecule and the nonadiabatic transitions would populate the triplet state. Such a treatment, successful for the collisional relaxation within atomic multiplets (see, e.g., Ref. [82]), where all other (widely spaced) states may be neglected, is not so well adapted to molecules: in the collisional complex, a large number of close-lying rovibronic levels becomes strongly mixed. The physical meaning of two individual states that cross at the well-defined intermolecular distance is not evident.

This problem has been discussed in a recent work by Freed and Tric,[83] where strong collisional interactions involving level-crossing effects ("perturbed mixing collisions") are considered together with long range interactions ("simple mixing collision") for which the first-order perturbation approximation is valid (see also Ref.[1]). The important point is the dependence on the β^2 parameter: for "simple mixing collisions" we have again the collisional cross-section σ_{isc} proportional to β^2 but in "perturbed mixing collisions" σ_{isc} attains the maximum value for relatively low values of β^2, the average cross-section shows thus a kind of saturation.

Similar conclusions have been deduced from the exact treatment of a simple molecular model: collisionally perturbed two-level system composed of a mixed state $|\sigma, J\rangle$ and a pure triplet state $|l, J'\rangle$ proposed by Grimbert et al.[38] By assuming, as in the Freed work,[11] the collisional coupling between $|\sigma\rangle$ and $|l\rangle$ equal to βV (where V is the collisional coupling between rotational levels in $\{s\}$ and $\{l\}$ manifolds) one obtains (for different types of the intermolecular potential) the analytical expressions for the $\sigma_{isc} = f(\beta^2)$. A new feature is a prediction of the temperature dependence of σ_{isc}.[84] The most important result concerns the dependence of $\sigma_{isc} = f(\beta^2)$ on the strength of external perturbations: for weak pertubers σ_{isc} is proportional to β^2 in the wide range, for stronger ones, the initial rapid increase of σ_{isc} is followed by much steeper dependence (which may be approximated by the linear dependence of σ_{isc} on $\ln \beta^2$). At last, for still stronger perturbations σ_{isc} attains rapidly an almost constant value of the order of gas-kinetic cross-sections, independent of the s–l mixing coefficient.

This conclusion will be useful in the analysis of experimental data.

2. Experimental Results

As mentioned above (Sec. I. B. 2,3), the long-lived fluorescence of molecules belonging to the strong-coupling intermediate case is efficiently quenched in collisions with inert partners (and still more efficiently self-quenched). The quenching rates are closely to the gas-kinetic collision rate in the case of biacetyl[33] and benzoquinone[31] and exceed them in the case of pyrimidine self-quenching $(k_q = 10^8 \text{ s}^{-1} \text{ torr}^{-1})$[30] and methylglyoxal self-quenching $(k_q = 8.10^7 \text{ s}^{-1} \text{ torr}^{-1})$[86], while for pyrazine-SF_6 collisions one obtains by combining Stern-Volmer parameters[29] and collision-free decay times[85]: $k_q = 6.10^7 \text{ s}^{-1} \text{ torr}^{-1}$.

Such a high quenching efficiency fits well into the Gelbart-Freed picture: the long-lived fluorescence is emitted from essentially triplet $(\beta^2 \simeq 1)$ with a very slight singlet admixture; the relaxation to closely lying pure triplet levels will thus occur at a rate practically equal to the relaxation rate within the triplet manifold[87]

In the small molecules belonging to the weak-coupling limit, the initially prepared state has a predominant singlet character $(\beta^2 \ll 1)$. As expected, the fluorescence quenching cross-sections are, in general, smaller than in the previous case and vary in wide limits. Unfortunately, the correlation between intramolecular parameters and quenching efficiencies cannot be done by comparing the behavior of different molecules: the intermolecular potential (the strength of the collisional perturbation) obviously depends not only on the collider but also on the excited species. The only way to check this correlation consists in the comparison of relaxation from different vibronic (rovibronic) levels of the same molecule, provided the s-l mixing coefficients for these levels have been previously determined.

