Resonance Raman scattering from a multilevel, thermally relaxing system*

S. Mukamel† and A. Nitzan

Department of Chemistry, Tel Aviv University, Tel Aviv, Israel
(Received 20 July 1976)

We consider light scattering from a multilevel system (e.g., a molecule) interacting with several heat baths. The Liouville space approach is employed and weak incident radiation intensity is assumed, whereas the light scattering process is described in the lowest appropriate order in the interaction between the molecule and the incident and emitted photons. The interaction with other radiation field modes as well as with the thermal baths is treated more fully, such as to account for the correct damping terms and their temperature dependence. The formalism is suited for light scattering from an impurity molecule in both gas and dense phases. The thermal baths induce relaxation within the manifold of excited states as well as transitions to nonradiative channels. Damping due to such transitions (as well as radiative damping) corresponds to interactions with zero temperature baths. The physical interpretation of such a bath depends on the nature of the particular damping process. Thermal relaxation within the excited manifold is induced by interaction with the environment represented by a bath of temperature T. Part of this interaction which is diagonal in the molecular space corresponds to the so-called "quasielastic collisions" and induces modulations of the molecular energy levels and broadening of the relaxed emission. The remainder, nondiagonal part induces actual transitions between the excited molecular energy levels. The formalism yields in a single calculation expressions for the cross section for both the coherent (Raman) scattering process and the relaxed luminescence and enables us to discuss the effects of different factors such as temperature and quenching processes on the relative yields for these processes. The formalism also allows for interference between different levels of the excited manifold due to coupling of several levels to the same bath, and makes it possible to study the effect of thermal relaxation on these interference phenomena.

I. INTRODUCTION

Resonance light scattering has been a subject of active study for a long time,[1] with the research effort focused both on developing its applications as an extremely useful spectroscopical tool and on understanding the nature of the phenomenon and the microscopic processes underlying the observed scattering. Even after almost half a century of development, the field is still plagued by controversies and misconceptions, particularly around the question of distinction between the so-called resonance Raman scattering and resonance fluorescence.[2-15] Actually, this problem of distinction apart from its purely semantic part has been settled by various workers, and an excellent discussion of its present standing has recently been given by Rousseau and Williams.[10] To settle the semantic problem at least for the present work we shall refer to the general phenomenon as resonance light scattering (RLS) and identify different components of the scattered radiation as resonance Raman scattering[16] (RRS) and resonance fluorescence (RF) parts. The identification depends on the nature of the experiment. In general, one can distinguish between two extreme types of experiments: long time (energy resolved) experiments[2-7,9,17-27] where a monoenergetic beam of infinite duration (as required by the uncertainty principle) and energy close to some resonance transition is scattered from the target under steady state conditions, with the scattered light being energy resolved; and short time (time resolved) experiments[8,28-34] where a broad band pulse of short duration is sent towards the molecule and the molecular response is followed as a function of time. In short time experiments the light scattered during the incident pulse lifetime may be identified as RRS while the rest of the emission which decays with a characteristic molecular lifetime may be called RF.[8] In a long time experiment the component of the scattered radiation with energy identical to the incident energy modulo the energy difference between the initial and final molecular energy levels may be identified as the Raman part (in the absence of inhomogeneous broadening this part is identical in width and form to the incident beam) while the rest of the scattered radiation constitutes the RF. It should be stressed that these definitions, though seemingly important from the practical point of view, are sometimes misleading as theoretical concepts. For example, in a long time scattering experiment with an isolated molecule, energy conservation implies that the scattered radiation cannot differ in energy from the incident beam. A short time experiment done on the same system still reveals in principle two components, fast and slow.[8]

In this paper we utilize the formalism of scattering theory in tetradic (Liouville space) operator language[35a] to describe long time energy resolved resonance light scattering from a system interacting with thermal baths. Weak intensity is assumed and the scattering cross section is obtained in the usual lowest order perturbation theory in the interaction between the molecule and the incident and emitted photons. The relaxation processes induced by the baths affect the light scattering process in several ways. First, interaction with pure sinks (zero temperature baths) will reduce the overall yield of the scattered emission. Such zero temperature baths represent inter- or intramolecular radiationless continua seated on molecular levels which are far below the excited spectral region (by "far below" we mean an energy spacing much larger than $k_B T$). Actually, if we neglect stimulated radiative processes, the radiative continuum may also be represented by such a zero temperature bath. Secondly,

within the spectroscopically interesting region interaction with the environment gives rise to thermal population and phase relaxation. Phase relaxation, caused by quasielectric collisions, leads to pressure broadening[35b] of the transitions, while inelastic processes result both in broadening and in population relaxation and in emission from levels other than the originally excited one. If we take into account the emission originated in all the levels connected in this way (the "spectroscopically interesting region" is defined such as to include all the levels emitting radiation which is monitored by our detector), these processes do not affect the total quantum yield for emission.

The scattering cross sections for a long time RLS experiment have been derived previously for the case of a single intermediate level by Huber, both for a molecule interacting with a surrounding solid[17,18] and for a molecule colliding with other particles in the gas phase.[19,20] Results similar to those given by Huber have been obtained by Hizhnyakov and Tehver[36] for resonance scattering from the zero phonon line associated with an electronic transition in an impurity molecule imbedded in a solid matrix. Essentially the scattering cross section was shown to be composed of two parts that may be identified as RRS and RF (see Sec. V). The RF part vanishes for an isolated molecule. Some attempts to extend the theory to the case of more than one intermediate state have also been made. Omont, Smith, and Cooper have considered RLS from a multiplet of rotational levels, both for the degenerate case[21] and for the case where the degeneracy is removed by a weak magnetic field.[22] The first work reduces essentially to the single intermediate level case by disregarding the radiation emitted following an inelastic collision. In the second work, Doppler broadening is assumed to smear both the absorbed and emitted intensity profiles, and resolution of the energy scattered from different parts of the excited manifold is not considered. Nitzan and Jortner[23] have considered RLS from an isolated molecule where the excited state manifold contains two coupled states, and studied the effects of interference between the transitions caused by the two states being coupled to the same radiative and radiationless continuua. Very recently Madden and Wennerstorm[37] have attempted to discuss RLS from a coupled multilevel manifold in terms of a molecular basis set which is diagonal in the coupling Hamiltonian. This procedure is clearly not valid in the case where the coupling is induced by an external thermal bath. Also, for an isolated molecule it results in expressions which are hard to interpret physically. Finally, Kubo, Takagawara, and Hanamura[38] have employed the formalism of the stochastic theory of line shapes to discuss relaxation effects in the one and two intermediate level problem. Their work has the same objective as our present work. Our treatment has the advantage of being totally microscopic. As such, it leads in a natural way to microscopic expressions for the various kinetic terms of the theory. This enables us to discuss specific models for the energy and the temperature dependence of these kinetic terms. It will be seen that these dependences play important roles in the qualitative and quantitative behavior of the scattering cross section. In addition, our formalism contains the possibility of interference between levels of the excited manifold which results from coupling of different levels to common baths. It thus becomes possible to study the effect of (incoherent) thermal relaxation on such interference effects.

Like other theories of this kind, our approach invokes the impact approximation, which holds only close enough to resonance. However, we generalize this approximation in a way that enables us to discuss excited manifolds extending in energy much further than the inverse correlation times of the thermal baths. In addition, two simplifying assumptions are made in this work. First, we disregard all sources of inhomogeneous broadening such as Doppler broadening in the gas phase and different impurity sites in solid matrices. Secondly, we consider nonpolarized incident radiation and sum over all polarizations of the scattered beam so that polarization effects and in particular depolarization ratios of the different components of the scattered radiation are not considered. Both assumptions may be relaxed as is done in the single intermediate level case.[19] It should be added that as our prime interest here lies in relative yields of RSL in different spectral regions, inhomogeneous broadening is relevant only to determine the feasibility of an experiment with the desired energy resolution.

As is well known, RRS often yields spectra of the scattered light much more structured and much better resolved than absorption or fluorescence spectra.[39,40] Care has to be taken to monitor only that part of the emission which corresponds to RRS, and different techniques have been devised for this purpose. Recently, Friedman and Hochstrasser[40] suggested that a controlled use of fluorescence quenchers may increase the quality of the RRS. Our formalism, which leads in the same calculation to cross sections for all relevant scattering and emission processes, enables us to discuss this point in a fully quantum mechanical way. It will be seen that the effect of a fluorescence quencher depends on whether the smearing in the spectrum is caused primarily by inelastic or quasielastic processes.

In Sec. II we describe the microscopic model used to discuss the scattering process. Section III contains an outline of the theory of light scattering in the tetradic $\mathcal{T}$ matrix formalism. In Sec. IV we derive the general formal expressions for the absorption and scattering cross sections in a thermally relaxing multilevel system, and in Sec. V we apply these results to the case of two intermediate levels in different conditions. The results are summarized and discussed in Sec. VI.

II. MODEL

A typical light scattering process from a nonisolated molecule should be described theoretically in terms of three elements; the incoming and outgoing photons, the molecular system, and the reservoirs coupled to the molecular system. These elements are represented by the energy level diagram of Fig. 1. The molecular sys-

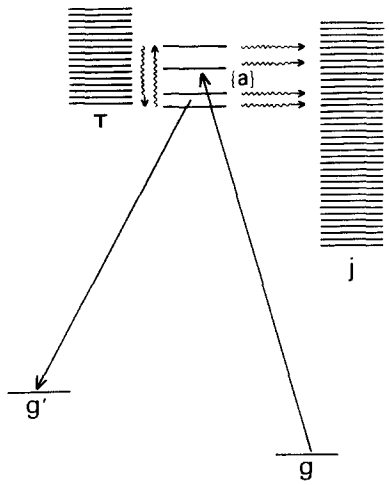

FIG. 1. Energy level model used in this paper. The continuum T denotes a thermal bath of temperature T. The continuum seated on the level j is one of several zero temperature baths which represents channels for irreversible damping. (a) is the manifold of optically active levels interacting with the baths. g and g' are the initial and final states of the scattering process.

tem is represented by a set of relevant energy levels; the initial (g) and final (g') levels, [41] and intermediate excited levels $\{a\}\cdot\{a\}$ represent this set of excited molecular states which are seated in the spectral region of interest and which are coupled radiatively to at least one of $\{g, g'\}$. We are interested in a resonance scattering process from discrete molecular levels, and therefore the relevant spectral region is well defined and the states in the set $\{a\}$ can be chosen to consist of a manifold of vibrational levels, which are interconnected by thermal relaxation within the excited molecular electronic state, or it can be a manifold of rotational levels or of Zeeman levels, which may be close enough to overlap within their radiative and nonradiative widths. In this latter case, we shall be able to study the effect on quantum mechanical interference phenomena of thermal relaxation between the closely spaced levels.

The reservoirs appearing in our model are represented by continua of levels and may be divided into two classes. The thermal bath denoted by the letter T in Fig. 1 is the reservoir which induces thermal relaxation between the levels of the manifold $\{a\}$. The other baths, seated on lower molecular levels j ($j = 1, 2\cdots$), represent radiative and nonradiative channels for the decay of the levels $\{a\}$ and to all practical purposes may be viewed as zero temperature baths.

The Hamiltonian for our model system may be written in the form

$$\tilde{H} = H_0 + U + V = H + V \,, \tag{II.1}$$

where

$$H_0 = \sum_a \epsilon_a |a\rangle\langle a| + \epsilon_g |g\rangle\langle g| + \epsilon_{g'} |g'\rangle\langle g'| + \sum_j \epsilon_j |j\rangle\langle j| + \sum_B H_B \,. \tag{II.2}$$

$\sum_B$ is the sum over all baths, including the radiation field. Also,

$$U = U_1 + U_2 + U_3 \,, \tag{II.3}$$

$$U_1 = \sum_{\substack{a \\ a \neq a'}} \sum_{a'} F_{aa'} |a\rangle\langle a'| \quad \text{(sums over } \{a\}) \,, \tag{II.4}$$

$$U_2 = \sum_{a,j} \sum (J_{ja} |j\rangle\langle a| + J_{aj} |a\rangle\langle j|) \tag{II.5}$$

(a goes over $\{a\}$, and j goes over lower molecular states), and

$$U_3 = \sum_\lambda K_\lambda |\lambda\rangle\langle\lambda| \quad (\lambda = \{a\}, \{j\}, g, g') \,. \tag{II.6}$$

F, J, and K are interaction Hamiltonians between the relevant molecular states and the baths. $F_{aa'}$, J_{ja}, and $K_\lambda = K_{\lambda\lambda}$ are the matrix elements of these interaction operators between the corresponding molecular states, and are still operators in the baths coordinates. The different baths are assumed to be uncorrelated, that is,

$$\langle FJ\rangle = \langle KJ\rangle = \langle KF\rangle = 0 \,,$$
$$\langle J_{ai} J_{bj}\rangle = \langle J_{aj} J_{bj}\rangle \delta_{ij} \,,$$
$$\langle J_{ai} J_{jb}\rangle = \langle J_{aj} J_{jb}\rangle \delta_{ij} \,, \tag{II.7}$$

where $\langle\ \rangle$ denote averages over the bath distributions. Physically the operators J are responsible for the decay of the states $\{a\}$ into radiative channels as well as into nonradiative channels seated on lower molecular states j. The corresponding baths consist of photon states in the case of radiative channels or any other continuous manifolds which may belong to the molecule itself and play the role of radiationless sinks. Thus, a particular j may represent a lower electronic state with the corresponding "bath" consisting of the quasicontinuous vibrational manifold seated on this state. All the j baths are taken as zero temperature baths representing irreversible damping, but this feature of the model is not necessary and can be relaxed without additional complication.

