ADVANCES IN CHEMICAL PHYSICS

EDITED BY

I. PRIGOGINE

AND

STUART A. RICE

VOLUME XL

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VOLUME XL

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

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ERRATA

The following corrections should be noted for Volume 37 of Advances in Chemical Physics, in the article entitled "Calculations of Observables in Metallic Complexes by the Molecular Orbital Theory" by G. de Brouckère, pages 203–304.

PAGE

206   Equation (1.4) should be:

$$E = \int \psi^* \mathcal{H} \psi \, d\tau \qquad \text{with } d\tau = dx_1.dx_2\ldots dx_N \qquad (1.4)$$

208   Equation (1.14) should be:

$$H_{pq}^{\text{eff}} = \int \chi_p^*(1) \mathcal{H}^{\text{eff}}(1) \chi_q(1) \, dv(1) \qquad (1.14)$$

216   The first line under the section heading should be:
    a. Diagonal Elements H_{pp}. As is emphasized in Sections I.D.2 and I.F.1,

217   Line 16, "total Hamiltonian" should be "effective Hamiltonian...."

223   Line 3, the fourth word should be "occupied."

228   In equation (2.12), the term $\bar{r}_p$ should be $\bar{r}_p$.

230   Below question 3 the correct sequence is:

$$\left[CH_2 \cdots C(CH_3) \cdots CH_2 \right]_2 - M(C_{2h}).$$
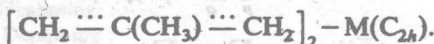
In the field of catalysis, it is well known that the oligomerization of butadiene is catalyzed by transition-metal complexes (Ni, Fe, Cr)[65–68]. For example, in the cyclodimerization of butadiene, the following intermediate is isolated[69]:

234   The first two entries in Table IA under "Orbitals" and their corresponding q_r numbers should be:

$$4s \qquad 0.03$$
$$4p \qquad -0.11$$

239   The section reference on the last line should be Section I.F.2.b.

241   The third line should be:
    b. Magnetic shielding or chemical shift σ (Section II.D.2.a)

242   On the second line below equations (2.20) the subscript should be: δ_{Cl}

243   Equation (2.22) should be:

$$q^\alpha = \sum_j \sum_p \sum_q n_j c_{pj}^* c_{qj} q_{pq}^\alpha + q_{\text{nucl}}^\alpha$$

$$= \sum_j n_j \left[\sum_p c_{pj}^2 q_{pp}^\alpha + \sum_q c_{qj}^2 q_{qq}^\alpha + \sum_{p,q} c_{pj}^* c_{qj} q_{pq}^\alpha + \sum_{q,l} c_{qj}^* c_{lj} q_{ql}^\alpha \right] + q_{\text{nucl}}^\alpha$$

$$(2.22)$$

PAGE

244 Equation (2.24) should be:

$$q^\alpha = \sum_j n_j \left[\sum_p c_{jp}^2 q_{pp}^\alpha + \sum_{p<q} c_{jp}^* c_{jq} q_{pq}^\alpha \right] + P \tag{2.24}$$

245 Equation (2.27) should be:

$$f_p = \sum_j n_j \left[c_{jp}^2 + c_{jp}^* \sum_{q \neq p} c_{jq} S_{pq} \right] \tag{2.27}$$

246 Equation (2.28) should be:

$$eqQ = 109.7 \sum_j \sum_p (2 - n_j) \left[c_{jp}^2 + \sum_{q>p} c_{jq}^* c_{jq} S_{pq} \right] \tag{2.28}$$

253 Equation (2.54) should be:

$$\int \eta_p^* \eta_q \, d\tau = \int \chi_p^* \chi_q \, d\tau - \frac{i}{2c} \left[\bar{H} \wedge \bar{R}_p \cdot \bar{R}_q \int \chi_p^* \chi_q \, d\tau - \bar{H} \wedge \bar{R}_{pq} \int \chi_p^* \bar{r}_p \chi_q \, d\tau \right] \tag{2.54}$$