To our knowledge, the only study of this kind has been carried out for CO $A^1\pi$ state, where the average mixing coefficients $\bar{\beta}_v^2$ characterizing vibronic levels $-v$ have been calculated from singlet-triplet coupling constants determined by the analysis of spectroscopic perturbations in the $A^1\pi-X^1\Sigma^+$ absorption spectra.[88,89] The results obtained under selective excitation of $v = 0 \div 8$ levels show a good correlation with $\bar{\beta}^2$: as expected from the treatment of Grimbert et al.[38]: σ_{isc} vary strongly in the case of He used as collision partner (from 0.5 Å^2 for $\bar{\beta}^2 = 10^{-3}$ to 3.5 Å^2 for $\bar{\beta}^2 = 0.1$), while for Ar this variation is strongly reduced (σ_{isc} changes from 10 to 25 Å^2) and for Kr the gas-kinetic quenching-cross-section is practically the same for all levels.

Recent, preliminary data on the fluorescence quenching from single rotational levels of CS $A^1\pi$ ($v = 0$) state of CS by O_2 and CO probably due to the intersystem crossing as in the case of CO[90] show little dependence of σ_{isc} on the mixing coefficients (k_q for O_2 increases from 6×10^6 to 8.4×10^6

sec^{-1} when β^2 varies from 0.09 to 0.19. This is not surprising in view of very high β^2 values and of strongly perturbing colliders used in this work (quenching rates closely to gas-kinetic collision rates). In NH_2 $^2A_1$ state, the electronic quenching rate is nearly the same for different vibronic levels[91] but the absence of spectroscopic information makes any discussion difficult. At last, in the case of the glyoxal self-quenching the rates of the intersystem crossing (about 0.1 of the rotational relaxation rates) do not vary in the significant way for low-lying ($\Delta E_{vib} < 1000$ cm^{-1}) vibronic levels of the ^1A_u state,[35,57] but for all these states the singlet-triplet perturbations are too weak to be detected by the high-resolution spectroscopy.

The collision-assisted predissociation in iodine B^3O_u+ state merits a detailed discussion. It is well known that B state is weakly coupled to the dissociative A $1u$ state by rotational and hyperfine-structure terms in the molecular Hamiltonian. The natural predissociation rate strongly depends on the vibrational quantum number (pronounced maxima for $v=5$ and $v=25$, a minimum for $v=15$), this dependence being due to a variation of the Franck-Condon factor.[92-94] The predissociation rate is enhanced by collisions. In absence of a detailed theoretical treatment of the collision-assisted I_2 predissociation, one can suppose that the asymmetric perturbation (breakdown of the orbital symmetry) in the collisional complex affects electronic and rotational wavefunctions but does not change the nuclear geometry.

As a matter of fact, the collisional cross-sections exhibit a clear dependence on the Franck-Condon factor. Their variation is relatively weak in the case of the very efficient self-quenching (σ varying between 55 and 90 Å^2)[94] and much more pronounced in the case of light atoms.[95-98] For He σ varies from 0.3 Å^2 for $v=15$ to 1.8 Å^2 for $v=25$ and to 1.34 Å^2 for $v=43$ (an intermediate value of the Franck-Condon factor).

We can conclude by repeating our initial remark: the amount of experimental data is still not sufficient and the further work is necessary. Moreover, in most actual studies carried out in the gas phase only the average cross-sections may be determined and this necessitates the averaging over the statistical distribution of velocities and of impact parameters in all theoretical treatments. From this point of view, crossbeam experiments, where the dependence of quenching cross-sections on the relative velocity of colliding particles (and even on the impact parameters, if the angular distribution of products is studies) may be determined, would be of highest interest.

D. Role of Strongly Mixed States (Problem of "Gates")

The collision-induced electronic relaxation is, in general, slow as compared to the rotational relaxation within a single vibronic state. This

implies that even under selective excitation of one rotational level in the $\{s\}$ manifold the thermal equilibrium between rotational levels populations is rapidly attained. The electronic relaxation will thus involve a large number of initial $\{s, J\}$ and final $\{l, J'\}$ levels (excepted for the case of anomalously efficient electronic relaxation[99]). Determination of differential cross sections for all $|s, J\rangle \rightarrow |s', J'\rangle$ and $|s, J\rangle \rightarrow |l', J'\rangle$ transitions would necessitate a selective excitation of a single rovibronic level $|s, J\rangle$ and selective monitoring of populations of all final levels in the single-collision conditions.