The operators F and K represent interactions between the molecule and its surroundings which cause thermal relaxation (corresponding to the temperature T of the surroundings) within the manifold $\{a\}$. F represents this part of the interaction which leads to actual transitions (t_1 processes) within $\{a\}$, while K stands for the part which corresponds to "elastic collisions" which do not change the molecular state (t_2 processes). Strictly speaking, F and K correspond to the same thermal bath and the relation $\langle FK\rangle = 0$ does not necessarily hold. The rationale behind disregarding this term is that within the rotating wave approximation F and K contain different Fourier components of the interaction and are therefore only weakly, if at all, correlated.

Finally, the operator V in Eq. (II.1) represents the interaction of the molecule with the incoming and the outgoing photons. The interaction with those modes of the radiation field which do not participate in the light scattering process is not included in V. Later in the

calculation, we apply a low order expansion in V, but interaction with the nonparticipating modes, which contribute to the radiative damping is taken to all orders. These radiative continua are considered to be among the zero temperature baths i displayed in Fig. 1.

In the dipole approximation V takes the form

$$V \propto \sum_{l,l'} \sum_{k\sigma} \frac{\epsilon_{ll'}}{\sqrt{\omega_k}} (a_{k\sigma} + a^*_{k\sigma}) \mathbf{e}_{k\sigma} \cdot \mu_{ll'} |l\rangle\langle l'| , \qquad \text{(II.8)}$$

where l, l' are molecular states; $\epsilon_{ll'} = \epsilon_l - \epsilon_{l'}$; ω_k is the frequency of a photon of wave vector k; σ is the polarization state of the photon; $\mathbf{e}_{k\sigma}$ is a unit vector in the direction of polarization; and $\mu_{ll'}$ is the molecular dipole matrix element.

In this paper we shall not be interested in polarization studies. The incident beam will be taken to be nonpolarized, and we shall average over the statistical mixture of incident beam polarizations and sum over the states of polarization of the scattered photon.

Equations (II.1)–(II.8) constitute the model in terms of which we discuss absorption line shapes and Raman scattering from molecules interacting with dissipative baths. In the next section we describe the formalism by which we approach this problem.

III. THEORETICAL APPROACH

In this section we present those aspects of the Liouville space approach to scattering and relaxation which will be useful for our discussion of Raman scattering from thermally reacting multilevel systems. Further details are found in the references.[42–44]

We consider light absorption and scattering in a system with ground state g and final state g'. In the diadic formalism the absorption cross section is given by

$$\sigma_g = -\frac{2\Omega}{\hbar c} \operatorname{Im} T_{gg} , \qquad \text{(III.1)}$$

where Ω is the normalization volume of the system (which is taken to infinity and is cancelled at the end of any calculation), c is the speed of light, and T is the diadic T operator defined in terms of the Green's operator $\tilde{G}(E) = (E - \tilde{H} + i\eta)^{-1}$ $(\eta \to 0+)$ by

$$T(E) = V + V\tilde{G}(E)V . \qquad \text{(III.2)}$$

The scattering cross section between states g and g' is given by

$$\sigma_{g\to g'} = \frac{2\pi}{\hbar} \frac{\Omega}{c} |T_{gg'}|^2 \delta(E_g - E_{g'}) . \qquad \text{(III.3)}$$

It should be noted that by $g(g')$ we denote here the molecular initial (final) state plus the incoming (outgoing) photon.

Turning now to the Liouville space formalism, we consider matrix elements of the tetradic $\mathcal{T}$ operator defined in terms of the tetradic equivalents of the interaction V (to be denoted $\mathcal{V}$) and the Green's function G (to be denoted $\mathcal{G}$),

$$\mathcal{T}(\omega) = \mathcal{V} + \mathcal{V}\mathcal{G}(\omega)\mathcal{V} . \qquad \text{(III.4)}$$

Matrix elements of $\mathcal{V}$ are given by

$$\mathcal{V}_{cd;ab} = V_{ca}\delta_{db} - \delta_{ca}V_{db} , \qquad \text{(III.5)}$$

while the tetradic Green's function is defined by

$$\mathcal{G}(\omega) = (\omega - \tilde{\mathcal{L}} + i\eta)^{-1} \quad (\eta \to 0^+), \qquad \text{(III.6)}$$

with the Liouville operator $\tilde{\mathcal{L}}$ satisfying

$$\tilde{\mathcal{L}}_{cd,ab} = \tilde{H}_{ca}\delta_{db} - \delta_{ca}\tilde{H}_{db} . \qquad \text{(III.7)}$$

The starting point for discussing line shapes and scattering profiles in the Liouville space formalism is the following equation satisfied by elements of the $\mathcal{T}$ matrix on the zero frequency shell[43,44]:

$$\mathcal{T}_{cc;aa}(0) = 2i \operatorname{Im} T_{aa}(E_a)\delta_{ca} + 2\pi i |T_{ca}(E_a)|^2 \delta(E_c - E_a) . \qquad \text{(III.8)}$$

For $g \neq g'$ we obtain by comparison to Eq. (III.3)

$$\sigma_{g\to g'} = -\frac{i}{\hbar} \frac{\Omega}{c} \mathcal{T}_{g'g';gg}(0) . \qquad \text{(III.9)}$$

For $g = g'$ we have

$$\mathcal{T}_{gg,gg}(0) = 2i \operatorname{Im} T_{gg}(E_g) + 2\pi i (|T_{g'g}(E_g)|^2 \delta(E_{g'} - E_g)_{g'\to g}$$

$$= -2\pi i \sum_{g'\neq g} |T_{g'g}(E_g)|^2 \delta(E_{g'} - E_g) , \qquad \text{(III.10)}$$

where we have used the optical theorem for the diadic T matrix

$$\pi \sum_{g'} |T_{g'g}(E_g)|^2 \delta(E_{g'} - E_g) = -\operatorname{Im} T_{gg}(E_g) . \qquad \text{(III.11)}$$

From Eq. (III.1), the first equality of Eq. (III.10) can be recast in the form

$$\mathcal{T}_{gg,gg}(0) = \frac{\hbar c}{i\Omega} \sigma_g + 2\pi i (|T_{g'g}(E_g)|^2 \delta(E_{g'} - E_g))_{g'\to g} . \qquad \text{(III.12)}$$

Evidently, the fully diagonal matrix element $\mathcal{T}_{gg,gg}(0)$ is singular (see also Appendix A). However, the singular term is of order $O(V^4)$ in the interaction with the incoming and outgoing photons. Therefore, as long as we limit ourselves to terms which are second order in this interaction, we can write

$$\sigma_g = \frac{i\Omega}{\hbar c} \mathcal{T}_{gg,gg}(0) \quad [\text{to } O(V^2)] . \qquad \text{(III.13)}$$

Equations (III.9) and (III.13) provide the desired expressions for the line shape and scattering cross section within the Liouville space formalism. In what follows we shall limit ourselves to weak exciting fields, for which it is enough to evaluate Eq. (III.9) to the fourth order and Eq. (III.13) to the second order in V.

The Liouville space formalism is specifically suited to evaluate cross sections averaged on a given initial distribution of a bath (or baths) interacting with the relevant system. We proceed to evaluate explicit expressions for $\langle\sigma_g\rangle$ and $\langle\sigma_{g\to g'}\rangle$, where $\langle\ \rangle$ donates averages over bath distributions.

Line shape. Starting from the identity [obtained from Eqs. (III.8) and (III.11)]

$$\sum_{g'} \sum_{\beta} \langle\langle g'\beta;\ g'\beta|\mathcal{T}|g\alpha;\ g\alpha\rangle\rangle = 0 , \qquad \text{(III.14)}$$

where g and g' denote, as before, the states of the relevant system, while α and β are bath initial and final states, we obtain

$$\sum_{g'\neq g}\sum_{\beta}\langle\langle g'\beta;\, g'\beta|\,\mathcal{T}\,|\,g\alpha;\, g\alpha\rangle\rangle = -\sum_{\beta}\langle\langle g\beta;\, g\beta|\,\mathcal{T}\,|g\alpha,\, g\alpha\rangle\rangle\ . \tag{III.15}$$

The operator $\mathcal{T}$ will be understood to be on the zero frequency shell [$\mathcal{T}=\mathcal{T}(0)$]. Taking thermal average on the initial bath states we obtain

$$\sum_{\alpha}\rho_{\alpha}\sum_{g'\neq g}\sum_{\beta}\langle\langle g'\beta;\, g'\beta|\,\mathcal{T}|g\alpha;\, g\alpha\rangle\rangle = -\sum_{\alpha}\rho_{\alpha}\sum_{\beta}\langle\langle g\beta;\, g\beta|\,\mathcal{T}|g\alpha;\, g\alpha\rangle\rangle\ . \tag{III.16}$$

For a single thermal bath of temperature T, $\rho_{\alpha}=\exp(-E_{\alpha}/k_BT)/\sum_{\alpha}\exp(-E_{\alpha}/k_BT)$. In our model we have one such bath and also several baths of zero temperature and ρ_{α} will be a product of the corresponding distributions. Now, the lhs of Eq. (III.16) is just proportional to the averaged line shape function,[45] and we obtain

$$\langle\sigma_g\rangle=\frac{i\Omega}{\hbar c}\,\langle\mathcal{T}\rangle_{gg,gg}\ . \tag{III.17}$$

The averaged tetradic $\mathcal{T}$ operator is

$$\langle\mathcal{T}\rangle=\sum_{\alpha}\rho_{\alpha}\sum_{\beta}\langle\langle\beta\beta|\,\mathcal{T}\,|\alpha\alpha\rangle\rangle \tag{III.18}$$

and is an operator in the molecular subspace. Introducing the Zwanzig projector[46]

$$C=\rho_B\,\mathrm{Tr}_B=\sum_{\alpha}\sum_{\beta}\rho_{\alpha}|\,\alpha\alpha\rangle\rangle\langle\langle\beta\beta|\ , \tag{III.19}$$

where Tr_B denotes trace over the irrelevant (baths) subspaces, and ρ_B is the baths density operator, we can recast Eq. (III.18) in the form

$$\langle\mathcal{T}\rangle=\mathrm{Tr}_B\,C\mathcal{T}C\rho_B\ . \tag{III.20}$$

It should be ketp in mind that Tr_B also includes trace over the states of the radiation field (corresponding to a zero temperature bath), excluding the incoming and the outgoing photons. In Eq. (III.4) the single $\mathcal{U}$ term on the rhs does not contribute to the relevant matrix elements as it does not couple states with equal numbers of photons. Restricting ourselves to the weak coupling limit, the absorption profile can be adequately discussed in the lowest (second) order in $\mathcal{U}$, and using a well known expression for the projected tetradic Green's function, the absorption line shape function is obtained in the form

$$\sigma_c=\frac{i\Omega}{c\hbar}\,(\langle\langle gg|\,\mathcal{U}\langle\mathcal{G}(\omega)\rangle\mathcal{U}|gg\rangle\rangle)_{\omega=0}\ , \tag{III.21}$$

with

$$\mathcal{G}(\omega)=(\omega-\mathcal{L}+i\eta)^{-1}\qquad(\eta\to0^{+})\ , \tag{III.22}$$

$$\langle\mathcal{G}(\omega)\rangle=\mathrm{Tr}_BC\mathcal{G}(\omega)C\rho_B=(\omega-\mathcal{L}_0^{sys}-\langle\mathcal{R}(\omega)\rangle)^{-1}\ , \tag{III.23}$$

$$\mathcal{R}(\omega)=\mathcal{U}+\mathcal{U}(1-C)(\omega-\mathcal{L}_0+i\eta)^{-1}(1-C)\mathcal{U}\ , \tag{III.24}$$

$$\langle\mathcal{R}(\omega)\rangle=\langle\langle\mathrm{Tr}_B|\,\mathcal{R}(\omega)\,|\rho_B\rangle\rangle = \sum_{\alpha}\sum_{\beta}\rho_{\alpha}\langle\langle\beta\beta|\,\mathcal{R}(\omega)\,|\alpha\alpha\rangle\rangle\ . \tag{III.25}$$

$\mathcal{L}$, $\mathcal{L}_0$, and $\mathcal{U}$ are the tetradic operators corresponding to H, H_0, and U of Eq. (II.1), $\mathcal{L}_0^{sys}$ corresponds to the operator H_0, Eq. (II.2), without the bath Hamiltonians but with this part of the radiation field Hamiltonian corresponding to the incoming and outgoing photons. In the notation where g and g' include these photon states, $H_0^{sys}=H_0-\sum_B H_B\cdot\langle\mathcal{R}(\omega)\rangle$ is the bath averaged level shift (tetradic) operator which is an operator in the molecular coordinates. Note that Eq. (III.24) is approximate: the correct expression should contain $\mathcal{L}=\mathcal{L}_0+\mathcal{U}$, instead of $\mathcal{L}_0$ in the denominator of the rhs. The approximation involved is the usual weak system–bath coupling involved in most calculations of this kind.