271 Equations (2.71) and (2.72) should be:

$$\langle \varphi_i | \bar{L}^M | \varphi_j \rangle = \sum_p \sum_q C_{ip}^L C_{jq}^L \langle \lambda_p | \bar{L}^M | \lambda_q \rangle \tag{2.71}$$

$$\langle \varphi_i | \bar{L}^M | \varphi_j \rangle \simeq \sum_{atom} \sum_{p,q \in atom} C_{ip}^L C_{jq}^L \langle \chi_p | \bar{L}^M | \chi_q \rangle \tag{2.72}$$

276 Equations (2.79) should be:

$$\phi_{ex}^{VII} = \left[S\alpha^2 \rightarrow V\alpha^2 \right]$$
$$\phi_{ex}^{VIII} = \left[D\beta^2 \rightarrow Sp^2 \right] \tag{2.79}$$
$$\phi_{ex}^{IX} = \left[S\alpha \rightarrow V\alpha \text{ and } D\beta \rightarrow Sp \right]$$

291 On the tenth line from the bottom, the correct wording is:
r^4 is the mean value of the fourth power of the electron orbital radius.

293 On line 19, the correct numbers are: 7250 cm^{-1} (+6350 cm^{-1} theoretically).

295 On the last line, the number should be: 5443 cm^{-1}.

299 Reference 69: G. Wilke and G. Bogdanovic
300 Reference 94: K. D. Carlson and C. M. Moser
    Reference 100: F. Grimaldi, A. Lecourt, and C. M. Moser
304 Reference 233: N. Rösch and K. H. Johnson

CONTENTS

DEPHASING OF
MOLECULAR VIBRATIONS
IN LIQUIDS

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CONTENTS

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1

I. INTRODUCTION

Vibrational phase relaxation in liquids is a problem that has attracted considerable attention during the last 5 to 10 years; advances in both experiment and theory have led to a much deeper understanding of the microscopic processes that cause dephasing and have demonstrated the usefulness of vibrational phase relaxation studies as a probe of liquid state structure and dynamics. On the experimental side, the most dramatic advance has been the development of coherent time-resolved picosecond techniques, but increasingly accurate isotropic Raman lineshape studies have allowed systematic investigation of the temperature, density, and concentration dependence of dephasing in liquids. On the theoretical side, a wide variety of increasingly sophisticated theories and models have been developed and compared with experimental results. In spite of all this recent activity, there are no really comprehensive surveys of the problem of phase relaxation in liquids. Diestler[1] has reviewed vibrational relaxation (both phase and population) with primary emphasis on the application of projection operator techniques to the study of a harmonic oscillor in a heat bath; references are given to much of the earlier experimental work. Three surveys of picosecond spectroscopy[2,3] have included brief sections on vibrational dephasing. A number of surveys of rotational relaxation in liquids[4] have included depolarized Raman lineshape measurements, but discussed only briefly the effect of vibrational dephasing on these experiments.

Dephasing can be described most simply for dilute gases. The vibrational wave function of a molecule is determined by its quantum state (i.e., the occupation numbers of the various normal modes) and by an overall phase. Collisions with other molecules can be either elastic or inelastic; inelastic collisions give rise to population relaxation, whereas elastic collisions give only phase shifts. Because the gas is taken to be dilute, collisions are separate binary events; during a series of such collisions the phase will change by different amounts depending on the relative momenta, orientations, and impact parameters of the interacting molecules. After a sufficient number of such elastic collisions, the phase of the wave function will have lost correlation with its initial value and, for an ensemble of molecules, will have a random distribution of values between 0 and 2π; phase relaxation has taken place.

The gas phase description is straightforward (although of course the actual collision dynamics may be complicated) because collisions are separate and the effect of each is given entirely by the resulting phase shift. In a liquid, molecular vibrations are well described by localized wave functions, but a given molecule interacts continuously with many

neighbors, thus the description of the dephasing is less simple. An understanding of dephasing in liquids is important for two reasons: first, probes of the vibrational motion provide information about the still poorly understood local structure and dynamics of molecular liquids; second, infrared or depolarized Raman studies of rotational relaxation also involve vibrational dephasing effects, which must be understood to separate out their contribution.

In Section II, the frequency- and time-domain experiments sensitive to dephasing are described and the correlation functions they determine are presented. In Section III a general theory for vibrational dephasing is given, which includes most formal theories developed to date as special cases; Section IV is devoted to the presentation and comparison of a number of theoretical models that have been developed. Section V summarizes recent experimental findings, emphasizing the five or six molecules that have been studied most extensively.