In real experiments using broadband fluorescence detection, the overall population of the vibronic level belonging to the $\{s\}$ manifold is monitored; in order to deduce therefrom the values of individual relaxation rates for $|s, J\rangle$ levels, we are usually obliged to make some simplifying assumptions. One can either assume that the overall relaxation rate is a weighted average of transition rates from all rotational levels or suppose that transitions occur uniquely between a limited number of strongly mixed levels playing the role of "gates" between $\{s\}$ and $\{l\}$ manifolds. The choice of the suitable approximation depends obviously on the character of the interstate coupling in the given molecular (or atomic) system.

As already mentioned (Section I.A), in the helium atom a significant singlet–triplet mixing occurs only for the quasidegenerate n^1F and n^3F states, which act effectively as "gates" between two manifolds of (practically) pure spin states.[8,12] A similar behavior would be expected in molecules when the coupling constant v_{sl} is much smaller than the average spacing between $|s, J\rangle$ and $|l, J\rangle$ states. A significant mixing takes place only in exceptional cases of an accidental $|s, J\rangle - |l, J\rangle$ degeneracy. A good example of such behavior is the $A^1\Sigma$ state of the BaO molecule. In the chemiluminescence spectrum of BaO (produced in the $Ba + N_2O$ reaction), the $P(46)$ and $R(44)$ lines of the $(1,1)$ and $(1,2)$ bands in the $A^1\Sigma - X^1\Sigma$ transition show anomalously high intensities under low perturbing-gas pressures ($P_{Ar} = 0.2$ torr). The radiative $A^1\Sigma$ state is populated by collision-induced transitions from the nonradiative $a^3\pi$ state. The $A^1\Sigma - a^3\pi$ coupling is extremely weak and a significant perturbation occurs only for the $A^1\Sigma(v = 1, J = 45)$ level. The anomalous intensity of emission is obviously due to its selective population in collision-induced transitions. As may be easily shown, such an effect is expected only when the transition rate $|\sigma, J\rangle \rightleftharpoons |\lambda, J\rangle$ between "gate" levels is of the same order of magnitude as the rotational relaxation rates within $\{s\}$ and $\{l\}$ manifolds and when the transition probabilities to other levels are vanishingly small.[100,101]

In the molecules with a stronger $s-l$ coupling, the spectral perturbations are not so "localized" and mixing coefficients are nonnegligible for a large number of rotational levels. The transitions would thus occur between many $|\sigma\rangle$ and $|\lambda\rangle$ levels. In the case of CO narrow-band excitation to the

$A^1\pi$ rotational levels, the collisionally induced $d^3\Delta$–$a^3\pi$ emission is composed of a large number of rotational lines, even in the low-pressure limit. It suggests a nonselective population of $\{l, J\}$ states in a good agreement with a relatively strong $A^1\pi$–$d^3\Delta$ coupling ($v_{sl} \approx 10$ cm^{-1}). On the other hand, a good correlation between cross sections for collisional depopulation of a given vibronic level $-v$ of the A state and average values of mixing coefficents for this level $-\beta_v^2$ suggests that transitions take place from (almost) all initially populated levels.

In polyatomic molecules belonging to the weak-coupling case (glyoxal, propynal) the density of rovibronic triplet levels $\{l, J'\}$, which may be collisionally coupled to the initially excited $|s, J\rangle$ state, is already so high that strong deviations from the average σ_{isc} value cannot be expected. As a matter of fact, the phosphorescence excitation spectra of glyoxal recorded under low gas pressure do not show any features corresponding to an anomalously high (or low) transition probabilities from individual rotational levels of the ^1A_u state to the ^3A_u state.[35]

E. Dependence of Collisional Relaxation Rates on the Intermolecular Potential

Systematic measurements of the fluorescence quenching rates as a function of the collision partner have been carried out for a number of diatomic and small polyatomic molecules: glyoxal,[35] propynal,[36] I_2,[95-98] SO_2^6 and OH.[102] In the first two cases, the quenching is due to the collision-induced intersystem crossing, in the third one, to the collision-assisted transition into a dissociative continuum. In the case of SO_2, both: $S_1 \rightsquigarrow T_1$ and $S_1 \rightsquigarrow S_0$ processes seem to be important, while for OH the final state has not been identified.