Scattering. The baths-averaged scattering cross section is given in the form

$$\sigma_{g\to g'}=-\frac{i\Omega}{\hbar c}\sum_{\beta}\sum_{\alpha}\rho_{\alpha}\langle\langle g'\beta;\, g'\beta|\,\mathcal{T}\,|\,g\alpha;\, g\alpha\rangle\rangle = -\frac{i\Omega}{\hbar c}\,\langle\langle g'g'|\,\langle\mathcal{T}\rangle\,|gg\rangle\rangle\ . \tag{III.26}$$

Here the lowest contributing order in $\mathcal{U}$ is $O(\mathcal{U}^4)$, and we may take

$$\langle\mathcal{T}\rangle=(\langle\mathcal{U}\mathcal{G}(\omega)\mathcal{U}\mathcal{G}(\omega)\mathcal{U}\mathcal{G}(\omega)\mathcal{U}\rangle)_{\omega=0}\ . \tag{III.27}$$

In what follows we invoke the following ansatz concerning the average in Eq. (III.27):

$$\langle\mathcal{T}\rangle=(\mathcal{U}\langle\mathcal{G}(\omega)\rangle\mathcal{U}\langle\mathcal{G}(\omega)\rangle\mathcal{U}\langle\mathcal{G}(\omega)\rangle\mathcal{U})_{\omega=0}\ . \tag{III.28}$$

This separation ansatz is usually applied very close to resonance, within the impact approximation.[47a] However, it can be shown[47b] that its range of validity is far wider than that of the impact approximation. Indeed Eq. (III.28) turns out to hold provided $d\langle\mathcal{R}(\omega)\rangle/d\omega\ll1$, with correction terms of this order. This condition may be satisfied, in principle in the entire spectral range of interest. This point is of great importance in the present model where the set of states $\{a\}$ may include states which are far from resonance for any exciting energy.

Equation (III.26), together with Eqs. (III.28) and (III.23)–(III.25), constitute our final formal result for the Raman scattering cross section within the weak coupling approximation.

It is seen now that within the approximation employed, both σ_g and $\sigma_{g\to g'}$ are given in terms of $\langle\mathcal{G}(\omega)\rangle_{\omega=0}$, which in turn is obtained once $\langle\mathcal{R}(\omega)\rangle$ is found. We next derive a general expression for $\langle\mathcal{R}(\omega)\rangle\equiv\bar{\mathcal{R}}(\omega)$. This is a tetradic operator in the molecular space with matrix elements given by

$$\langle\langle a,\, b|\,\bar{\mathcal{R}}(\omega)\,|\,c,\, d\rangle\rangle = \sum_{\alpha}\sum_{\beta}\rho_{\alpha}\langle\langle a\beta;\, b\beta|\,\mathcal{R}(\omega)\,|\,c\alpha;\, d\alpha\rangle\rangle = \sum_{\alpha}\sum_{\beta}\rho_{\alpha}\langle\langle a\beta;\, b\beta|\,\mathcal{U}(\omega-\mathcal{L}_0)^{-1}\mathcal{U}|\,c\alpha,\, d\alpha\rangle\rangle\ . \tag{III.29}$$

If

$$\mathcal{U}=\sum_B\mathcal{U}_B\quad\text{(sum over baths)}\ , \tag{III.30}$$

Then

$$\bar{\mathcal{R}}(\omega)=\sum_B \bar{\mathcal{R}}^B(\omega)\ , \tag{III.31}$$

where

$$\langle\langle ab\,|\bar{\mathcal{R}}^B(\omega)\,|\,cd\rangle\rangle$$

$$=\sum_\alpha\sum_\beta \rho_\alpha^B\langle\langle a\beta,\ b\beta\,|\,\mathcal{U}^B(\omega-\mathcal{L}_0)^{-1}\mathcal{U}^B\,|\,c\alpha,d\alpha\rangle\rangle\ . \tag{III.32}$$

Here α, β correspond in each case to the states of the particular bath involved.

Let us focus now on a particular bath and omit the index B during the rest of the discussion. The tetradic operator $\mathcal{U}$ corresponds to a diadic of the general form

$$U=\sum_{kl} U^{kl}\,|k\rangle\langle l|\ , \tag{III.33}$$

where U^{kl} are operators in the bath coordinates ($U^{kl}=(U^{lk})^\dagger$), and where k, l go over all the molecular levels. Using the general properties of $\mathcal{U}$ as a Liouville operator, we obtain the following relations:

$$\mathcal{U}\,|c\alpha;\ d\alpha\rangle\rangle=\sum_{k\delta}\left(U^{kc}_{\delta\alpha}\,|k\delta;\ d\alpha\rangle\rangle-U^{dk}_{\alpha\delta}\,|c\alpha;\ k\delta\rangle\rangle\right)\ ,$$

$$\langle\langle a\beta;\ b\beta\,|\,\mathcal{U}=\sum_{k\delta}\left(U^{ak}_{\beta\delta}\langle\langle k\delta;\ b\beta\,|-U^{kb}_{\delta\beta}\langle\langle a\beta;\ k\delta\,|\right)\ , \tag{III.34}$$

where

$$U^{kl}_{\beta\delta}=\langle\beta\,|\,U^{kl}\,|\,\delta\rangle\ . \tag{III.35}$$

Equations (III. 32) and (III. 34) now lead to the result

$$\langle\langle ab\,|\bar{\mathcal{R}}(\omega)\,|\,cd\rangle\rangle=\sum_\alpha \rho_\alpha\Big\{\delta_{bd}\sum_{k\delta}U^{ak}_{\alpha\delta}U^{kc}_{\delta\alpha}(\omega-\epsilon_{kb}-\omega_{\delta\alpha}+i\eta)^{-1}+\delta_{ac}\sum_{k\delta}U^{kb}_{\delta\alpha}U^{dk}_{\alpha\delta}(\omega-\epsilon_{ak}-\omega_{\alpha\delta}+i\eta)^{-1}$$

$$-\sum_\delta U^{ac}_{\delta\alpha}U^{db}_{\alpha\delta}(\omega-\epsilon_{cb}-\omega_{\alpha\delta}+i\eta)^{-1}-\sum_\delta U^{db}_{\alpha\delta}U^{ac}_{\delta\alpha}(\omega-\epsilon_{ad}-\omega_{\delta\alpha}+i\eta)^{-1}\Big\}\ , \tag{III.36}$$

where $\epsilon_{ad}=\epsilon_a-\epsilon_d$ and $\omega_{\delta\alpha}=\omega_\delta-\omega_\alpha$ are energy differences between energy levels of the molecule and the bath, respectively.

It will prove convenient to express the sums appearing in Eq. (III. 36) as bath correlation functions. To this end we convert the energy denominators in Eq. (III. 36) to exponentials using the relation

$$(A+i\eta)^{-1}=-i\int_0^\infty dt\exp(iAt) \tag{III.37}$$

and then replace ω_α and ω_δ by H_B operating on the corresponding bath states. Then the δ summation yields (taking also $\omega=0$)

$$\langle\langle ab\,|\bar{\mathcal{R}}(\omega=0)\,|\,cd\rangle\rangle=-i\int_0^\infty dt\Big\{\delta_{bd}\sum_k\exp(-i\epsilon_{kb}t)\langle U^{ak}(t)U^{kc}(0)\rangle+\delta_{ac}\sum_k\exp(-i\epsilon_{ak}t)\langle U^{dk}(0)U^{kb}(t)\rangle$$

$$-\exp(-i\epsilon_{cb}t)\langle U^{db}(0)U^{ac}(t)\rangle-\exp(-i\epsilon_{ad}t)\langle U^{db}(t)U^{ac}(0)\rangle\Big\}\ . \tag{III.38}$$

To end this section, we note that the operators U^{kl} appearing in Eq. (III. 38) are given explicitly in the model introduced in Eqs. (II. 1)–(II. 6).

Thus,

$$U^{aa'}=F_{aa'}\ , \tag{III.39a}$$

$$U^{ja}=J_{ja}\ , \tag{III.39b}$$

and

$$U^{\lambda\lambda}=K_\lambda\quad(\lambda=\{a\},\ g,\ g')\ . \tag{III.39c}$$

This concludes our formal discussion. The absorption line shape σ_g, Eq. (III. 21), and the scattering cross section $\sigma_{g\to g'}$, Eqs. (III. 26) and (III. 28), can be calculated using Eqs. (III. 23) and (III. 38). In the next section we present the general results from this calculation.

IV. GENERAL RESULTS

The formalism presented in the previous section is now applied to yield general expressions for the absorption and scattering cross sections within the model described in Sec. II.

Absorption line shape. Equations (III. 21), (III. 23), and (II. 8), together with the resolution of the identity in the molecular space $\sum_{kl}|kl\rangle\rangle\langle\langle kl|=1$, yield

$$\sigma_g=\frac{i\Omega}{c\hbar}\,\mathbf{a}^\dagger\mathbf{M}\,\mathbf{a}\ , \tag{IV.1}$$

where

$$\mathbf{a}=\begin{pmatrix}\langle\langle a_1 g\,|\,\mathcal{V}\,|\,gg\rangle\rangle\\ \langle\langle a_2 g\,|\,\mathcal{V}\,|\,gg\rangle\rangle\\ \vdots\\ \langle\langle a_n g\,|\,\mathcal{V}\,|\,gg\rangle\rangle\\ \langle\langle g a_1\,|\,\mathcal{V}\,|\,gg\rangle\rangle\\ \langle\langle g a_2\,|\,\mathcal{V}\,|\,gg\rangle\rangle\\ \vdots\\ \langle\langle g a_n\,|\,\mathcal{V}\,|\,gg\rangle\rangle\end{pmatrix}=\begin{pmatrix}V_{a_1 g}\\ V_{a_2 g}\\ \vdots\\ V_{a_n g}\\ -V_{g a_1}\\ -V_{g a_2}\\ \vdots\\ -V_{g a_n}\end{pmatrix}\ , \tag{IV.2a}$$

$$\mathbf{a}^\dagger=(V_{g a_1}\cdots V_{g a_n},\ -V_{a_1 g}\cdots-V_{a_n g})\ . \tag{IV.2b}$$

Here $a_1\cdots a_n=\{a\}$ is the set of optically active molecular levels in the spectral region of interest. Also, the

matrix **M** is given as the inverse of

$$\mathbf{M}^{-1} = -\begin{pmatrix} \epsilon_{a_1 g} + \bar{R}_{a_1 g, a_1 g} & R_{a_1 g, a_2 g} & \cdots & \bar{R}_{a_1 g, g a_n} \\ \bar{R}_{a_2 g, a_1 g} & \epsilon_{a_2 g} + \bar{R}_{a_2 g, a_2 g} & & \vdots \\ \vdots & & \ddots & \vdots \\ \bar{R}_{g a_n, a_1 g} & \cdots & & \epsilon_{g a_n} + \bar{R}_{g a_n, g a_n} \end{pmatrix}, \tag{IV.3}$$

with

$$\bar{R}_{ab,cd} = \langle\langle ab | \bar{R}(\omega = 0) | cd \rangle\rangle , \tag{IV.4}$$

which is given in a general form by Eqs. (III.38) and (III.39), and explicitly in Appendix B. It should be noted that the input necessary for the calculation of an absorption profile according to this scheme includes the molecular energy level diagram, the radiative couplings $V_{a_i g}$ $(i = 1 \ldots n)$ and time correlation functions of the molecular interactions with the different baths.

Scattering. Equations (III.26), (III.28), (III.23), and (II.8) lead to

$$\begin{aligned} \sigma_{g \to g'} &= -\frac{i\Omega}{c\hbar} \langle\langle g'g' | \mathcal{U} \langle \mathcal{G}(\omega = 0) \rangle \\ &\quad \times \mathcal{U} \langle \mathcal{G}(\omega = 0) \rangle \mathcal{U} \langle \mathcal{G}(\omega = 0) \rangle \mathcal{U} | gg \rangle\rangle \\ &= \frac{i\Omega}{c\hbar}\, \mathbf{b}^{\dagger} \mathbf{N} (\mathbf{A}_1 \mathbf{K}_1 \mathbf{B}_1 + \mathbf{A}_2 \mathbf{K}_2 \mathbf{B}_2)\, \mathbf{M}\, \mathbf{a} . \end{aligned} \tag{IV.5}$$

b is of the same form as **a**, Eq. (IV.2b), with g' replacing g. Similarly, the matrix **N** is identical in form to **M** given by Eq. (IV.3), only g' replaces g here. $\mathbf{B}_1$ is a matrix of $2n$ columns and n^2 rows (n is the number of states in $\{a\}$) given by

$$\mathcal{B}_1 = \begin{pmatrix} \mathcal{U}_{a_1 a_1; a_1 g} & \mathcal{U}_{a_1 a_1; a_2 g} & \cdots & \mathcal{U}_{a_1 a_1; a_n g} & \mathcal{U}_{a_1 a_1; g a_1} & \cdots & \mathcal{U}_{a_1 a_1; g a_n} \\ \vdots & & & & & & \vdots \\ \mathcal{U}_{a_1 a_1; a_1 g} & & & & & & \vdots \\ \mathcal{U}_{a_2 a_1; a_1 g} & & & & & & \vdots \\ \vdots & & & & & & \vdots \\ \mathcal{U}_{a_2 a_n; a_1 g} & & & & & & \vdots \\ \vdots & & & & & & \vdots \\ \mathcal{U}_{a_n a_1; a_1 g} & & & & & & \vdots \\ \vdots & & & & & & \vdots \\ \mathcal{U}_{a_n a_n; a_1 g} & \cdots & & \cdots & & \cdots & \mathcal{U}_{a_n a_n; g a_n} \end{pmatrix} . \tag{IV.6}$$

