

ON THE NATURE OF INTRAMOLECULAR DEPHASING PROCESSES IN POLYATOMIC MOLECULES

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Intramolecular dephasing processes in polyatomic molecules are discussed with relation to coherent transient spectroscopy, radiationless transitions, multiphoton molecular processes, and overtone spectroscopy. A distinction is made between proper and improper dephasing processes (PDP, IDP) depending on whether they arise due to changes in populations or not. It is shown that the type of experiment and, consequently, the way we partition the hamiltonian are closely related to this distinction. We consider several experimental and theoretical approaches for studying intramolecular dynamics and discuss under what conditions it is necessary and useful to introduce explicitly dephasing interactions.

1. Introduction

The development of new spectroscopic techniques and their application to the studies of polyatomic molecules [1-8] [‡] have induced recently an increased activity directed towards understanding the nature of intramolecular interactions and processes in highly excited polyatomic molecules.

As a result of these studies, there is now a tendency in the literature to classify intramolecular coupling terms and relaxation phenomena as dephasing processes DP ("T₂" type), and relaxation of populations RP ("T₁" type). Such a classification is based on an analogy with other fields (e.g. magnetic resonance in condensed phases [11], pressure broadening in dilute gases [12-14], etc.) where the distinction between T₁ and T₂ is well established. We note, however, that since the dynamics of highly excited polyatomic molecules may be extremely complicated, and since it is treated theoretically by many different approaches [‡], there is often an ambiguity in the usage of this classification of intramolecular interactions into DP and RP.

It is our purpose in the present paper to give a more

precise definition of dephasing, "T₂" type intramolecular interactions in large molecules. We shall show that this definition is not unique but rather depends to a large extent on our level of theoretical description, which, in turn, is determined by the type and quality of the available experimental information. Thus, the choice of a *complete* or a *reduced* description of the system (i.e. with fewer degrees of freedom) and the kind of basis set we adopt are often dictated by the experimental observables and they will inevitably influence our classification of the intramolecular interactions. In section 2 we give a general definition of proper and improper dephasing processes and discuss the recent experimental techniques which yield information regarding molecular dephasing phenomena. In section 3 we discuss RP versus DP for systems where we adopt a full dynamical description (i.e. including all degrees of freedom). It is shown that the basic formulation of radiationless processes as well as coherent transient phenomena in large molecules usually falls into this category. In section 4 we discuss systems with a reduced description. It is demonstrated how the explicit introduction of proper dephasing interactions can be avoided by using a larger (i.e. a less reduced) description. Studies of unimolecular reactions, multiphoton processes and overtone spectra usually require such a description.

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[‡] For a recent review, see ref. [9]; see also papers in ref. [10].

[‡] For recent reviews, see ref. [15].

2. Basic features of dephasing phenomena

A dephasing process is any process which causes the decay of a phase coherence (i.e. off diagonal density matrix element), which is usually produced by the interaction of the molecular system with the radiation field. Dephasing processes are important whenever we have a system interacting with a radiation field, as they affect the nature of the radiation-matter interaction and thus influence the experimental observables, making the dephasing amenable to direct observation by various experimental techniques such as line-shape and relaxation experiments in magnetic resonance [11], absorption [12-14], fluorescence and Raman spectroscopy (both time and frequency resolved) [16-19] etc.

Some of the new experimental techniques which were recently applied to extract information regarding dephasing phenomena in large molecules are:

- (1) Coherent transient experiments performed both in the gas phase and in low temperature solids [1-4].
- (2) Nonlinear, time-resolved spectroscopy (e.g. induced Raman) in the liquid and solid phases [5-6].
- (3) Overtone spectroscopy of large molecules in the gas and liquid phase [7,8].
- (4) Studies of multiphoton molecular processes in the infrared (multiphoton absorption, laser chemistry, etc.) [9,10].

The importance of intramolecular dephasing effects is two-fold: (1) they affect crucially the dynamics of all molecular radiative processes; (2) as they are amenable to experimental observation, then with a suitable theoretical interpretation they may be used to obtain useful dynamical information regarding intramolecular interactions.