In all cases, a reasonable agreement has been found between relaxation rates and the strength of attractive van der Waals interactions described by the semiempirical formulas in terms of ionization potentials, polarizibilities and dipole moments of colliding molecules.[36, 103]

More recently, Parmenter et al.[44, 104] proposed the correlation between collisional cross-sections (for a wide variety of relaxation processes) in $A^* + M$ collisions and the potential energy well ϵ_{A^*M}. The form of this dependence is given by:

$$\sigma_M = C \exp\left[\frac{\epsilon_{A^*M}}{kT} \right] \tag{27}$$

If supposed that ϵ_{A^*M} may be approximated by a geometric mean between

$\epsilon_{A \cdot A \cdot}$ and ϵ_{MM} (known for a number of small molecules) one obtains:

$$\sigma_M = C \exp\left[\delta\left(\frac{\epsilon_{MM}}{k} \right)^{1/2} \right]$$

(28)

where $\delta = (\epsilon_{A \cdot A \cdot}/kT^2)^{1/2}$ is constant for a given excited species.

This formula may be directly checked, and excellent correlations are found for a large number of literature data as long as the rotational and electronic relaxation is considered.[44] The model fails for the vibrational relaxation of small molecules, this failure being obviously due to an important role of repulsive interactions in the case of "strong" collisions necessary for the induction of vibrational transitions.

The important conclusion from the Parmenter work is a close relation between rotational and electronic relaxation, both of them depending mainly on attractive part of the intermolecular potential. This may be clearly seen in the case of glyoxal, where the cross-sections for the collision-induced intersystem crossing[35] and for the rotational relaxation[105] are correlated. We consider this result as a strong argument in favor of the model discussed in Section II and based on the assumption that the electronic relaxation is induced by long-range interaction through a reversible rotational relaxation and dephasing processes.

In the further discussion[104] the authors assume that the parameter δ deduced from experimental results using (28) gives directly the depth of the potential well for $A^* - A^*$ interactions $\epsilon_{A \cdot A \cdot}$. This statement is controversial: experimental data for I_2[95-98] show a strong dependence of δ on the vibrational level in the $B^3O_u +$ state.[104] The same is true for the $A^1\pi$ state of CO. This difference can be hardly explained by the dependence of the intermolecular forces on the vibrational quantum number.

From our point of view, δ depends not only on the $\epsilon_{A \cdot A \cdot}$ potential but also on the intramolecular parameters of the A^* excited species, relevant for a particular relaxation process. As discussed before [Section II.D.1; (19)] we expect more complex relations between rotational and electronic relaxation rates than a simple proportionality supposed in (28). As a matter of fact neither in glyoxal nor in iodine can both processes be described by the same set of parameters.

As previously we will insist on the necessity of further experimental studies. The most significant results would be obtained by a simultaneous determination of rotational, vibrational, and electronic relaxation rates from a well-defined excited states of model molecules as a function of the collision partner.

IV. NEW PROBLEMS AND PERSPECTIVES

In the last section we emphasized very often the scarcity of available experimental data and a need of more detailed studies in a direct line of previous works. It seems, nevertheless, that an essential progress may be attained only by the extension of the research field to new techniques and to new problems. In the following sections we attempt to outline—in a very subjective way—some of the most promising perspectives. Since only the first steps have been made and the number of reported experimental results is extremely limited, we will focus our attention on expected rather than at already accomplished works.