A_1 is a matrix with n^2 columns and $2n$ rows given by

$$A_1 = \begin{pmatrix} \mathcal{U}_{a_1 g'; a_1 a_1} & \cdots & \mathcal{U}_{a_1 g'; a_1 a_n} & \cdots & \mathcal{U}_{a_1 g'; a_n a_1} & \cdots & \mathcal{U}_{a_1 g'; a_n a_n} \\ \mathcal{U}_{a_2 g'; a_1 a_1} & & & & & & \vdots \\ \vdots & & & & & & \vdots \\ \mathcal{U}_{a_n g'; a_1 a_1} & & & & & & \vdots \\ \mathcal{U}_{g' a_1; a_1 a_1} & & & & & & \vdots \\ \vdots & & & & & & \vdots \\ \mathcal{U}_{g' a_n; a_1 a_1} & \cdots & & \cdots & & \cdots & \mathcal{U}_{g' a_n; a_n a_n} \end{pmatrix} . \tag{IV.7}$$

$\mathbf{K}_1$ is an $n^2 \times n^2$ square matrix of the operator $\langle G(\omega = 0) \rangle$ within the set $\{a\}$. Using the notation $\bar{\mathcal{G}} = \langle \mathcal{G}(\omega = 0) \rangle$, the matrix $\mathbf{K}_1$ takes the form

$$\mathbf{K}_1 = \begin{pmatrix} \bar{\mathcal{G}}_{a_1 a_1; a_1 a_1} & \cdots & \bar{\mathcal{G}}_{a_1 a_1; a_1 a_n} & \cdots & \bar{\mathcal{G}}_{a_1 a_1; a_n a_1} & \cdots & \bar{\mathcal{G}}_{a_1 a_1; a_n a_n} \\ \vdots & & & & & & \vdots \\ \bar{\mathcal{G}}_{a_1 a_n; a_1 a_1} & & & & & & \vdots \\ \vdots & & & & & & \vdots \\ \bar{\mathcal{G}}_{a_n a_1; a_1 a_1} & & & & & & \vdots \\ \vdots & & & & & & \vdots \\ \bar{\mathcal{G}}_{a_n a_n; a_1 a_1} & \cdots & & \cdots & & \cdots & \bar{\mathcal{G}}_{a_n a_n; a_n a_n} \end{pmatrix} . \tag{IV.8}$$

The matrix $\mathbf{B}_2$ has two rows and $2n$ columns and is given by

$$\mathbf{B}_2 = \begin{pmatrix} \upsilon_{gg';a_1g} & \cdots & \upsilon_{gg';a_ng} & \upsilon_{gg';ga_1} & \cdots & \upsilon_{gg';ga_n} \\ \upsilon_{g'g;a_1g} & \cdots & \upsilon_{g'g;a_ng} & \upsilon_{g'g;ga_1} & \cdots & \upsilon_{g'g;ga_n} \end{pmatrix} . \tag{IV.9}$$

A_2 is a $2n \times 2$ matrix having the form

$$\mathbf{A}_2 = \begin{pmatrix} \upsilon_{a_1g';gg'} & \upsilon_{a_1g';g'g} \\ \vdots & \vdots \\ \upsilon_{a_ng';gg'} & \upsilon_{a_ng';g'g} \\ \upsilon_{g'a_1;gg'} & \upsilon_{g'a_1;g'g} \\ \vdots & \vdots \\ \upsilon_{g'a_n;gg'} & \upsilon_{g'a_n;g'g} \end{pmatrix} . \tag{IV.10}$$

Finally, $\mathbf{K}_2$ is a square matrix of order 2 given by

$$\mathbf{K}_2 = \begin{pmatrix} \bar{\mathcal{G}}_{gg';gg'} & \bar{\mathcal{G}}_{gg';g'g} \\ \bar{\mathcal{G}}_{g'g;gg'} & \bar{\mathcal{G}}_{g'g;g'g} \end{pmatrix} . \tag{IV.11}$$

The explicit forms of the matrices $\mathbf{A}_1$, $\mathbf{B}_1$, $\mathbf{K}_1$ and $\mathbf{A}_2$, $\mathbf{B}_2$, $\mathbf{K}_2$ can be obtained from the definition of υ [Eq. (III.5)] and from Eq. (III.23). Contributions to the matrix $\mathbf{B}_1$ are obtained from

$$\begin{aligned} \upsilon_{ab,cg} &= -\delta_{ac} V_{gb} , \\ \upsilon_{ab,gd} &= \delta_{bd} V_{ag} . \end{aligned} \tag{IV.12}$$

Similarly, the terms of A_1 are given by

$$\begin{aligned} \upsilon_{ag,cd} &= -\delta_{ac} V_{dg} , \\ \upsilon_{gb,cd} &= \delta_{bd} V_{gc} . \end{aligned} \tag{IV.13}$$

The matrices $\mathbf{B}_2$ and $\mathbf{A}_2$ become

$$\mathbf{B}_2 = \begin{pmatrix} 0 & \cdots & 0 & -V_{a_1g'} & \cdots & -V_{a_ng'} \\ V_{g'a_1} & \cdots & V_{g'a_n} & 0 & \cdots & 0 \end{pmatrix} . \tag{IV.14}$$

$$\mathbf{A}_2 = \begin{pmatrix} V_{a_1g} & 0 \\ \vdots & \vdots \\ V_{a_ng} & 0 \\ 0 & -V_{ga_1} \\ \vdots & \vdots \\ 0 & -V_{ga_n} \end{pmatrix} . \tag{IV.15}$$

The matrix $\mathbf{K}_1$ is obtained as the inverse of

$$\mathbf{K}_1^{-1} = -\begin{pmatrix} \bar{\mathcal{R}}_{a_1a_1;a_1a_1} & \bar{\mathcal{R}}_{a_1a_1;a_1a_2} & \cdots & \bar{\mathcal{R}}_{a_1a_1;a_1a_n} & \cdots & \bar{\mathcal{R}}_{a_1a_1;a_na_1} & \cdots & \bar{\mathcal{R}}_{a_1a_1;a_na_n} \\ \bar{\mathcal{R}}_{a_1a_2;a_1a_1} & \epsilon_{a_1a_2} + \bar{\mathcal{R}}_{a_1a_2;a_1a_2} & & & & & & \\ \vdots & & \ddots & & & & & \\ \bar{\mathcal{R}}_{a_1a_n;a_1a_1} & & & \epsilon_{a_1a_n} + \bar{\mathcal{R}}_{a_1a_n;a_1a_n} & & & & \\ \vdots & & & & \ddots & & & \\ \bar{\mathcal{R}}_{a_na_1;a_1a_1} & & & & & \epsilon_{a_na_1} + \bar{\mathcal{R}}_{a_na_1;a_na_1} & & \\ \vdots & & & & & & \ddots & \\ \bar{\mathcal{R}}_{a_na_n;a_1a_1} & & & & & & & \bar{\mathcal{R}}_{a_na_n;a_na_n} \end{pmatrix} . \tag{IV.16}$$

where again $\epsilon_{a_1a_2} = \epsilon_{a_1} - \epsilon_{a_2}$. Finally, the matrix $\mathbf{K}_2$ is the diagonal square matrix

$$\mathbf{K}_2 = \begin{pmatrix} (\epsilon_{g'} - \epsilon_g - \bar{\mathcal{R}}_{gg';gg'})^{-1} & 0 \\ 0 & (\epsilon_g - \epsilon_{g'} - \bar{\mathcal{R}}_{g'g;g'g})^{-1} \end{pmatrix} . \tag{IV.17}$$

The necessary elements of $\bar{\mathcal{R}}$ are given in Appendix B.

Equation (IV.5), together with Eqs. (IV.6), (IV.7), and (IV.14)–(IV.17), provide an explicit result for the scattering cross section in terms of the radiative interactions V_{a_ig} $(i = 1 \cdots n)$ and the correlation functions of the interactions between the molecule and the baths.

V. SIMPLE MODEL RESULTS

In this section we apply the general results obtained in the previous section to particular cases. After briefly outlining the results obtained when the manifold $\{a\}$ consists of a single level, we shall focus attention on the two level model (two levels in $\{a\}$), which is the simplest model with both t_1 and t_2 processes occurring within the manifold of intermediate states. We shall discuss in terms of this model the temperature effect and the effect of quenching on the yields of the different emission modes in the resonance light scattering process. Also, this model can be utilized to discuss the effect of thermal relaxation on intramolecular interference effects.

A summary of some notations used in this section is provided in Appendices C and D.

Single intermediate level. This case was formerly studied by Huber.[17–20] Recently, Mukamel, Jortner, and Ben-Reuven[48] have studied the same problem within

the Liouville space framework. From the general results of Sec. IV, we obtain the absorption line shape with a single intermediate level $|s\rangle$ by putting in Eq. (IV.1), cf. Eqs. (IV.2)–(IV.4),

$$\mathbf{a} = \begin{pmatrix} V_{sg} \\ -V_{gs} \end{pmatrix}, \quad \mathbf{a}^+ = (V_{gs}, \ -V_{sg}) , \tag{V.1}$$

and

$$\mathbf{M} = -\begin{pmatrix} \epsilon_{sg} + \bar{\mathcal{R}}_{sg;sg} & 0 \\ 0 & -\epsilon_{sg} + \bar{\mathcal{R}}_{gs;gs} \end{pmatrix}^{-1} . \tag{V.2}$$

The necessary matrix elements of $\bar{\mathcal{R}}$ are obtained from Appendix B. The final result for the absorption cross section is

$$\sigma_g = \frac{2\Omega}{c\hbar} |V_{sg}|^2 \frac{\Gamma}{\tilde{\epsilon}_{sg}^2 + \Gamma^2} , \tag{V.3}$$

where

$$\tilde{\epsilon}_{sg} = \epsilon_s - \epsilon_g + D_{sg} \tag{V.4}$$

is the shifted energy difference,

$$D_{sg} = \mathrm{Im} \int_0^\infty dt \Big\{ \sum_j \exp(-i\epsilon_{gj} t) \langle J_{js}(0) J_{js}(t) \rangle + \exp(i\epsilon_{sg} t) [\langle K_s(0) K_s(t) \rangle + \langle K_g(t) K_g(0) \rangle - \langle K_s(0) K_g(t) \rangle - \langle K_s(t) K_g(0) \rangle] \Big\} \tag{V.5}$$

is the total energy shift, and

$$\Gamma = \Gamma_j + \kappa \tag{V.6}$$

is the total width associated with the $g \rightarrow s$ transition, where the shorthand notation

$$\Gamma_j \equiv \sum_j \Gamma_{sj} = \sum_j \frac{1}{2} \int_{-\infty}^{\infty} \exp(i\epsilon_{gj} t) \langle J_{sj}(t) J_{js}(0) \rangle \tag{V.7}$$

stands for the contribution to the width of the level s related to its decay to continuous channels associated with lower molecular levels j. Finally,

$$\kappa = \frac{1}{2} \int_{-\infty}^{\infty} \exp(i\epsilon_{sg} t) [\langle K_s(0) K_s(t) \rangle + \langle K_g(t) K_g(0) \rangle - \langle K_s(0) K_g(t) \rangle - \langle K_s(t) K_g(0) \rangle] \tag{V.8}$$

is the contribution to the width of the $g \rightarrow s$ transition associated with t_2-type modulation of the energy levels s and g. In the classical limit where K_s and K_g commute with each other, Eq. (V.8) takes the form

$$\kappa = \frac{1}{2} \int_{-\infty}^{\infty} \exp(i\epsilon_{sg}(t) \langle (K_s(0) - K_g(0)) (K_s(t) - K_g(t)) \rangle , \tag{V.8'}$$

which has an obvious physical interpretation. In many discussions of t_2 contributions to line broadening, K_g is disregarded. In the classical limit this can be understood as redefining the operator K.

The scattering cross section associated with the single intermediate level $|s\rangle$ is obtained from Eq. (IV.5) using Eqs. (V.1) and (V.2) (and their $g \rightarrow g'$ equivalents) and in addition

$$\mathbf{B}1 = (-V_{gs}, \ V_{sg}) , \quad \mathbf{A}_1 = \begin{pmatrix} -V_{sg'} \\ V_{g's} \end{pmatrix} , \tag{V.9}$$

$$\mathbf{K}_1 = -R^{-1}_{ss;ss} = (2i\Gamma_j)^{-1} , \tag{V.10}$$

$$\mathbf{B}_2 = \begin{pmatrix} 0 & -V_{sg'} \\ V_{g's} & 0 \end{pmatrix} , \quad \mathbf{A}_2 = \begin{pmatrix} V_{sg} & 0 \\ 0 & -V_{gs} \end{pmatrix} , \tag{V.11}$$

$$\mathbf{K}_2 = \begin{pmatrix} (-\tilde{\epsilon}_{gg'} + i\kappa_g)^{-1} & 0 \\ 0 & (\tilde{\epsilon}_{gg'} + i\kappa_g)^{-1} \end{pmatrix} , \tag{V.12}$$

with

$$\tilde{\epsilon}_{gg'} = \epsilon_g - \epsilon_{g'} + \mathrm{Im} \int_0^\infty dt \exp(-i\epsilon_{gg'} t) I_g , \tag{V.12'}$$

$$\kappa_g = \mathrm{Re} \int_0^\infty dt \exp(-i\epsilon_{gg'} t) I_g = \frac{1}{2} \int_{-\infty}^{\infty} dt \exp(-i\epsilon_{gg'} t) I_g , \tag{V.12''}$$

$$I_g = \langle K_g(t) K_g(0) \rangle + \langle K_{g'}(0) K_g(t) \rangle - \langle K_{g'}(0) K_g(t) \rangle - \langle K_{g'}(t) K_g(0) \rangle . \tag{V.12'''}$$