A number of related subjects are not discussed or are only mentioned briefly. Vibrational population relaxation can in some cases contribute to dephasing; studies of population relaxation in solid matrices have been reviewed by Legay[5]; Refs. 2 and 3 discuss picosecond investigations of liquids. Vibrational lineshapes of molecules in solids and matrices[6] are not discussed, although the problem is closely related to the liquid state dephasing problem, and comparative studies should prove interesting. Lineshapes in hydrogen-bonded liquids[7,8] are not covered. Coherence effects in nuclear magnetic resonance[9] are quite closely related to vibrational dephasing on a formal level, but fall outside the scope of this review, as do the recent coherent optical studies[10-12] of solids and gases.

II. EXPERIMENTAL PROBES OF VIBRATIONAL DEPHASING

Vibrational dephasing is accessible to experiment primarily through two types of measurement: spectral line shape determinations and coherent picosecond excitation studies. The former method is older and easier to carry out experimentally, but the interpretation is sometimes ambiguous; the latter technique is difficult experimentally, but in some cases gives cleaner results. In this section we outline the theory underlying these two types of experiment and determine the microscopic correlation functions that can be obtained from them.

A. Spectral Lineshape Studies

The scattering of light can be described either classically[13] or quantum mechanically.[14] The starting point here is the quantum mechanical ex-

pression derived by Placzek[15,16] for the differential scattering cross-section for Raman scattering into solid angle $d\Omega$ and frequency range $d\omega$ about ω:

$$\frac{d^2\sigma}{d\Omega\,d\omega} = \left(\frac{2\pi}{\lambda}\right)^4 \sum_{i,f} |\langle i|\,\hat{\varepsilon}_I \cdot \underline{\alpha} \cdot \hat{\varepsilon}_s\,|f\rangle|^2\, \rho_i\, \delta(\omega - \omega_{fi}) \tag{2.1}$$

Here λ is the wavelength of the scattered light, $\hat{\varepsilon}_I$ and $\hat{\varepsilon}_S$ are the polarization directions of incident and scattered light, and $\underline{\alpha}$ is the polarizability tensor of the scattering medium. The initial and final states of the system with energies E_i and E_f are i and f; $\hbar\omega_{fi} = E_f - E_i$, and ρ_i is the probability that the system is initially in state i. The scattering intensity, which is proportional to this cross-section, can then be expressed in terms of time correlation functions using the procedure outlined by Gordon[16]: first, the delta function in (2.1) is Fourier transformed to give

$$I(\omega) \propto \sum_{i,f} \int_{-\infty}^{\infty} dt e^{i(\omega - \omega_n)t} |\langle i|\,\hat{\varepsilon}_I \cdot \underline{\alpha} \cdot \hat{\varepsilon}_s\,|f\rangle|^2\, \rho_i$$

$$= \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{i,f} \langle i|\, e^{iE_i t/\hbar}\hat{\varepsilon}_I \cdot \underline{\alpha} \cdot \hat{\varepsilon}_s e^{-iE_f t/\hbar}\,|f\rangle$$

$$\otimes \langle f|\,\hat{\varepsilon}_I \cdot \underline{\alpha} \cdot \hat{\varepsilon}_s\,|i\rangle\rho_i \tag{2.2}$$

The Heisenberg representation of an operator $\underline{\alpha}$ is

$$\underline{\alpha}(t) = e^{i\mathscr{H}t/\hbar}\underline{\alpha}e^{-i\mathscr{H}t/\hbar} \tag{2.3}$$

Equation 2.2 thus becomes

$$I(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{i,f} \langle i|\,\hat{\varepsilon}_I \cdot \underline{\alpha}(t) \cdot \hat{\varepsilon}_s\,|f\rangle\langle f|\,\hat{\varepsilon}_I \cdot \underline{\alpha} \cdot \hat{\varepsilon}_s\,|i\rangle\rho_i \tag{2.4}$$

The sum over i with weighting ρ_i is simply the equilibrium ensemble average $\langle\ \rangle_{eq}$ of the operator inside the brackets; thus

$$I(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \hat{\varepsilon}_I \cdot \underline{\alpha}(t) \cdot \hat{\varepsilon}_s \hat{\varepsilon}_I \cdot \underline{\alpha} \cdot \hat{\varepsilon}_s\rangle_{eq} \tag{2.5}$$

The subscript "eq" is dropped except where confusion may result.