A. Electronic Relaxation in van der Waals Complexes

Recent developments of the supersonic-nozzle technique opened a new field: the study of dynamics of electronically excited van der Waals complexes.[106] This problem is closely related to that of collisions involving electronically excited molecules. The analogy clearly appears when the system composed of an excited molecule A* and of a perturber M is described in the reference of its center of mass. The electronic excitation of the free molecule (followed by a collision) corresponds to the electronic transition between ground- and excited-state dissociative continua (Fig. 5).
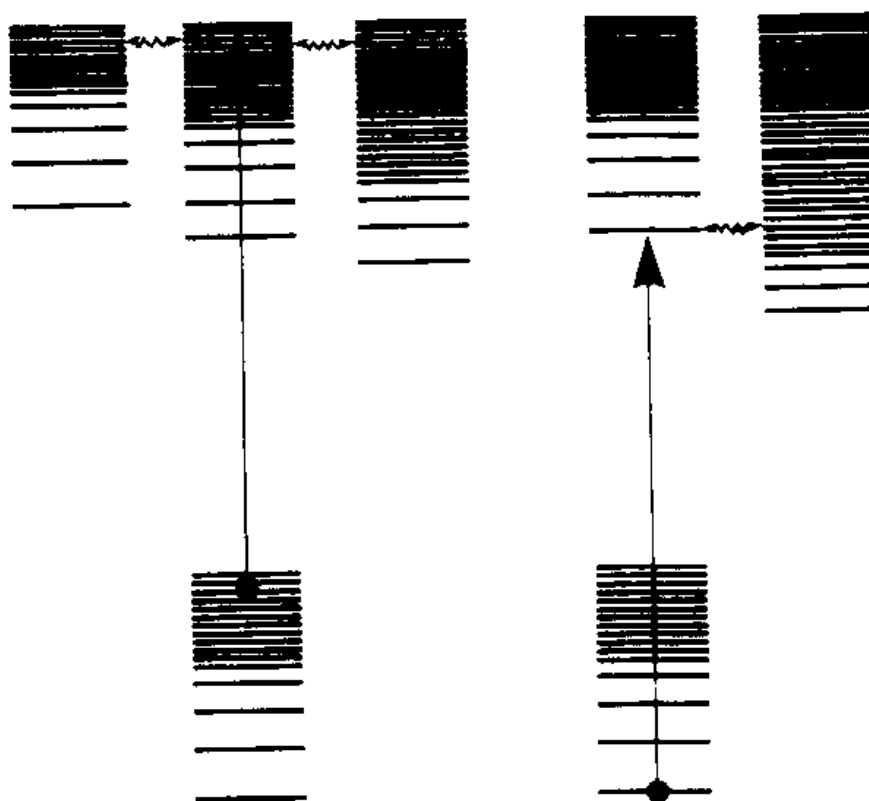

Fig. 5. Schematic representation of optical transitions and coupling patterns in the M···A system. Excitation of the free A molecule (at left) and of the van der Waals complex (at right).

Collision-induced $|s\rangle \rightarrow |l\rangle$ transitions in the excited molecule M will result from the coupling between dissociative continua of the $|s\rangle$ and $|l\rangle$ states of the M $\ldots$ A* complex. This coupling strength depends on the relative velocities of colliders, impact parameters, orientation of molecular axes, etc. The theoretical treatment of the problem necessitates thus an averaging over the statistical distribution of all relevant parameters.

The direct excitation of the complex formed in the ground electronic state prepares the same system in its bound state $|s\rangle$ isoenergetic with dissociative continua of lower $\{s'\}$ and $\{l\}$ states. We are dealing here with a much simpler problem of the coupling between a discrete state with a well-defined geometry and a limited number of continua. Experimental[107,108] and theoretical[109,110] studies of the I_2. He complex excited to higher vibronic levels of the $I_2B^3O_u+$ state showed a highly selective character of the coupling: the bound state of the I_2. He complex corresponding to v vibrational quanta of the I $\cdots$ I vibration is strongly coupled to the dissociative continuum of the neighbor v-1 vibrational state and very weakly to all other states. The excited complex decays thus almost exclusively through the vibrational predissociation:

$$I_2(v) \cdot He \rightarrow I_2(v-1) + He$$
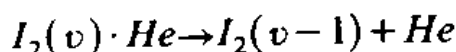
We may expect that the electronic predissociation of the excited complex will be also highly selective. If the initially excited $|s\rangle$ state is the vibrationless level of the $\{s\}$ electronic manifold, the coupling to lower lying vibronic levels of the $\{l\}$ manifold will induce the transition:

$$A^*(s) \cdot He \rightarrow A^*(l) + He$$
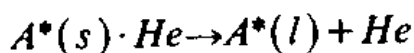
The identification of final (l) states populated in the dissociation process (relatively easy in absence of collisional relaxation in molecular beams) would be of higher interest for the understanding of coupling mechanisms.

On the other hand, if the initial excitation prepares one of higher vibronic states in the $\{s\}$ manifold, this state will be coupled to the lower $\{s'\}$ levels as well, as to the $\{l\}$ levels. The vibrational relaxation within the $\{s\}$ manifold will thus compete with the electronic $|s\rangle \rightarrow \{l\}$ relaxation process.