The final result for the scattering cross section is obtained in the form

$$\sigma_{g \rightarrow g'} = \frac{2\Omega}{c\hbar} |V_{sg} V_{sg'}|^2 \frac{1}{\tilde{\epsilon}_{sg}^2 + \Gamma^2} \left[\frac{\Gamma^2 + \epsilon_{sg} \epsilon_{sg'}}{\tilde{\epsilon}_{sg'}^2 + \Gamma^2} \frac{\kappa_g}{\tilde{\epsilon}_{gg'}^2 + \kappa_g^2} + \frac{\Gamma^2/\Gamma_j + \Gamma\epsilon_{gg'}(\tilde{\epsilon}_{sg} - \tilde{\epsilon}_{sg'})/(\tilde{\epsilon}_{gg'}^2 + \kappa_g^2)}{\tilde{\epsilon}_{sg'}^2 + \Gamma^2} \right] . \tag{V.13}$$

In most cases κ_g is very small so that the first term in the square brackets is sharply peaked at $\tilde{\epsilon}_g = \tilde{\epsilon}_{g'}$. In the second term we can take $\epsilon_{gg'}(\tilde{\epsilon}_{sg} - \tilde{\epsilon}_{sg'})/(\tilde{\epsilon}_{gg'}^2 + \kappa_g^2) = -1$. In this approximation we get

$$\sigma_{g \rightarrow g'} = \frac{2\Omega}{c\hbar} \frac{|V_{sg} V_{sg'}|^2}{\tilde{\epsilon}_{sg}^2 + \Gamma^2} \left[\frac{\kappa_g}{\tilde{\epsilon}_{gg'}^2 + \kappa_g^2} + \frac{\kappa}{\Gamma_j} \frac{\Gamma}{\tilde{\epsilon}_{sg'}^2 + \Gamma^2} \right] . \tag{V.14}$$

For $\kappa_g \rightarrow 0$ we obtain

$$\sigma_{g \rightarrow g'} = \frac{2\Omega}{c\hbar} \frac{|V_{sg} V_{sg'}|^2}{\tilde{\epsilon}_{sg}^2 + \Gamma^2} \left(\pi\delta(\epsilon_g - \epsilon_{g'}) + \frac{\kappa}{\Gamma_j} \frac{\Gamma}{\tilde{\epsilon}_{sg'}^2 + \Gamma^2} \right) . \tag{V.14'}$$

This result was originally obtained by Huber. Note that multiplying by the density of final state $\rho(\epsilon_{g'})$ and integrating over $\epsilon_{g'}$ we obtain (using $\pi |V_{sg'}|^2 \rho(\epsilon_{g'}) = \Gamma^f$ = radiative width for the transition to the final state) $\int d\epsilon_{g'} \rho(\epsilon_{g'}) \sigma_{g \rightarrow g'} = \Gamma^f (\Gamma/\Gamma_j) |V_{sg}|^2 (\tilde{\epsilon}_{sg}^2 + \Gamma^2)^{-1}$, whereas the total quantum yield

$$y = \frac{\int d\epsilon_{g'} \rho(\epsilon_{g'}) \sigma_{g \rightarrow g'}}{\sigma_g} = \frac{\Gamma^f}{\Gamma_j} \equiv \frac{\Gamma^f}{\sum_j \Gamma_{sj}} \tag{V.15}$$

is just the energy independent ratio of the radiative width to the total damping width of the level s, and is

not affected by the interaction which gives rise to κ.

Two intermediate levels. The application of the general formulas of Sec. IV to the case of two intermediate levels is as straightforward as in the case of single intermediate level but naturally more cumbersome. In Appendix C we summarize the notations used for the different kinetic coefficients and energy shift terms encountered in this calculation. For simplicity we take $K_g = K_{g'} = 0$ so that the result is the two level generalization of Eq. (V.15).

The intermediate levels are denoted $|s\rangle$ and $|r\rangle$ with $\epsilon_r > \epsilon_s$. Utilizing the results of Sec. IV, we obtain the following expressions for the vectors and matrices appearing in Eqs. (IV.1) and (IV.5):

$$\mathbf{M} = \begin{pmatrix} -\mathbf{m}^* & \mathbf{0} \\ \mathbf{0} & \mathbf{m} \end{pmatrix}, \tag{V.16}$$

$$\mathbf{m} = \begin{pmatrix} \bar{\epsilon}_{rg} + i\Gamma_r & d_j + i\gamma_j \\ d_j + i\gamma_j & \bar{\epsilon}_{sg} + i\Gamma_s \end{pmatrix}^{-1}, \tag{V.17}$$

$$\Gamma_r = \Gamma_{rs}(\epsilon_{gs}) + \Gamma_{rj}(\epsilon_{gr}) + \kappa_r(\epsilon_{gr}), \tag{V.18}$$

$$\Gamma_s = \Gamma_{rs}(\epsilon_{gr}) + \Gamma_{sj}(\epsilon_{gj}) + \kappa_s(\epsilon_{gs}), \tag{V.19}$$

$$\mathbf{K}_1 = \begin{pmatrix} 2i(\Gamma_{rs}+\Gamma_{rj}) & i\gamma + d_j & i\gamma_j - d_j & -2i\Gamma_{rs}\exp(-\beta\epsilon) \\ i\gamma_j + d_j & i(\Gamma_{rj}+\Gamma_{sj}+\kappa) - \bar{\epsilon} & 0 & i\gamma_j - d_j \\ i\gamma_j - d_j & 0 & i(\Gamma_{rj}+\Gamma_{sj}+\kappa) + \bar{\epsilon} & i\gamma_j + d_j \\ -2i\Gamma_{rs} & i\gamma_j - d_j & i\gamma_j + d_j & 2i(\Gamma_{rs}\exp(-\beta\epsilon) + \Gamma_{sj}) \end{pmatrix}^{-1}, \tag{V.20}$$

$$\mathbf{K}_2 = \begin{pmatrix} (-\epsilon_{gg'} + i\eta)^{-1} & 0 \\ 0 & (\epsilon_{gg'} + i\eta)^{-1} \end{pmatrix}, \tag{V.21}$$

$$\mathbf{A}_1 = \begin{pmatrix} -V_{rg'} & -V_{sg'} & 0 & 0 \\ 0 & 0 & -V_{rg'} & -V_{sg'} \\ V_{g'r} & 0 & V_{g's} & 0 \\ 0 & V_{g'r} & 0 & V_{g's} \end{pmatrix}, \tag{V.22}$$

$$\mathbf{B}_1 = \begin{pmatrix} -V_{gr} & 0 & V_{rg} & 0 \\ -V_{gs} & 0 & 0 & V_{rg} \\ 0 & -V_{gr} & V_{sg} & 0 \\ 0 & -V_{gs} & 0 & V_{sg} \end{pmatrix}, \tag{V.23}$$

$$\mathbf{A}_2 = \begin{pmatrix} V_{rg} & 0 \\ V_{sg} & 0 \\ 0 & -V_{gr} \\ 0 & -V_{gs} \end{pmatrix}, \tag{V.24}$$

$$\mathbf{B}_2 = \begin{pmatrix} 0 & 0 & -V_{rg'} & -V_{sg'} \\ V_{g'r} & V_{g's} & 0 & 0 \end{pmatrix}, \tag{V.25}$$

$$\mathbf{a} = \begin{pmatrix} V_{rg} \\ V_{sg} \\ -V_{gr} \\ -V_{gs} \end{pmatrix}. \tag{V.26}$$

b and **N** are obtained from **a**, Eq. (V.26), and **M**, Eqs. (V.16)–(V.19), respectively, by replacing g by g' everywhere.

The parameters appearing in Eqs. (V.17)–(V.20) are defined in terms of time correlation functions of the interactions between the molecule and the different baths (including intramolecular baths), as obtained from Appendix B. A summary of all the relevant correlation functions and their properties is provided in Appendix C. As shown there, it turns out that the decay constants Γ^2 and κ^2 can be expressed in terms of Γ^1 and κ^1, while γ^2 and d^2 do not appear in the calculation. In Eqs. (V.17)–(V.20) we omitted the upper index 1 on all the quantities Γ, γ, and d. The same is true for $\kappa_r (= \kappa_{rr}$ of Appendix C) and $\kappa_s (= \kappa_{ss})$ appearing in Eqs. (V.18)–(V.19), while $\kappa = \kappa(\epsilon)$ appearing in Eq. (V.20) is defined by Eq. (C21a) with $\omega = \epsilon$. Next, the energy dependence of these parameters should be noted. The energy arguments of the parameters Γ and κ appearing in **M** are explicitly written in Eqs. (V.18)–(V.19). It is seen that Γ_{rj} and Γ_{sj} can be taken as constants because their argument ϵ_{gj} changes little when the energy of the incoming photon (included in ϵ_g) is swept through the spectroscopically interesting region. (This statement is based on the assumption that $\epsilon_{rj}, \epsilon_{sj} \gg \epsilon_{rs}$.) On the other hand, ϵ_{gr} and ϵ_{gs} vary strongly as a function of ϵ_g in the spectroscopically interesting region because ϵ_g is of the same order as ϵ_r or ϵ_s. Thus the energy dependence in $\Gamma_{rs}(\epsilon_{gs})$, $\Gamma_{rs}(\epsilon_{gr})$, $\kappa_r(\epsilon_{gr})$, and $\kappa_s(\epsilon_{gs})$ has to be considered. d_j and γ_j appearing in Eq. (V.17) have ϵ_{gj} as their energy argument and may be taken as constants. In **K** we have $\Gamma_{rs} = \Gamma_{rs}(\epsilon)$ $(\epsilon = \epsilon_{rs} = \epsilon_r - \epsilon_s)$, $\Gamma_{aj} = \Gamma_{aj}(\epsilon_{aj})$ $(a = r, s)$, $\kappa = \kappa(\epsilon)$, and γ_j and d_j have either ϵ_{sj} or ϵ_{rj} as their arguments. All these parameters do not depend on ϵ_g or $\epsilon_{g'}$. Moreover, in the same approximation in which $\gamma(\epsilon_{gj})$ and (ϵ_{gj}) are taken to be independent on ϵ_g in the spectral region of interest, we also have $\gamma(\epsilon_{rj}) = \gamma(\epsilon_{sj})$ and $d(\epsilon_{rj}) = d(\epsilon_{sj})$. Finally, the shifted energies appearing in Eqs. (V.17) and (V.19) are

$$\bar{\epsilon}_{rg} = \epsilon_{rg} + D_{rs}(\epsilon_{gs}) + D_{rj}(\epsilon_{gj}) + \eta_{rr}(\epsilon_{gr}), \tag{V.27}$$

$$\bar{\epsilon}_{sg} = \epsilon_{sg} + D_{rs}(\epsilon_{gr}) + D_{sj}(\epsilon_{gj}) + \eta_{ss}(\epsilon_{gs}), \tag{V.28}$$

$$\bar{\epsilon} = \bar{\epsilon}_{rs} = \epsilon_{rs} + D_{rj}(\epsilon_{sj}) - D_{sj}(\epsilon_{rj}) + \eta(\epsilon). \tag{V.29}$$

Here also functions of ϵ_{gj}, ϵ_{rj}, and ϵ_{sj} may be regarded as constants [e.g., $D_{sj}(\epsilon_{gj}) \simeq D_{sj}(\epsilon_{rj})$] while the energy dependence of functions of ϵ_{gs} and ϵ_{gr} must be taken into account.

Utilizing Eqs. (V.16), (V.17), (V.25), (V.26) with Eq. (IV.1) we obtain an explicit expression for the ab-

sorption cross section,

$$\sigma_g = -\frac{2\Omega}{\hbar c}\,\mathrm{Im}\{[(\tilde{\epsilon}_{rg}-i\Gamma_r)(\tilde{\epsilon}_{sg}-i\Gamma_s)-(d_j-i\gamma_j)^2]^{-1}\}$$
$$\times(V_{gr},\ V_{gs})\begin{pmatrix}-\tilde{\epsilon}_{sg}+i\Gamma_s & d_j-i\gamma_j\\ d_j-i\gamma_j & -\tilde{\epsilon}_{rg}+i\Gamma_r\end{pmatrix}\begin{pmatrix}V_{rg}\\ V_{sg}\end{pmatrix}. \tag{V.30}$$

We note in passing that this result [like the result (V.3)] does not rely on the separation approximation, Eq. (III.28), and is not subjected to the restriction $d\langle R(\omega)\rangle/d\omega \ll 1$.

Turning now to the calculation of the scattering cross section, it is convenient to separate the contribution from the term involving $\mathbf{K}_2$ in Eq. (IV.5) into two parts. Inserting the relation

$$\mathbf{K}_2 = PP\,\frac{1}{\epsilon_{gg'}}\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix} - i\pi\delta(\epsilon_{gg'})\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \tag{V.31}$$

into Eq. (IV.5), we obtain

$$\sigma_{g\to g'} = -\frac{i\Omega}{c\hbar}(R_F+R_R) \equiv \sigma^{RF}_{g\to g'} + \sigma^{RR}_{g\to g'}, \tag{V.32}$$

where the resonance Raman term is

$$R_R = -i\pi\mathbf{b}^\dagger\mathbf{N}\mathbf{A}_2\mathbf{B}_2\mathbf{M}\mathbf{a}\,\delta(\epsilon_g-\epsilon_{g'}), \tag{V.33}$$

while the resonance fluorescence term is

$$R_F = R_{F1}+R_{F2}, \tag{V.34}$$

with

$$R_{F1} = \mathbf{b}^\dagger\mathbf{N}\mathbf{A}_1\mathbf{K}_1\mathbf{B}_1\mathbf{M}\mathbf{a} \tag{V.35}$$

and

$$R_{F2} = \mathbf{b}^\dagger\mathbf{N}\mathbf{A}_2\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix}\mathbf{B}_2\mathbf{M}\mathbf{a}\,PP\,\frac{1}{\epsilon_{gg'}}. \tag{V.36}$$

It can be shown that the coefficient of the principal part term in Eq. (V.36) vanishes for $\epsilon_g=\epsilon_{g'}$, so that $PP(1/\epsilon_{gg'})$ may be replaced simply by $1/(\epsilon_g-\epsilon_{g'})$.