In analogy with collisional dephasing [14] let us distinguish between proper and improper intramolecular dephasing processes (PDP, IDP respectively). PDP are "true" dephasing processes not arising from decay of population whereas IDP arise from changes in population. This distinction is not unique but rather operational. The experimentalist will distinguish between PDP and IDP according to his ability (or inability, respectively) to measure some lifetime associated with the dephasing. This ability depends, of course, on the type and limitations of the particular experiment, which makes the distinction between PDP

and IDP not entirely rigorous.

From a theoretical viewpoint, PDP are caused by *diagonal* coupling terms in the hamiltonian which do not affect the populations in which we are interested, whereas IDP comes from off diagonal coupling terms which affect both the populations and coherences [11-14]. The occurrence of PDP coupling terms thus depends on the way we partition our hamiltonian and our choice of a basis set.

We shall now turn to a more quantitative definition of dephasing. Suppose we have a large system with n degrees of freedom, characterized by a hamiltonian $H(Q)$, ($Q \equiv Q_1, Q_2 \dots Q_n$). (Q may denote the internal degrees of freedom of an isolated molecule or of a group of molecules.) Let us now make a distinction between two types of theoretical approaches towards solving the dynamics of such a system.

(I) Full dynamical (though, possibly approximate) treatment, including all the degrees of freedom (Q).

(II) A reduced description in terms of fewer degrees of freedom where the effects of the rest are taken into account in some approximate way.

In sections 3 and 4 we shall consider in detail each of these approaches and specify under what circumstances it is necessary or useful to use them and what are the consequences regarding the nature of the dephasing phenomena.

3. A full dynamical approach

A full dynamical treatment (I) of a many-body problem is usually feasible whenever the system is small enough (few degrees of freedom) or when we adopt a simple model (e.g. collection of harmonic oscillators) for the system. Let us further classify such treatments into two classes depending on the basis set which we choose.

(IA) *Partitioning of the hamiltonian*

Here we partition $H(Q)$ into two parts

$$H(Q) = H_0(Q) + H'(Q). \quad (1)$$

We now adopt a basis $\{|m\rangle\}$ of eigenstates of H_0 . $H'(Q)$ can always be taken to be traceless, i.e. we can easily include all the diagonal elements of H' in H_0 . Thus we have

$$H_0 = \sum_m |m\rangle E_m \langle m|,$$

and

$$H' = \sum_{m \neq n} |m\rangle V_{mn} \langle n|. \quad (2)$$

If we now consider H' as causing transitions between the $\{|m\rangle\}$ states we see that there are no PDP terms. H' is *off diagonal* and any dephasing is accompanied by changes in populations and is thus an IDP.

(IB) Exact diagonalization

Here we solve for the exact eigenstates $\{|j\rangle\}$ of $H(Q)$. Using this basis set, we have for the probability amplitude of the system to be in a state $|b\rangle$ at time t if it starts in a state $|a\rangle$ at time $t = 0$ [20,15].

$$\langle b|a(t)\rangle = \sum_j \langle b|j\rangle \langle j|a\rangle \exp(-iE_j t). \quad (3)$$

Any time evolution of $|\langle b|a(t)\rangle|^2$ thus arises since the initial state $|a\rangle$ and the final state $|b\rangle$ are not eigenstates of H . The time evolution is thus always a dephasing of the $|a\rangle$ wavepacket and there are no RP (in the $\{|j\rangle\}$ basis set).