First significant results have been obtained for the $I_2 \cdot$ He complex in the $I_2B^3O_u+$ state. As mentioned above, all vibronic levels with $v \geqslant 1$ are vibrationally predissociated; the predissociation is evidenced by the emission of the I_2 $(v-1)$ fluorescence under a selective excitation of the $I_2 \cdot$ He(v) state. However, no fluorescence could be detected when the vibrationless level of the complex (vibrationally nonpredissociated) was

excited. This effect has been tentatively explained by the electronic predissociation (slow as compared to the vibrational predissociation of higher levels, but much more rapid than the radiative decay rate) transferring the molecule to the dissociative A state[111]

$$I^*_2(B) \cdot He \rightarrow I^*_2(A) + He \rightarrow I + I + He$$
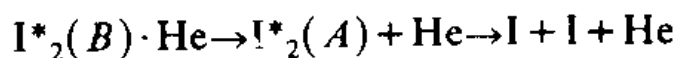
The analogy with the collision-assisted predissociation of I_2 B state is in fact very close.

This result can be probably generalized for a large class of molecules. It is interesting to note that in the fluorescence-excitation spectra of helium supersonic jets containing "large" (statistical-limit) molecules the lines of van der Waals complexes appear with a high intensity,[112] while these bands are absent or very weak in the case of "small" or "intermediate-case" molecules such as chromyl chloride,[113] biacetyl,[114,115] and glyoxal.[116] All molecules belonging to the latter group exhibit a very efficient fluorescence quenching in collisions, one can thus suppose that the absence of fluorescence from excited complexes is also due to the induction of electronic relaxation.

The case of glyoxal complexes with He and Ar has been studied in more detail.[117] In the fluorescence excitation spectrum, no lines corresponding to the $C_2H_2O_2 \cdot X$ complexes could be detected in the vicinity of the $^1A_u - {}^1A_g 0^0_0$ transition, while they appear with a non-negligible intensity in transitions to higher vibronic levels of the ^1A_u state. In contrast to it, the phosphorescence excitation spectrum in the 0^0_0 spectral region is composed mainly of bands corresponding to $C_2H_2O_2 \cdot X$ complexes. As could be expected, the 0^0 level of the complex lying below the 0^0 level of the free molecule yields on dissociation free molecules in high vibronic levels of the phosphorescent ^3A_u state but not in the fluorescent ^1A_u state. From higher vibronic levels of the complex ^1A_u state both deactivation channels are opened; the observed branching ratio between ^1A_u and ^3A_u products depends on relative probabilities of transitions to strongly coupled but sparse lower ^1A_u levels and to weakly coupled but dense ^3A_u ones.

B. Electronic Relaxation of Photofragmentation Products

The photodissociation of van der Waals complexes may be considered as prototype of more complex processes occurring during the photofragmentation of a polyatomic molecule: $ABC + h\nu \rightarrow (ABC)^{**} \rightarrow AB^* + C$. As in the previous case, we expect a close correlation between initially prepared state of the parent molecule and the energy distribution in AB^* and C fragments. However, after the breakdown of the B—C, the frag-

ments are still closely together and their interaction during the separation ("half-collision") process may induce the relaxation in fragments. Observed populations would be modified with respect to the initial ones.

This problem has been discussed in recent theoretical[118,119] and experimental[120] studies of photodissociation phenomena, but the experimental material is still very poor. We can give as an example the case of CH_3ONO photodissociation by the far-ultraviolet radiation ($\lambda = 1100 + 1300 \text{Å}$) yielding the NO fragment in the $A^2\Sigma^+(v=0 \div 3)$, $C^2\pi(v=0)$ and $D^2\Sigma^+(v=0)$ states. The relative population of the $A(v=3)$ level is anomalously high and, since the efficient $C(v=0) \rightarrow A(v=3)$ and $D(v=0)$ collisional relaxation is known, the anomaly may be tentatively explained by the electronic relaxation during the dissociative "half-collision."[121]

As in the case of van der Waals complexes, the relation between the dissociation process:

$$(AB^{**}--C) \rightarrow AB^* + C$$
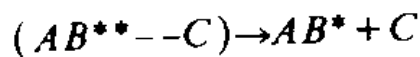
and the collisional relaxation:

$$AB^{**} + C --- \rightarrow AB^* + C$$

is very close. One can hope that with further developments in laser and crossed-beam techniques, a comparative study of both processes will be possible at least for simple molecular systems (e.g., HCN photodissociation and $H + CN^*$ collisions).