Equations (V.32)–(V.36) can be utilized for numerical computation of the different contributions to the scattering cross section, using Eqs. (V.16)–(V.29). Results of such computations will be given and discussed in a future publication. In what follows we shall consider the analytical result obtained for a simpler model in which the interference terms d_j and γ_j appearing in the expressions for the matrices $\mathbf{K}_1$, $\mathbf{M}$, and $\mathbf{N}$ are assumed to vanish. For simplicity we also take $V_{sg}=V_{gs}=V_{sg'}=V_{g's}\equiv V_s$, $V_{rg}=V_{gr}=V_{rg'}=V_{g'r}\equiv V_r$, and $\Gamma_{sj}=\Gamma_{rj}\equiv\Gamma_j$. Then a straightforward application of Eqs. (V.16)–(V.29) and (V.32)–(V.36) yields

$$\sigma^{RF}_{g\to g'} = \frac{2\Omega}{c\hbar}\Big\{V_r^4\Big[2\tilde{\gamma}'\,I(n_1)I(m_1)+\frac{I(m_1^*n_1)}{\epsilon_g-\epsilon_{g'}}\Big]+V_s^4\Big[2\gamma'\,I(n_2)I(m_2)+\frac{I(m_2^*n_2)}{\epsilon_g-\epsilon_{g'}}\Big]$$
$$+V_r^2V_s^2\Big[2\Gamma'_{rs}I(n_2)I(m_1)+2\tilde{\Gamma}'_{rs}I(n_1)I(m_2)+I\Big(\frac{(n_2-n_1^*)(m_2-m_1^*)}{\epsilon+2\tilde{\Gamma}_j i}\Big)+\frac{I(m_1^*n_2+m_2^*n_1)}{\epsilon_g-\epsilon_{g'}}\Big]\Big\}, \tag{V.37}$$

where

$$A' = \frac{A}{2(\gamma\tilde{\gamma}-\Gamma_{rs}\tilde{\Gamma}_{rs})} \qquad (A=\gamma,\ \tilde{\gamma},\ \Gamma_{rs},\ \tilde{\Gamma}_{rs}), \tag{V.38}$$

$$\tilde{\Gamma}_{rs} = \Gamma_{rs}\exp(-\beta\epsilon), \tag{V.39a}$$

$$\gamma = \Gamma_{rs}+\Gamma_j, \tag{V.39b}$$

$$\tilde{\gamma} = \tilde{\Gamma}_{rs}+\Gamma_j, \tag{V.39c}$$

$$\tilde{\Gamma}_j = \Gamma_j+\tfrac{1}{2}\kappa, \tag{V.39d}$$

$$m_l = (-E_l+i\gamma_l)^{-1}, \quad n_l = (-E'_l+i\gamma'_l)^{-1}, \quad l=1,2, \tag{V.40a}$$

$$E_1 = \epsilon_{rg}, \quad \gamma_1 = \Gamma_{rs}(\epsilon_{gs})+\Gamma_j+\kappa_r(\epsilon_{jr}), \tag{V.40b}$$

$$E_2 = \epsilon_{sg}, \quad \gamma_2 = \Gamma_{rs}(\epsilon_{gr})+\Gamma_j+\kappa_s(\epsilon_{gs}), \tag{V.40c}$$

$$E'_1 = \epsilon_{rg'}, \quad \gamma'_1 = \Gamma_{rs}(\epsilon_{g's})+\Gamma_j+\kappa_r(\epsilon_{g'r}), \tag{V.40d}$$

$$E'_2 = \epsilon_{sg'}, \quad \gamma'_2 = \Gamma_{rs}(\epsilon_{g'r})+\Gamma_j+\kappa_s(\epsilon_{g's}), \tag{V.40e}$$

and where $I(x)$ stands for $\mathrm{Im}(x)$. In these results and henceforth we omit the tilde sign denoting shifted energy levels.

The result for the scattering cross section takes particularly simple forms in the two extreme temperature limits $kT\ll\epsilon$ and $kT\gg\epsilon$.

Low temperature limit. Here $\tilde{\Gamma}_{rs}=\tilde{\Gamma}'_{rs}=0$, $\tilde{\gamma}=\Gamma_j$, $\tilde{\gamma}'=1/2\gamma$, $\gamma'=1/2\Gamma_j$, and $\Gamma'_{rs}=\Gamma_{rs}/2\gamma\Gamma_j$.

Equation (V.37) then yields

$$\sigma^{RF}_{g\to g'} = \frac{2\Omega}{c\hbar}\Big\{V_r^4\Big[\frac{I(n_1)I(m_1)}{\gamma}+\frac{I(m_1^*n_1)}{\epsilon_g-\epsilon_{g'}}\Big]$$
$$+V_s^4\Big[\frac{I(n_2)I(m_2)}{\Gamma_j}+\frac{I(m_2^*n_2)}{\epsilon_g-\epsilon_{g'}}\Big]+V_s^2V_r^2\Big[\frac{\Gamma_{rs}}{\gamma\Gamma_j}I(n_2)I(m_1)+I\Big(\frac{(n_2-n_1^*)(m_2-m_1^*)}{\epsilon+2i\tilde{\Gamma}_j}\Big)+\frac{I(m_1^*n_2+m_2^*n_1)}{\epsilon_g-\epsilon_{g'}}\Big]\Big\}. \tag{V.41}$$

Utilizing Eqs. (V.40a)–(V.40e), we obtain the explicit forms for the coefficients of V_r^4 and V_s^4 in this expression:

$$\frac{I(n_l)I(m_l)}{a}+\frac{I(m_l^*n_l)}{\epsilon_g-\epsilon_{g'}} = \frac{1}{(E_l^2+\gamma_l^2)(E_l'^2+\gamma_l'^2)}\Big(\frac{\gamma_l\gamma_{l'}}{a}+\frac{\gamma'_lE_l-\gamma_lE'_l}{\epsilon_g-\epsilon_{g'}}\Big), \quad l=1,2. \tag{V.42}$$

Here $a=\gamma$, Γ_j for $l=1$, 2, respectively. If γ_l, γ_l' are not too large, this expression will contribute mainly in the region $E_l \sim E_l' \sim 0$. Thus we get contribution to the coefficient of V_r^4 for $E_g \sim E_{g'} \sim \epsilon_r$. Putting this into the expressions (V.40b) and (V.40d) for γ_1, γ_1', we obtain $\gamma_1 \simeq \gamma_1' \simeq \Gamma_{rs} + \Gamma_j + \kappa_r(0) = \gamma + \kappa_r(0)$. Also for $\gamma_1 \simeq \gamma_1'$ we have $(\gamma_1' E_1 - \gamma_1 E_1')/(\epsilon_g - \epsilon_{g'}) = -\gamma_1$. Equation (V.42) then leads to

$$\frac{I(n_1)I(m_1)}{\gamma} + \frac{I(m_1^* n_1)}{\epsilon_g - \epsilon_{g'}} = \frac{1}{(\epsilon_{rg}^2 + \gamma_1^2)(\epsilon_{rg'}^2 + \gamma_1^2)} \frac{\gamma_1}{\gamma} \kappa_r(0) \,. \tag{V.43}$$

Similarly, the coefficient of V_s^4 is appreciable only for $\epsilon_g \simeq \epsilon_{g'} \simeq \epsilon_s$. For this energy $\gamma_2 \simeq \gamma_2' \simeq \Gamma_{rs}(-\epsilon) + \Gamma_j + \kappa_s(0)$. By Eq. (C14), $\Gamma_{rs}(-\epsilon)$ $(= \Gamma_{rs}'(-\epsilon)$ of Appendix C) is zero at $k_B T \ll \epsilon$ and $\gamma_2 \simeq \gamma_2' \simeq \Gamma_j + \kappa_s(0)$. Then

$$\frac{I(n_2)I(m_2)}{\Gamma_j} + \frac{I(m_2^* n_1)}{\epsilon_g - \epsilon_{g'}} = \frac{1}{(\epsilon_{sg}^2 + \gamma_2^2)(\epsilon_{sg'}^2 + \gamma_2^2)} \frac{\gamma_2 \kappa_s(0)}{\Gamma_j} \,. \tag{V.44}$$

The expression for the low temperature resonance fluorescence cross section then becomes

$$\sigma_{g\to g'}^{RF} = \frac{2\Omega}{c\hbar} \left\{ \frac{V_r^4}{(\epsilon_{rg}^2 + \gamma_1^2)(\epsilon_{rg'}^2 + \gamma_1^2)} \frac{\gamma_1}{\gamma} \kappa_r + \frac{V_s^4}{(\epsilon_{sg}^2 + \gamma_2^2)(\epsilon_{sg'}^2 + \gamma_2^2)} \frac{\gamma_2}{\Gamma_j} \kappa_s \right.$$
$$\left. + V_s^2 V_r^2 \left[\frac{\Gamma_{rs}}{\gamma \Gamma_j} I(n_2)I(m_1) + I\left(\frac{(n_2 - n_1^*)(m_2 - m_1^*)}{\epsilon + 2i\bar{\Gamma}_j} \right) + \frac{I(m_1^* n_2 + m_2^* n_1)}{\epsilon_g - \epsilon_{g'}} \right] \right\} \,, \tag{V.45}$$

with

$$\gamma_1 = \Gamma_{rs} + \Gamma_j + \kappa_r = \gamma + \kappa_r \,, \tag{V.46}$$

$$\gamma_2 = \Gamma_j + \kappa_s \,, \tag{V.47}$$

and, from Appendix C,

$$\kappa_a \equiv \kappa_a(0) = \frac{1}{2} \int_{-\infty}^{\infty} dt \, \langle K_a(t) K_a(0) \rangle \,, \quad a = r, \; s \,. \tag{V.48}$$

High temperature limit. Here $\Gamma_{rs} = \bar{\Gamma}_{rs}$, $\gamma = \bar{\gamma}$, $\gamma' = \bar{\gamma}' = \frac{1}{2}\gamma/(\gamma^2 - \Gamma_{rs}^2)$ and $\Gamma_{rs}' = \bar{\Gamma}_{rs}' = \frac{1}{2}\Gamma_{rs}/(\gamma^2 - \Gamma_{rs}^2)$. Equation (V.37) now leads to

$$\sigma_{g\to g'}^{RF} = \frac{2\Omega}{c\hbar} \left\{ V_r^4 \left[\frac{\gamma}{\gamma^2 - \Gamma_{rs}^2} I(n_1)I(m_1) + \frac{I(m_1^* n_1)}{\epsilon_g - \epsilon_{g'}} \right] + V_s^4 \left[\frac{\gamma}{\gamma^2 - \Gamma_{rs}^2} I(n_2)I(m_2) + \frac{I(m_2^* n_2)}{\epsilon_g - \epsilon_{g'}} \right] \right.$$
$$\left. + V_s^2 V_r^2 \left[\frac{\Gamma_{rs}}{\gamma^2 - \Gamma_{rs}^2} (I(n_1)I(m_2) + I(n_2)I(m_1)) + I\left(\frac{(m_2 - m_1^*)(n_2 - n_1^*)}{\epsilon + 2i\bar{\Gamma}_j} \right) + \frac{I(m_1^* n_2 + m_2^* n_1)}{\epsilon_g - \epsilon_{g'}} \right] \right\} \,. \tag{V.49}$$

Approximations similar to those made above now lead to

$$\frac{I(m_1^* n_1)}{\epsilon_g - \epsilon_{g'}} = -\frac{I(n_1)I(m_1)}{\gamma + \kappa_r} \,, \tag{V.50a}$$

$$\frac{I(m_2^* n_2)}{\epsilon_g - \epsilon_{g'}} = -\frac{I(n_2)I(m_2)}{\gamma + \kappa_s} \,. \tag{V.50b}$$

If we make the additional assumption that $\Gamma_{rs}(\omega)$ and $\kappa_a(\omega)$ $(a = r, \; s)$ do not depend on their energy arguments throughout all the interesting spectral region (such an assumption can be consistent of course only in the high temperature limit) and that $\kappa_r = \kappa_s \equiv \bar{\kappa}$ (so that $\gamma_1 = \gamma_2 = \gamma_1' = \gamma_2' = \gamma + \bar{\kappa}$), it can be shown by straightforward algebraic manipulations that

$$\frac{I(m_1^* n_2 + m_2^* n_1)}{\epsilon_g - \epsilon_{g'}} = -I\left[\frac{(m_2 - m_1^*)(n_2 - n_1^*)}{\epsilon + 2(\gamma + \bar{\kappa})i} \right] \,. \tag{V.51}$$

With these approximations made, Eq. (V.49) yields

$$\sigma_{g\to g'}^{RF} = \frac{2\Omega}{c\hbar} \left\{ [V_r^4 I(n_1)I(m_1) + V_s^4 I(n_2)I(m_2)] \frac{\bar{\kappa}/\gamma + (\Gamma_{rs}/\gamma)^2}{\gamma(1 + \bar{\kappa}/\gamma)[1 - (\Gamma_{rs}/\gamma)^2]} \right.$$
$$\left. + V_s^2 V_r^2 \left[[I(n_1)I(m_2) + I(n_2)I(m_1)] \frac{\Gamma_{rs}/\gamma}{\gamma[1 - (\Gamma_{rs}/\gamma)^2]} + 2(\Gamma_{rs} + \kappa_{rs}) \operatorname{Re} \frac{(m_2 - m_1^*)(n_2 - n_1^*)}{(\epsilon + 2\bar{\Gamma}_j i)(\epsilon + 2(\gamma + \bar{\kappa})i)} \right] \right\} \,. \tag{V.52}$$

The last term in Eq. (V.52) obtained by using $\bar{\Gamma}_j = \Gamma_j + \kappa$, $\gamma = \Gamma_j + \Gamma_{rs}$, and $\kappa = 2\,(\bar{\kappa} - \kappa_{rs})$ as given by Eq. (C21a).