Two different experiments can be carried out, one in which $\hat{\varepsilon}_I$ and $\hat{\varepsilon}_S$ are parallel (giving $I_\parallel(\omega)$), and one in which they are perpendicular ($I_\perp(\omega)$). The isotropic and anisotropic lineshapes are defined as

$$I_{iso}(\omega) = I_\parallel(\omega) - \tfrac{4}{3}I_\perp(\omega)$$
$$I_{aniso}(\omega) = I_\perp(\omega) \tag{2.6}$$

They are related to the mean polarizability

$$\alpha \equiv \tfrac{1}{3} \operatorname{Tr} \underline{\alpha} \tag{2.7}$$

and the polarizability anisotropy

$$\underline{\beta} = \underline{\alpha} - \alpha \mathcal{J} \tag{2.8}$$

through[13]

$$I_{\text{iso}}(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \alpha(t)\alpha(0) \rangle \tag{2.9}$$

$$I_{\text{aniso}}(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \operatorname{Tr} \underline{\beta}(t) \cdot \underline{\beta}(0) \rangle$$

The system polarizabilities α and $\underline{\beta}$ may be approximated as the sum of the mean polarizabilities or polarizability anisotropies of the molecules in the system. This corresponds to the neglect of pair and higher-order collision-induced polarizabilities,[14] which affect primarily the high-frequency wings of the spectrum.

The isotropic spectrum includes both low-frequency quasielastic scattering contributions (which are centered on the incident frequency and correspond to Rayleigh-Brillouin scattering) and higher-frequency vibrational Raman contributions (which arise from the dependence of α on vibrational coordinates and are therefore centered a distance $\pm\omega_0$ from the incident laser frequency, where ω_0 is the vibrational frequency). This latter part of the spectrum may be expressed as

$$I_{\text{iso}}(\omega) \propto \left| \frac{\partial \alpha}{\partial Q} \right|^2 \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{j=1}^{N} \langle Q_i(t)Q_j(0) \rangle \tag{2.10}$$

where j is summed over the N molecules in the system and Q_i is the vibrational coordinate of interest on molecule i. It is clear from (2.10) that the isotropic Raman spectrum provides a direct probe of the vibrational dephasing process as it is reflected in the correlation function $\langle \sum_j Q_i(t)Q_j(0) \rangle$. It is frequently assumed that the phases of the vibrations on neighboring molecules are uncorrelated; it is shown in Section III.A that this is not generally true. If, however, this correlation is neglected as a first approximation, the lineshape becomes

$$I(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \langle Q_i(t)Q_i(0) \rangle \tag{2.11}$$

and depends only on the separate dephasing of each molecule. In the case where the correlation function of $Q_i(t)$ is exponential

$$\langle Q_i(t)Q_i(0) \rangle \approx \langle Q_i^2 \rangle \exp(-t/\tau_v) \tag{2.12}$$

the isotropic spectrum is a Lorentzian with a full width at half height (FWHH) of $2/\tau_v$ sec^{-1} or $(\pi c \tau_v)^{-1}$ cm^{-1}.

The anisotropic spectrum includes low-frequency (rotational Raman) and higher-frequency (vibrational Raman) contributions. The latter can be written

$$I_{\text{aniso}}(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \left\langle \text{Tr} \sum_{j=1}^{N} \frac{\partial \beta_i(t)}{\partial Q_i} \cdot \frac{\partial \beta_j(0)}{\partial Q_j} Q_i(t) Q_j(0) \right\rangle. \quad (2.13)$$