C. Magnetic-Field Effects

There exists, in the past few years an increasing interest in the influence of external (magnetic and electric) fields on the dynamics of excited molecular states. This interest is not surprising if we are reminded of the role played by this kind of studies in the development of the atomic physics. We will limit our discussion to the phenomena related to the collisional electronic relaxation; application of magnetic fields in the studies of predissociation[93] and of dephasing processes in isolated molecules[122] will not be treated here.

As far, as collisionally perturbed molecular systems are concerned one can distinguish two kinds of phenomena which seem not to be directly related:

1. Level-anticrossing effects taking place in relatively strong magnetic fields.
2. So-called "magnetic fluorescence quenching" observed in weak magnetic fields.

The mechanism of the level-anticrossing is relatively well understood, while the nature of the weak-field effect is still subject to controversions.

1. Level-Anticrossing and Electronic Relaxation

The level-crossing and anticrossing phenomena have been observed for the first time for hyperfine components of atomic energy levels.[123] The level-anticrossing spectroscopy was then applied to the study of very weak singlet–triplet (or doublet–quadruplet) coupling in atoms[11, 12] and in diatomic molecules (see, e.g., Refs. 124 and 125 and references therein).

We consider the case of $|s\rangle$ and $|l\rangle$ levels so weakly coupled that their mixing is vanishingly small $(v_{sl} \ll \epsilon_{sl})$. The effect of the magnetic field on the spin–orbit coupling (i.e., on the v_{sl} constant) can be usually neglected, the magnetic-field effect consists simply in the Zeeman shift of the $m_s \neq 0$ component of the paramagnetic (e.g., triplet) state, which may induce the crossing of the $|s\rangle$ and $|l\rangle$ levels. In the vicinity of the crossing point $(\epsilon_{sl}(H) \rightarrow 0)$ both states are strongly mixed and give origin to a pair of $|\sigma\rangle$ and $|\lambda\rangle$ states sharing radiative and nonradiative widths of $|s\rangle$ and $|l\rangle$ levels. This implies the change of the fluorescence intensity from the $|s\rangle$ state populated by optical excitation or by electric discharge, when the magnetic field is scanned across the crossing point (optically detected level-anticrossing signal). The major part of the early work was carried out in collision-free conditions and the decay of excited species was essentially radiative. In this case, the v_{sl} coupling constants can be directly deduced from the widths of anticrossing signals. It has been, however, observed in course of this work[17, 18] that anticrossing signals are substantially modified (broadened in most cases) by collisions with inert partners (ground-state He atoms in the case of the n^1D–n^3D anticrossing in He). This influence may be explained by two closely related effects:

1. A rapid decay of coherence between initially prepared states due to pure dephasing and reversible relaxation between rotational levels and/or magnetic sublevels.
2. A nonlinear dependence of the transition probabilities between σ and λ states on their mixing coefficients α^2 and β^2.

The level-anticrossing techinque offers thus a unique possibility for detailed studies of electronic relaxation, because intramolecular parameters which determine the relaxation rate (the spacing of zero order $|s\rangle$ and $|l\rangle$ levels and of quasi-stationary $|\sigma\rangle$ and $|\lambda\rangle$ states, the mixing coefficients α^2 and β^2) vary in a well-defined way with the strength of the magnetic field.