Radiationless processes in isolated large molecules involving electronic to vibrational energy relaxation are usually treated within the framework of a full dynamical approach [15]. The reason that this can be done is that these problems are usually treated using sufficiently simple models so that a full dynamical treatment (within the simplified model) is feasible. A typical molecular level scheme consists of three zero-order Born–Oppenheimer electronic states $|g\rangle$, $|s\rangle$ and $|l\rangle$. $|g\rangle$ and $|s\rangle$ refer to the ground state and the first excited singlet state whereas $\{|l\rangle\}$ denotes the levels corresponding to a lower lying excited state (say a triplet manifold). Usually $|g\rangle$ is coupled to $|s\rangle$ via radiative coupling whereas $|s\rangle$ and $|l\rangle$ are coupled via non-radiative (nuclear kinetic energy, spin–orbit) couplings. As $|g\rangle$, $|s\rangle$ and $|l\rangle$ denote a *complete collection of quantum numbers* we can choose our zeroth order hamiltonian H_0 to be diagonal in this Born–Oppenheimer representation whereas the coupling terms are off diagonal V_{gs} , V_{sl} . As a result all the relaxations are viewed as transitions of populations.

Furthermore, since the coupling is provided by the

electronic degrees of freedom, it is possible in many cases to get the essential features of these processes by using a harmonic model for the nuclear motion. This model is sufficiently simple to enable a full dynamical treatment, thus no PDP needs to be considered, as all diagonal parts of the hamiltonian are put into H_0 . Such a description is of the type IA mentioned above.

The present discussion is applicable also for the coherent transient spectroscopy in isolated electronically excited large molecules [3,4,21]. The dephasing there arises completely from off diagonal coupling (i.e. it is an IDP). Of course, it is always possible (at least in principle) to switch between methods IA and IB. Thus by diagonalizing the complete hamiltonian with regard to V_{sl} we can get the true molecular states $\{|j\rangle\}$ and the time evolution may then be viewed as a pure dephasing of wavepackets of these states [15,22].

In conclusion, when adopting a full dynamical treatment we may either have only PR and IDP (IA) or have only PDP (IB) depending on our choice of a basis set. This of course does not change the physics of the problem and has to do with our convenience in the theoretical description.

4. A reduced description

In many problems (e.g. lineshapes in condensed phases) [11,23–25] it is practically impossible to have a full description as it may require a macroscopic number of degrees of freedom. Usually one then adopts a reduced description, i.e. the degrees of freedom (Q) are separated into two groups: relevant ones Q_S the “system”, and the rest Q_R the “bath” [26–30]. H is then partitioned according to

$$H = H_S(Q_S) + H_R(Q_R) + H_{SR}(Q_S, Q_R). \quad (4)$$

(Note the basic difference between this partitioning and eq. (2). Here H_S and H_R are defined in different phase spaces whereas H_0 and H' in (2) were both defined in the complete phase space.) One then tries to obtain a reduced description in terms of Q_S alone where the effects of Q_R are taken into account in some approximate way.

If we now switch to the interaction representation in $H(Q_R)$ [29] we have

$$\tilde{H}(t) = e^{iH_R t} (H_S + H_{SR}) e^{-iH_R t}. \quad (5)$$

Let us expand \tilde{H} in a complete basic set ($|a\rangle$, $|b\rangle$, etc.) in the phase space of Q_S i.e.

$$\tilde{H} = \sum_{a,b} |a\rangle \langle a| (H_S)_{ab} \langle b| + \sum_{a,b} |a\rangle \langle a| F_{ab}(Q_R, t) \langle b|, \quad (6)$$

where

$$F_{ab}(Q_R, t) = \langle a| e^{iH_R t} H_{SR}(Q_S, Q_R) e^{-iH_R t} |b\rangle, \quad (7)$$

and (...) denotes a matrix element involving integration only of Q_S . In eq. (6) the size of the matrices H_S and F is determined by the phase space of Q_S , however, each matrix element F_{ab} is a time dependent operator in Q_R . There are now several ways to proceed in order to obtain a simple manageable treatment.

(IIA) Exact classical treatment of Q_R

If the size of Q_R is not too large we can assign classical trajectories to $Q_R(t)$, thus each F_{as} becomes an ordinary function of time rather than an operator. This is a common situation in pressure broadening in the binary collision approximations (BCA) [14].