For a molecule with a threefold or higher axis in the direction $\mathbf{u}_i$, this expression can be simplified[13] to give

$$I_{\text{aniso}}(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{j=1}^{N} \langle \tfrac{1}{2}[3(\mathbf{u}_i(t) \cdot \mathbf{u}_j(0))^2 - 1] Q_i(t) Q_j(0) \rangle$$

$$= \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{j=1}^{N} \langle P_2(\mathbf{u}_i(t) \cdot \mathbf{u}_j(0)) Q_i(t) Q_j(0) \rangle$$

$$\approx \int_{-\infty}^{\infty} dt e^{i\omega t} \langle P_2(\mathbf{u}_i(t) \cdot \mathbf{u}_i(0)) Q_i(t) Q_i(0) \rangle \quad (2.14)$$

where P_2 is the second Legendre polynomial. In the last step of (2.14) we neglected the phase correlation between neighboring molecules (as discussed for the isotropic Raman line). The anisotropic Raman spectrum depends on rotational as well as vibrational relaxation; thus it is a less useful probe of the pure dephasing processes. On the other hand, the vibrational contribution must be understood and separated out if accurate information on rotational motion is to be extracted from measured depolarized Raman lineshapes.

The infrared absorption line shape $I_{\text{IR}}(\omega)$ is given[16] by an expression analogous to (2.1):

$$I(\omega) = 3 \sum_{i,f} |\langle f| \, \hat{\varepsilon} \cdot \mathbf{\mu} \, |i\rangle|^2 \rho_i \delta(\omega_{fi} - \omega) \quad (2.15)$$

where $\hat{\varepsilon}$ is a unit vector along the polarization direction of the incident radiation (this direction can be averaged over for ordinary unpolarized incident radiation), and $\mathbf{\mu}$ is the dipole moment operator for the system. An analogous transformation to that outlined above for the Raman lineshape gives[16]

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \mathbf{\mu}(t) \cdot \mathbf{\mu}(0) \rangle \quad (2.16)$$

If the dipole moment of the system is approximated as the sum of dipole moments on the individual molecules, the absorption intensity near the

vibrational frequency ω_0 is given by

$$I(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{j=1}^{N} \left\langle \frac{\partial \mu_i(t)}{\partial Q_i} \cdot \frac{\partial \mu_j(0)}{\partial Q_j} Q_i(t) Q_j(0) \right\rangle$$

$$\propto \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{j=1}^{N} \langle \mathbf{u}_i(t) \cdot \mathbf{u}_j(0) Q_i(t) Q_j(0) \rangle$$

$$\approx \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \mathbf{u}_i(t) \cdot \mathbf{u}_i(0) Q_i(t) Q_i(0) \rangle \qquad (2.17)$$

Here again, as in the anisotropic Raman scattering case, the lineshape is affected by both rotational and vibrational relaxation.

B. Coherent Picosecond Excitation Experiments

Although the study of isotropic Raman linewidths provides a direct and useful probe of vibrational dephasing, the interpretation of these experiments is sometimes clouded by the presence of hot bands, isotope splittings, and other sources of inhomogeneous broadening. In such cases, the recently developed picosecond pulse techniques[2,3] are very useful; a carefully designed experiment allows the determination of the contribution of purely homogeneous broadening to an inhomogeneous line. The principle of these experiments is as follows: a short (picosecond) laser pulse creates a coherent superposition of vibrationally excited molecules; a second probe pulse then measures the amplitude still present after a time t_D, through coherent anti-Stokes Raman scattering. In this section we outline the theory of pulsed picosecond dephasing experiments, with the emphasis less on experimental details than on the fundamental question of what microscopic properties are determined by a given experiment. A fuller discussion is given in Ref. 17.

The electric field of the incident laser beam is characterized by wave vector k_L and frequency ω_L; it has the form

$$\tfrac{1}{2} E_L \exp\left[i(k_L x - \omega_L t)\right] + \text{c.c.} \qquad (2.18)$$

Suppose there are a number of distinct types of molecules (e.g., isotopes) in the system with frequencies ω_j, $j = 1, 2, \ldots, n$. Through stimulated Raman scattering, the laser field generates a Stokes field

$$\tfrac{1}{2} E_S \exp\left[i(k_S x - \omega_S t)\right] + \text{c.c.} \qquad (2.19)$$

and a coherent superposition of vibrations q_j for each species j:

$$q_j = \tfrac{1}{2} Q_j \exp\left[i(k_j x - \omega_j t)\right] + \text{c.c.} \qquad (2.20)$$

The stimulated excitation mechanism ensures that $k_j = k_L - k_S$ for all species present. E_S and Q_j are generated through the interaction of the