This technique has been recently applied to glyoxal, a classical example of a polyatomic molecule corresponding to the weak-coupling limit. Under

a selective excitation of single rotational levels of the vibrationless ^1A_u 0^0 state (gas pressure corresponding to a few collisions per lifetime), each anticrossing event induces a drop of the fluorescence intensity and an enhancement of phosphorescence. Because of the $\Delta J = 0$ selection rule, the anticrossing spectra are entirely different for each rotational level. They contain a large amount of purely spectroscopic information concerning the density and distribution of (l, J) triplet states which may couple to the $|s, J\rangle$ state, the spin-orbit and spin-rotation coupling constants, etc.[126] Still more important, from our point of view, is the possiblility to deduce from the signal shapes for different gas pressures the detailed form of the dependence of quenching cross-sections σ_{isc} on the level spacing and mixing coefficients.[127]

2. Fluorescence Quenching in Weak Magnetic Fields

This effect has been recently reported for several small molecules but detailed studies have been carried out only for glyoxal,[128-133] while for CS^{134} and $NO_2^{135,136}$ a more general discussion seems to be still premature in view of the limited amount of data and of the extreme complexity of their spectra.

The characteristic features of the weak-field effect in glyoxal may be summarized in the following way:

1. In the collision-free conditions the fluorescence lifetime and yield are unchanged (initially reported data suggesting a shortening of the collision free lifetime are not confirmed in further works[130-133]). On the other hand, cross-sections for the collision-induced intersystem crossing are increased by about 40% for all collision partners,

2. The effect is practically independent of the excitation wavelength in a wide frequency range ($\Delta E_{vib} = 0 + 1000$ cm^{-1}).[132] No significant difference was found, either, when different rotational levels have been selectively pumped.[133]

3. For all exciting wavelengths, the effect is saturated in the magnetic field of the order of 800 G.

The contrast with previously discussed level-anticrossing effects is striking. Moreover, the triplet-level densities (of the order of 1/cm^{-1}) and singlet-triplet coupling constants ($v_{sl} \le 10^{-2}$ cm^{-1}) deduced from level-anticrossing experiments[126] show that in the magnetic fields $H \le 1$ kG (corresponding to Zeeman shifts of ~ 0.1 cm^{-1}) a significant modification of mixing coefficients is highly improbable. These arguments seem to be strong enough to rule out the explanation of the weak-field effect by the level-anticrossing mechanism.[1,129]

Another possible explanation, proposed by Stannard[137] and by Küttner et al.[132] consists in the magnetic mixing of the triplet sublevels (T_x, T_y, T_z). Since in absence of rotation and of external fields, the singlet state is coupled to one of the triplet components,[138] their mixing will increase the density of final states and the efficiency of collisional transitions. It has been shown[133] that rotation (except for very high K values) cannot entirely mix T_x, T_y and T_z states, while this mixing is induced by the magnetic field and is complete (the field effect saturates) when the spin–rotation coupling is broken (the molecular analog of the Paschen–Bak effect). From direct observation of Zeeman effect in the ^3A_u–^1A_g absorption spectrum[133] corroborated by the value of the spin–rotation coupling constant deduced from level-anticrossing experiments[126] the magnetic-field strength necessary for induction of the Paschen–Bak effect would be of the order of 500 G.

If this interpretation of the weak-field effect is correct (its confirmation in the case of other molecules would be necessary), application of weak magnetic fields in the study of collisional electronic relaxation opens new, interesting possibilities: without affecting the structure of $\{s\}$ levels, the weak magnetic field modifies the character of the $\{l\}$ manifold.

V. FINAL CONCLUSIONS

The analysis of actually available experimental data shows that the simple model proposed in Section II accounts for the fundamental properties of the collision-induced electronic relaxation. Let us summarize some of the most important points:

1. The reversible character of electronic relaxation (detectable for obvious reasons only in the case of diatomic molecules) is now a well-established experimental fact.
2. The efficiency of collisions for induction of $|s\rangle \rightarrow |l\rangle$ transitions is closely related to the s–l coupling strength in the isolated molecule, even if the details of this relation are still not completely elucidated.
3. The electronic and rotational relaxation are closely related: in both cases the efficiency of collisions may be correlated to the attractive part of the intermolecular potential.

We emphasized the scarcity and dispersion of experimental data and a need in further studies extended to new molecular systems and applying modern techniques (highly selective optical excitation, crossed-beam experiments, external field effects).

We discussed also the relation between collisional relaxation and processes occuring in "half-collisions" (dissociation of molecules and of

van der Waals complexes). We expect a rapid development of work in this area.

At last, it must be kept in mind that the electronic collisional relaxation represents a specific case of collisional processes involving electronically excited species such as electronic-energy transfer and reactive collisions.

Acknowledgments

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