(IIB) Stochastic approach for the bath

If the phase space of Q_R is very large (in condensed phases it is actually macroscopic) one can treat the $F_{ab}(t)$ as stochastic functions thus obtaining a stochastic equation of motion (e.g. line shapes in liquids or solids) [23–25]. Such equations may be solved by a variety of methods (see, e.g., ref. [31]).

(IIC) Derivation of master equations

Since we are interested only in system operators (i.e. operators depending only on Q_S) we may try to develop a closed equation of motion for the reduced system density matrix σ , which is obtained from the general S + R density matrix ρ by tracing it over the bath variables. The derivation of the master equation may be accomplished using Zwanzig projection operators in Liouville space [27] or the Cumulant expansion [24]. The resulting master equation has usually the form

$$d\sigma/dt = -i[H_S, \sigma] - \int_0^t d\tau R(t-\tau)\sigma(\tau), \quad (8)$$

or

$$d\sigma/dt = -i[H_S, \sigma] - \tilde{R}(t)\sigma(t), \quad (9)$$

depending on the approximations used. R and \tilde{R} are system operators which may be expressed in terms of our hamiltonian (6). A general discussion of these two types of master equations and their range of applicability has been given recently [32].

The success of the master equation approach depends on the choice of the appropriate system degrees of freedom Q_S so that their motion will be weakly correlated with that of the bath. Otherwise we have to solve self-consistently for the system and bath [26]. A possible reason for weak correlation is separation of time scales (the bath variable change much faster or slower than the motions of the system), although other reasons may hold (e.g. a large bath which is not affected by the system) [23–25,32]. In each of these reduced descriptions, we usually cannot avoid having diagonal interaction terms of the form $|a\rangle F_{aa} \langle a|$ in the hamiltonian where F_{aa} is an ordinary function of time (IIA), a stochastic random function of time (IIB) or a bath operator (IIC). These diagonal terms will contribute to PDP without affecting the populations in the system. Thus, adopting a reduced description requires usually the introduction of PDP. Conversely, when we have a reduced description including PDP we can usually increase the number of dynamical variables and avoid the necessity of treating PDP. This is an important point as it gives us flexibility in our choice of the theoretical description.

Let us consider now two typical reduced dephasing descriptions and show how by increasing the system phase space (Q_S) we can avoid the PDP completely.

A first example: an n state jump model

Consider a level scheme consisting of a ground state $|g\rangle$ and a group of n excited states $\{|l\rangle\}$ with energies E_l . Let us further assume that due to some perturbations (collisional, intermolecular interactions in condensed phases, etc.) the system can jump randomly between the various n states [23–25]. Assuming that all n states are radiatively coupled to g we now wish to calculate the line shape for absorption. Two limits are clear: when the transition rate γ between the $\{|l\rangle\}$ states is very slow compared to their energy spread Δ , the line shape consists of a sum of contributions due to the various levels. As a result, the line shape will then reflect the energy spread (Δ) of the

$\{|l\rangle\}$ states. However, when $\gamma \gg \Delta$ then a motional narrowing occurs and the line collapses to a Lorentzian at the mean energy of the $\{|l\rangle\}$ manifold. This state of affairs may be viewed in two different ways.

(i) In the stochastic Liouville treatment of Kubo [24,25] and Anderson and Weiss [23], the system is viewed as a 2-level system with a randomly fluctuating frequency. The random jump is then viewed as a PDP.

(ii) Alternatively, we can consider the system as an $n + 1$ level system and write a master equation (generalized Bloch equation) with transition rates between populations (RP).

Both approaches will result in the same expressions for the line shape. This example demonstrates how by using a more complete description with more states ($n + 1$ states versus 2) we can eliminate the necessity of having PDP. For the sake of illustration let us take the case $n = 2$ (i.e. a two state jump model). The stochastic Liouville viewpoint with a randomly fluctuating frequency (i) is discussed by Kubo in detail [24, 25]. Let us consider here the more complete approach (ii). Using a three-level description we may write an effective Hamiltonian of the form

$$H = |g\rangle E_g \langle g| + |a\rangle (\epsilon - \frac{1}{2}i\gamma) \langle a| + |b\rangle (-\epsilon - \frac{1}{2}i\gamma) \langle b| + \frac{1}{2}i\gamma (|a\rangle \langle b| + |b\rangle \langle a|), \quad (10)$$

where $|a\rangle$ and $|b\rangle$ denote the two excited states having energies $\pm\epsilon$, and γ is their relaxation rate.