The following comments should be made at this point.

(a) Equation (V.37) with Eq. (V.45) for the low temperature limit and Eq. (V.52) in the high temperature limit constitute our final results for the cross section for resonance fluorescence (or the "redistributed emission") $\sigma_{g\to g'}^{RF}$ for the case $d_j = \gamma_j = 0$ (interstate coupling caused by interaction of the two states with the same bath is disre-

garded). Also the assumptions mentioned before, Eq. (V.37) and those following Eq. (V.50), were made for simplicity.

(b) In many applications the last term of Eq. (V.52) can be neglected relative to the other terms. For $\epsilon \gg \Gamma$, $\gamma + \bar{\kappa}$ this term is of order Γ/ϵ^2 (Γ denotes here the order of a width) while the other terms are $O(1/\Gamma)$ and are much larger. In this case the high temperature *RF* cross section becomes

$$\sigma^{RF}_{g\to g'} = \frac{2\Omega}{c\hbar}\left(V_r^4 I(n_1)I(m_1) + V_s^4 I(n_2)I(m_2)\,\frac{\bar{\kappa}/\gamma + (\Gamma_{rs}/\gamma)^2}{\gamma(1+\bar{\kappa}/\gamma)[1-(\Gamma_{rs}/\gamma)^2]} + V_s^2 V_r^2[I(n_1)I(m_2) + I(n_2)I(m_1)]\,\frac{\Gamma_{rs}/\gamma}{\gamma[1-(\Gamma_{rs}/\gamma)^2]}\right) . \quad (V.53)$$

(c) Both the low temperature result, Eq. (V.45), and the high temperature result, Eqs. (V.52) and (V.53), contain "direct" terms, proportional to V_s^4 and V_r^4 and corresponding to excitation and emission in the vicinity of the same spectral line, and "transfer" terms proportional to $(V_s V_r)^2$ and corresponding to absorption near one spectral line and emission near another. It is seen that the transfer term proportional to $I(m_2)\,I(n_1)$, which corresponds to excitation near the lower level s and emission near the higher level r, is missing, as expected, in the low temperature expression.

(d) The most serious approximation involved in obtaining these results is the factorization invoked in Eq. (III.28). In choosing parameters to enter in Eq. (V.37), it is important to remember that these results hold provided $d\Re(\omega)/d\omega \ll 1$. Therefore, for example, a model in which $\Gamma_{rs}(E)$ and $\kappa(E)$ do not vanish at $T \to 0$, the limit $E \to 0$ cannot be applied in the low temperature case because of the discontinuity in the widths implied by Eqs. (C14) and (C18). Another drawback involved in the factorization ansatz is that it leads to an expression for the scattering cross section which is no longer positive definite as the original expression (III.3) was. Actually computed values may become negative (in the low T limit) in regions of very small cross section, and of course have to be discarded. In the high T limit the factorization ansatz may become exact and under these conditions no negative results are encountered.

(e) For $V_r = \Gamma_{rs} = 0$, both Eqs. (V.45) and (V.52) lead to

$$\sigma^{RF}_{g\to g'} = \frac{2\Omega}{c\hbar}\,\frac{V_s^4(\Gamma_f+\kappa_s)(\kappa_s/\Gamma_f)}{[\epsilon_{sg}^2+(\Gamma_f+\kappa_s)^2][\epsilon_{sg'}^2+(\Gamma_f+\kappa_s)^2]} , \quad (V.54)$$

where κ_s should be calculated for the corresponding temperature. This result is identical to the *RF* term in Eq. (V.14) for the single excited level case (where $\Gamma = \Gamma_f + \kappa_s$).

(f) In calculating matrix elements of $\Re$, we took the molecule–bath interaction up to second order. This, together with the assumption of weak dependence of $\Re(E)$ on E, leads to the characteristic Lorentzian forms appearing in the expressions for the absorption line shape and the scattering cross section. This, however, has a serious deficiency as it predicts nonzero emission in energies larger than the incident energy even in the zero temperature limit.

(g) As is well known, a nonperturbative treatment of terms of the kind (II.6) with K_λ being of first order in the phonon coordinates leads to the typical asymmetric line shapes with phonon sidebands associated with impurity states in solids. If we disregard such terms and take for K_λ only terms nonlinear in the bath coordinates the results can be interpreted as contributions from zero phonon lines only.[36] Also, the low temperature result is probably appropriate for discussing ratios between emission intensities in direct and transfer lines and between *RR* and *RF* processes. This point needs further justification, however.

(h) It is important to note that keeping the energy arguments of $\kappa_a(\omega)$ ($a = r, s$) and $\Gamma_{rs}(\omega)$ was essential for obtaining the results at the low temperature limit. Assigning an energy independent t_2-type width to each level as is often done in stochastic theories is fundamentally wrong for low temperatures where relations like Eqs. (C14) and (C18) imply considerable energy dependence of these widths. One should keep in mind that such relations also impose a lower bound on the temperature range for which the theory is valid as the condition $d\bar{\Re}(\omega)/d\omega \ll 1$ implies that

$$\frac{|\Re(|\omega|)|}{k_B T}\,\exp\left(-\frac{|\omega|}{k_B T}\right) \ll 1 \quad (V.55)$$

has to be satisfied for all $E < 0$. This however, is not a very restrictive condition as in most cases $\Re(E) \sim 0$ for E, $T \to 0$.

In order to obtain the total cross section for the resonance light scattering, we have to add to $\sigma^{RF}_{g\to g'}$ also the Raman scattering cross section $\sigma^{RR}_{g\to g'}$. Under the same assumptions which lead to Eqs. (V.37), (V.41), and (V.49), Eqs. (V.32)–(V.33) yield

$$\sigma^{RR}_{g\to g'} = \frac{2\Omega}{c\hbar}\,\delta(\epsilon_g - \epsilon_{g'})\,|m_1 V_r^2 + m_2 V_s^2|^2 . \quad (V.56)$$

The temperature dependence of this expression comes only through the temperature dependence of the relaxation widths appearing in m_1 and m_2.

Finally, to have a complete picture we write the line shape function under the same assumptions. Equation (IV.1) leads to

$$\sigma_g = -\frac{2\Omega}{c\hbar}\,(V_r^2 I(m_1) + V_s^2 I(m_2)) , \quad (V.57)$$

which is, as should be expected in the absence of interference terms, a sum of two simple Lorentzian terms.

Expressions (V.32), (V.37) [with its extreme temperature limits, Eqs. (V.41) and (V.49)], and (V.56) constitute our final result for the RLS cross section in a two intermediate level system without interstate coupling. Equation (V.57) is the absorption cross section for the same case.

We are now in a position to discuss the effect of

radiationless damping contributions to Γ_j on the relative magnitude of terms in the absorption and scattering cross section. We shall limit this discussion here to the simplest case, delaying detailed numerical investigation to later work. We thus focus attention on the approximate high temperature expression with $\kappa_r = \kappa_s = \bar{\kappa}$ and with $V_s^2 = V_r^2 \equiv V^2 \propto \Gamma_{\rm rad}^i$ ($\Gamma_{\rm rad}^i$ is the radiative width associated with emission to the initial state and we assume the state s and r to be close enough in energy to correspond to the same density of photon states for transitions to the ground state). We also note that when comparing the absorption and scattering cross section, $\alpha_{g\to g'}$ should be multiplied by the density of final states $\rho(g')$. Denoting $V^2\rho(g') = (1/\pi)\Gamma_{\rm rad}^f$ (where $\Gamma_{\rm rad}^f$ is the radiative width associated with emission to the final state), we finally obtain

$$\sigma_{g\to g'}\rho(\epsilon_{g'}) \propto \frac{\Gamma_{\rm rad}^i \Gamma_{\rm rad}^f}{\pi}\left(\pi\delta(\epsilon_g - \epsilon_{g'})|m_1+m_2|^2 + \frac{\bar{\kappa}/\gamma + (\Gamma_{rs}/\gamma)^2}{\gamma(1+\bar{\kappa}/\gamma)(1-(\Gamma_{rs}/\gamma)^2)}(I(n_1)I(m_1)+I(n_2)I(m_2)) + \frac{\Gamma_{rs}/\gamma}{\gamma(1-(\Gamma_{rs}/\gamma)^2)}(I(n_1)I(m_2)+I(n_2)I(m_1))\right) \quad (V.58)$$

and

$$\sigma_g \propto -\Gamma_{\rm rad}^i(I(m_1)+I(m_2)) = \Gamma_{\rm rad}^i(\bar{\kappa}+\gamma)(|m_1|^2+|m_2|^2) \quad (V.59)$$

with the same proportionality coefficient in Eqs. (V.58) and (V.59). The expression (V.58) for the scattering cross section contains five terms. The first corresponds to coherent scattering. The next two can be interpreted as describing emission from the level (r or s) which is originally excited, while the last two describe absorption to one level and emission from the other. Integrating over $\epsilon_{g'}$ and noting that $\int d\epsilon_{g'} I(n_l) = \pi$ ($l = 1, 2$), while $I(m_l) = (\bar{\kappa}+\gamma)|m_l|^2$, we obtain from Eq. (V.58)

$$\int d\epsilon_{g'}\sigma_{g\to g'}\rho(\epsilon_{g'}) \propto \Gamma_{\rm rad}^i\Gamma_{\rm rad}^f\left[|m_1+m_2|^2 + \frac{\bar{\kappa}/\gamma+(\Gamma_{rs}/\gamma)^2}{1-(\Gamma_{rs}/\gamma)^2}(|m_1|^2+|m_2|^2) + \frac{(\bar{\kappa}/\gamma+1)(\Gamma_{rs}/\gamma)}{1-(\Gamma_{rs}/\gamma)^2}(|m_2|^2+|m_1|^2)\right]. \quad (V.60)$$

Consider now excitation in the vicinity of the level r, whereas the m_2 terms in Eq. (V.60) and (V.59) can be neglected. [The error involved in neglecting $|m_2|^2$ is of the same order of the term disregarded in going from (V.52) to (V.53)]. The integrated scattering cross section then becomes

$$\int d\epsilon_{g'}\sigma_{g\to g'}\rho(\epsilon_{g'}) = \Gamma_{\rm rad}^i\Gamma_{\rm rad}^f|m_1|^2\frac{\gamma+\bar{\kappa}}{\Gamma_j}. \quad (V.61)$$

Dividing by $\sigma_g \simeq \Gamma_{\rm rad}^i(\bar{\kappa}+\gamma)|m_1|^2$, we obtain the quantum yield

$$y_f = \frac{\Gamma_{\rm rad}^f}{\Gamma_j}. \quad (V.62)$$

The same result is obtained for excitation near level s. Numerical calculations based on our more general expressions show that the quantum yield is indeed independent on the incident photon energy through all the spectral region in a model where the decay rates associated with levels s and r are taken to be equal and providing interference terms are absent.[49] This result is a generalization of the similar result obtained for a single molecular resonance [Eq. (V.15)].

More interesting predictions are obtained by comparing the magnitudes of the different terms in Eq. (V.60). The following features are readily observed: (a) The two direct terms are equal in magnitude, and the same is true for the two transfer terms. This result corresponds to the high temperature limit, and is due to the fact that we took $V_r = V_s$. (b) The relative intensity of transfer terms and direct terms is

$$\frac{I_{\rm trans}}{I_{\rm dir}} = \frac{(\bar{\kappa}/\gamma+1)(\Gamma_{rs}/\gamma)}{\bar{\kappa}/\gamma+(\Gamma_{rs}/\gamma)^2}. \quad (V.63)$$

Note that $I_{\rm dir}$ was taken to contain only redistributed radiation. If we include the coherent scattering also, we obtain for $|m_1+m_2|^2 \simeq |m_1|^2+|m_2|^2$ (nonoverlapping resonances)

$$\frac{I_{\rm trans}}{\tilde{I}_{\rm dir}} = \frac{\Gamma_{rs}}{\gamma} \quad (V.64)$$

$\tilde{I}_{\rm dir}$ denotes the sum of the coherent and the "direct" redistributed scattering terms. (c) The relative yield between the coherent and the redistributed radiation is given, again for $|m_1+m_2|^2 \simeq |m_1|^2+|m_2|^2$, by

$$\frac{I_{\rm coh}}{I_{\rm red}} = \frac{1-(\Gamma_{rs}/\gamma)^2}{(1+\Gamma_{rs}/\gamma)(\bar{\kappa}/\gamma+\Gamma_{rs}/\gamma)}. \quad (V.65)$$

Three kinetic coefficients are involved in these ratios: Γ_{rs}, the rate of thermal relaxation within the excited state manifold due to inelastic transitions; $\bar{\kappa}$, level modulation and broadening due to quasielastic interactions with the surrounding medium; and $\gamma = \Gamma_{rs} + \sum_j \Gamma_j$, where $\sum_j \Gamma_j$ is the rate of damping of the excited state manifold caused by interaction with radiative and radiationless channels, including collision induced damping.