The line shape is (assuming both levels have the same transition dipole) [20]:

$$L(\omega) = \text{Im}(G_{aa} + G_{bb} + G_{ba} + G_{ab}), \quad (11)$$

where

$$G(\omega) = (E_g + \omega - H)^{-1}, \quad (12)$$

using the Dyson equation [20]

$$G = G_0 + G_0 V G, \quad (13)$$

we find

$$G_{aa} = (\omega - \omega_0 + \epsilon + \frac{1}{2}i\gamma)/A(\omega),$$

$$G_{bb} = (\omega - \omega_0 - \epsilon + \frac{1}{2}i\gamma)/A(\omega),$$

$$G_{ab} = G_{ba} = \frac{1}{2}i\gamma/A(\omega) \quad (14)$$

where

$$A(\omega) = (\omega - \omega_0 - \epsilon + \frac{1}{2}i\gamma)(\omega - \omega_0 + \epsilon + \frac{1}{2}i\gamma) + \frac{1}{4}\gamma^2.$$

Substitution of eqs. (14) in (11) results in

$$L(\omega) = \gamma\epsilon^2 / [(\omega - \omega_0 - \epsilon)^2(\omega - \omega_0 + \epsilon)^2 + \gamma^2\omega^2]. \quad (15)$$

This is the same result obtained by Kubo [23,24] for the two state jump model.

Second example: pressure broadening in the binary collision approximation

Another typical example is the pressure broadening in the BCA [14]. Let us consider an atom A interacting with the radiation field and being perturbed by binary collisions with B atoms. Let us further assume that B cannot induce electronic inelastic transitions in A. The line shape for the transition $A + h\nu \rightarrow A^*$ will then be broadened due to the collisional interactions with B. The conventional way for calculating the line shape of A is to treat the motion of B classically and the broadening is viewed as a dephasing (since no inelastic transitions occur). This kind of approach is a reduced description (of type IIA above) of the line shape in terms of the internal degrees of freedom of A alone.

Let us now consider the same system to be an ensemble of AB molecules [33]. This amounts to including the translational degrees of freedom in the system variables. If we solve for the true molecular states of AB and A^*B , the level scheme will now consist of two (or more) continua due to the translation (and perhaps also bound states). Using this basis set, the broadening is seen to arise due to different transitions in these continua involving transfer of energy to or from the translation. (A collision occurs during the atom-field interaction and the off resonance energy comes or goes into the translation.) Since in line shape measurements the translational and angular distribution after a collision of $A + B$ is not resolved, and since the lifetime of A^* is not changed by these collisions it is convenient to view this situation as a dephasing and the picture of transitions between two continua does not add much in practice. However when the same collisions are studied in molecular beams, then the angular and translational distribution of $A + B$ after the collision are monitored and then both the experimentalist and the theoretician will look at these same collisions as "inelastic" (RP type) involving translational energy change, and not as merely "dephasing" events.

We shall now consider the implication of the above discussion and examples on the nature of dephasing processes in large molecules.

When treating the dynamics of collisionally perturbed large molecules, and of molecules in condensed phases it is obvious that we need to look for a reduced description in terms of the phase space of a single or a few molecules. In such a case, depending on the nature of the problem one usually adopts one of the reduction approaches discussed above. As a result, proper dephasing processes appear naturally in such descriptions (e.g. radiationless transitions and coherent spectroscopy in condensed phases) [3–6,15].

Let us consider now the dynamics of isolated highly vibrationally excited molecules in the ground electronic state. This dynamics is the key problem in the theoretical understanding of unimolecular reactions, isomerizations, laser chemistry, etc. Recent experiments in multiphoton infrared processes [9,10,34,35] and high overtone spectroscopy [8,36] reveal information regarding this dynamics. In the harmonic approximation the molecular states are described by the occupation numbers ν_i of the various normal modes. Thus a general state in the harmonic approximation is $|\nu_1\nu_2\dots\nu_n\rangle$. This basis set is usually suitable for the description of the molecule at low energies (e.g. ordinary infrared spectra). However all intramolecular processes at higher energies are caused by the anharmonicities (i.e. the difference between the true and the harmonic hamiltonians). This makes it impossible to solve even approximately the full dynamical problem (unlike radiationless transitions in electronically excited molecules, where a zero order harmonic treatment is often satisfactory). It is thus desirable to look for a reduced description involving few degrees of freedom. Examples are:

- (1) In unimolecular decompositions and isomerizations we may define a reaction coordinate connected with the bonds being formed or broken. This will usually involve only few of the molecular normal modes.
- (2) In multiphoton processes we have usually few normal modes carrying oscillator strength and interacting with the radiation field [34,35].
- (3) Local modes have been suggested for the description of overtone spectra in several molecules [7, 36,37].

A natural approach to these problems is to develop a master equation for the density matrix of few modes

of interest chosen to be "the system". Let us then write for a general state $|\nu_1\nu_2\dots\nu_a,\nu'_a+1,\dots,\nu'_n\rangle \equiv |\mathbf{v}_S, \mathbf{v}_R\rangle$, where \mathbf{v}_S refers to the relevant (system) modes and the \mathbf{v}_R to the rest.

The whole collection of states having the same \mathbf{v}_S but differing by \mathbf{v}_R are thus considered to be a *single level* in our reduced description. We now adopt the partitioning of the hamiltonian given by eqs. (4)–(7); where $H_S + H_R$ constitute the harmonic hamiltonian and H'_{SR} is the anharmonic part of H . We thus have

$$(H_S + H_R)|\mathbf{v}_S, \mathbf{v}_R\rangle = [E_S(\mathbf{v}_S) + E_R(\mathbf{v}_R)]|\mathbf{v}_S, \mathbf{v}_R\rangle. \quad (16)$$

Eq. (6) now assumes the form:

$$H = \sum_{\mathbf{v}_S} |\mathbf{v}_S\rangle E_S(\mathbf{v}_S) \langle \mathbf{v}_S| + \sum_{\mathbf{v}_S \neq \mathbf{v}'_S} |\mathbf{v}'_S\rangle F'_{\mathbf{v}'_S \mathbf{v}_S}(\mathbf{Q}_R, t) \langle \mathbf{v}_S| + \sum_{\mathbf{v}_S} |\mathbf{v}_S\rangle F_{\mathbf{v}_S \mathbf{v}_S}(\mathbf{Q}_R, t) \langle \mathbf{v}_S|. \quad (17)$$

where

$$F'_{\mathbf{v}'_S \mathbf{v}_S}(\mathbf{Q}_R, t) = \langle \mathbf{v}'_S | e^{iH_R t} H_{SR} e^{-iH_R t} | \mathbf{v}_S \rangle. \quad (18)$$

The second and third terms in H arise due to the anharmonicities. The second term causes transitions between states of the system (changing \mathbf{v}_S) and is thus responsible for changes in populations and a dephasing which arises due to these changes (RP and IDP respectively). The third term is diagonal in the system phase space. It induces transitions between the bath states by coupling states with different \mathbf{v}_R , thus causing the energy of the \mathbf{v}_S states to fluctuate, resulting in a proper dephasing PDP.

We thus see that in these problems, since we are adopting a reduced description it is natural to have PDP which should be considered in any theoretical model. However, the previous examples which we have considered (n state jump model and the pressure broadening) show that PDP can often be eliminated by using a more complete dynamical description. The question of what kind of approach to adopt for a given problem thus depends on the amount of experimental information which determines the appropriate reduction scheme.

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