In the limit $\Gamma_j \to \infty$ (Γ_{rs}/γ, $\bar{\kappa}/\gamma \to 0$), Eqs. (V.63)–(V.65) lead to

$$\frac{I_{\rm trans}}{I_{\rm dir}} \xrightarrow{\Gamma_j\to\infty} \frac{\Gamma_{rs}}{\bar{\kappa}}, \quad (V.66)$$

$$\frac{I_{\rm trans}}{\tilde{I}_{\rm dir}} \xrightarrow{\Gamma_j\to\infty} \frac{\Gamma_{rs}}{\Gamma_j}, \quad (V.67)$$

and

$$\frac{I_{\rm coh}}{I_{\rm red}} \xrightarrow{\Gamma_j\to\infty} \frac{\Gamma_j}{\bar{\kappa}+\Gamma_{rs}}. \quad (V.68)$$

In the limit $\Gamma_j \to 0$ ($\gamma \to \Gamma_{rs}$), which can only approximately hold since a small radiative width must persist, we obtain

$$\frac{I_{\text{trans}}}{I_{\text{dir}}} \xrightarrow{\Gamma_j \to 0} 1 , \tag{V.69}$$

$$\frac{I_{\text{trans}}}{\tilde{I}_{\text{dir}}} \xrightarrow{\Gamma_j \to 0} 1 , \tag{V.70}$$

and

$$\frac{I_{\text{coh}}}{I_{\text{red}}} \xrightarrow{\Gamma_j \to 0} \frac{\Gamma_j}{\Gamma_{rs}+K} . \tag{V.71}$$

Finally, in the absence of any interaction with the surrounding medium $\Gamma_{rs}=\bar{\kappa}=0$ and Eq. (V.65) implies $I_{\text{coh}}/I_{\text{red}}=\infty$ (i.e., $I_{\text{red}}=0$).

These results, obtained under highly simplifying assumptions, contain all the qualitative features of the effect of medium induced relaxation on the resonance light scattering in the absence of interference phenomena:

(1) For an isolated molecule, only coherent scattering exists and the cross section for redistributed emission is zero. Note that the presence of collision induced damping does not change this conclusion. (By damping we refer to irreversible transitions out of the manifold $\{a\}$.)

(2) When the interaction with the surrounding medium increases this may affect $\bar{\kappa}$ and Γ_{rs} and also Γ_j through collision induced damping.

(3) For a weak medium molecule interaction we usually have $\bar{\kappa} \gg \Gamma_{rs} \gg$ (collision induced damping). If no intramolecular damping channels exist, $\Gamma_j \to 0$ and Eqs. (V.69)–(V.71) account for the relative intensities.

(4) When Γ_j increases, Eqs. (V.66)–(V.68) imply that the intensity of the transfer lines is reduced relative to that of the direct lines (for $\bar{\kappa} \gg \Gamma_{rs}$ this holds both for $I_{\text{trans}}/I_{\text{dir}}$ and $I_{\text{trans}}/\tilde{I}_{\text{dir}}$). For a many level system, such effect practically reduces the number of observed lines in the scattered light spectrum and may effectively bring structure to a previously structureless spectrum. (Note that in a multilevel system the number of transfer lines is much larger than that of direct lines.) This may be the effect seen by Friedman and Hochstrasser.[40]

It is interesting to note that for $\bar{\kappa} \ll \Gamma_{rs}$ (such that molecule–medium interaction is more effective in inducing inelastic transitions) $I_{\text{trans}}/I_{\text{dir}}$ increases when $\Gamma_j \to \infty$. This is in contrast to whay may be anticipated from simple kinetic arguments. Consider the model

$$G \xrightarrow{k'} R,$$

$$R \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S ,$$

$$R \xrightarrow{k} F_1 ,$$

$$S \xrightarrow{k} F_2 . \tag{V.72}$$

Here k' corresponds to the rate of populating the state R, k_1, and k_2 are rates for relaxation between S and R and k is the rate of damping of the $\{S, R\}$ manifold. This model yields the steady state populations

$$R = \frac{k'G}{k_1 + k + k_1(k_1/k_2 + k)} ,$$

$$S = \frac{k_1}{k_2 + k} R , \tag{V.73}$$

so that $S/R = k_1/(k_2+k)$. For $k \to 0$, $S/R \to k_1/k_2$, while for $k \to \infty$, $S/R \to k_1/k \to 0$, so that fast damping rate supresses the transfer of population from R to S. This is contrary to the result (V.66) (for $\bar{\kappa} \ll \Gamma_{rs}$) but agrees with (V.64). The somewhat surprising result implied by Eq. (V.66) is caused by the fact that for $\bar{\kappa}=0$ both I_{trans} and I_{dir} depend on Γ_{rs} and actually I_{dir} is of higher order in the interaction which leads to Γ_{rs} than I_{trans}. It should be added that in principle both $I_{\text{trans}}/I_{\text{dir}}$ and $I_{\text{trans}}/\tilde{I}_{\text{dir}}$ are measurable quantities.

VI. CONCLUSION

In this paper we have presented the solution for a model for nonpolarized resonance light scattering from a thermally relaxing multilevel system in the absence of inhomogeneous broadening. This model takes into account both thermal relaxation within the excited state manifold and damping into channels outside this manifold and can be used to discuss interference between levels of the excited manifold.

The main general results for the absorption line shape and the scattering cross section are given in Sec. IV, with the necessary $\bar{R}$ matrix elements given in Appendix B. General results for the one and two intermediate states models are given in Eqs. (V.3), (V.13), and (V.14) (single intermediate level) and Eqs. (V.16)–(V.30) and (V.32)–(V.36) (two intermediate levels). The particular case where cross coupling terms arising from interaction of different excited levels with the same baths are disregarded is further discussed in Eqs. (V.37)–(V.57). In particular, analytic results displaying the effect of damping on the relative yields of different emission modes are given and discussed at the end of Sec. V. The more general results are of course amenable to numerical computations which will be presented in a future publication.

The results (V.63)–(V.71) which show the effect of damping on the relative yields were obtained in a model where interference terms are disregarded and therefore should correspond in a sense to a classical kinetic scheme. The agreement between Eqs. (V.73) and (V.64) shows that this is indeed the case. It should be realized though that the present quantum mechanical approach is useful even for this simple case as it gives information about the energy distribution of the scattered radiation and shows the way in which quasielastic interactions affect the scattering process.

The simple model results presented in Sec. V clearly show that RLS cross sections and relative yields contain a large amount of information concerning the rates of the different relaxation processes involving the excited state manifold. Indeed, it has been demonstrated[24,25,31] that such relative yields can be used to estimate the rates of extremely fast radiationless transitions from excited electronic states of large molecules. More

information can be obtained in systems where relative yields of coherent and relaxed emission are obtained. The model presented here should be very useful in analyzing such data.

ACKNOWLEDGMENT

We are grateful to Professor A. Ben Reuven and Professor J. Jortner for stimulating discussions, and to Dr. J. Friedman for reading the manuscript and for useful comments.

APPENDIX A: ON THE SINGULARITY OF FULLY DIAGONAL TERMS OF THE TETRADIC τ MATRIX

The line shape function $\sigma_g(E_g)$, being a physically observable quantity, is of course analytic and well behaved. From Eqs. (III. 10) and (III. 11) we have

$$\frac{1}{\pi}\,\mathrm{Im}\,T_{gg}(E_g) = -\sum_{g'} |T_{g'g}(E_g)|^2\,\delta(E_g - E_{g'})\,, \tag{A1}$$

$$\frac{i}{2\pi}\,\mathcal{T}_{gg,gg}(0) = -\sum_{g'\neq g} |T_{g'g}(E_g)|^2\,\delta(E_{g'} - E_g)\,. \tag{A2}$$

The quantities on the lhs of Eqs. (A1) and (A2) differ from each other by a singular term, and therefore at least one of them has to be singular. Since the absorption line shape is related to the depletion of radiation intensity in the forward direction due to the presence of the absorber, it may be thought that $T_{gg,gg}(0)$ given by Eq. (A2) is the experimentally measured and therefore nonsingular quantity (remember that g stands for both the molecular and the photon states). The following consideration shows that it is actually $\mathrm{Im}\,T_{gg}(E_g)$ which is the nonsingular quantity. If $\delta\phi$ is a solid angle in the forwarded direction, the absorbed intensity may be defined by

$$\begin{aligned} I_{\text{absorbed}} &= \lim_{\delta\phi\to 0} \sum_{g'\neq\delta\phi} |T_{g'g}|^2\,\delta(E_{g'} - E_g) \\ &= \lim_{\delta\phi\to 0}\left(\sum_{\substack{g' \\ (\text{all } g')}} |T_{g'g}|^2\,\delta(E_{g'} - E_g) \right. \\ &\quad \left. - \sum_{g'\in\delta\phi} |T_{g'g}|^2\,\delta(E_{g'} - E_g)\right) \\ &= \lim_{\delta\phi\to 0}\left(-\,\mathrm{Im}\,T_{gg} - |T_{gg}|^2\rho(E_g)\,\delta\phi\right) \\ &= -\,\mathrm{Im}\,T_{gg}\,. \end{aligned}$$

Here $g' \neq \delta\phi$ means that the wave vector of the emitted photon is not in the solid angle $\delta\phi$. We see that it is $\mathrm{Im}\,T_{gg}$ which is related to the proper definition of the measurable absorbed intensity and it is therefore the nonsingular quantity.

APPENDIX B: THE MATRIX $\bar{\mathcal{R}}$

For the absorption and scattering problems we need matrix elements of $\bar{\mathcal{R}}$ of three kinds: (1) those within the subset $\{a\}$; (2) those within the subset $\{g, g'\}$; and (3) elements between mixed pairs ag and $a'g$ or ag' and $a'g'$. Explicit expressions for these elements can be obtained from Eqs. (III. 38) and (III. 39):

$$\begin{aligned} &\langle\langle a_1 a_2|\bar{\mathcal{R}}(\omega=0)|a_3 a_4\rangle\rangle \equiv \bar{\mathcal{R}}_{a_1a_2;a_3a_4} \\ &= -i\int_0^\infty dt\left\{\delta_{a_2a_4}\left(\sum_{a'\neq a_1,a_3}\exp(-i\epsilon_{a'a_2}t)\langle F_{a_1a'}(t)F_{a'a_3}(0)\rangle + \sum_j \exp(-i\epsilon_{ja_2}t)\langle J_{a_1j}(t)J_{ja_3}(0)\rangle\right.\right. \\ &\quad \left.+\,\delta_{a_1a_3}\exp(-i\epsilon_{a_1a_2}t)\langle K_{a_1}(t)K_{a_1}(0)\rangle\right) + \delta_{a_1a_3}\left(\sum_{a'\neq a_2,a_4}\exp(-i\epsilon_{a_1a'}t)\langle F_{a_4a'}(0)F_{a'a_2}(t)\rangle\right. \\ &\quad \left.\left.+\sum_j \exp(-i\epsilon_{a_1j}t)\langle J_{a_4j}(0)J_{ja_2}(t)\rangle + \delta_{a_2a_4}\exp(-i\epsilon_{a_1a_2}t)\langle K_{a_2}(0)K_{a_2}(t)\rangle\right)\right. \\ &\quad -\exp(-i\epsilon_{a_3a_2}t)\langle F_{a_4a_2}(0)F_{a_1a_3}(t)\rangle(1-\delta_{a_2a_4})(1-\delta_{a_1a_3}) - \exp(-i\epsilon_{a_1a_4}t)\langle F_{a_4a_2}(t)F_{a_1a_3}(0)\rangle \\ &\quad \left.\times(1-\delta_{a_2a_4})(1-\delta_{a_1a_3}) - \exp(-i\epsilon_{a_1a_2}t)[\langle K_{a_2}(0)K_{a_1}(t)\rangle + \langle K_{a_2}(t)K_{a_1}(0)\rangle]\,\delta_{a_1a_3}\delta_{a_2a_4}\right\}\,, \end{aligned} \tag{B1}$$

$$\bar{\mathcal{R}}_{gg';g'g} = \bar{\mathcal{R}}_{g'g;gg'} = 0\,, \tag{B2a}$$

$$\bar{\mathcal{R}}_{gg';g'g} = -i\int_0^\infty dt\exp(-i\epsilon_{gg'}t)[\langle K_g(t)K_g(0)\rangle + \langle K_{g'}(0)K_{g'}(t)\rangle - \langle K_{g'}(0)K_g(t)\rangle - \langle K_{g'}(t)K_g(0)\rangle]\,, \tag{B2b}$$

$\bar{\mathcal{R}}_{g'g;g'g}$ = same with g and g' interchanged,

$$\begin{aligned} \bar{\mathcal{R}}_{a_1g;a_2g} = -i\int_0^\infty dt\left\{\sum_{a'\neq a_1,a_2}\exp(-i\epsilon_{a'g}t)\langle F_{a_1a'}(t)F_{a'a_2}(0)\rangle + \sum_j \exp(-i\epsilon_{jg}t)\langle J_{a_1j}(t)J_{ja_2}(0)\rangle\right. \\ \left.+\,\delta_{a_1a_2}\exp(-i\epsilon_{a_1g}t)[\langle K_{a_1}(t)K_{a_1}(0)\rangle + \langle K_g(0)K_g(t)\rangle - \langle K_g(0)K_{a_1}(t)\rangle - \langle K_g(t)K_{a_1}(0)\rangle]\right\}\,, \end{aligned} \tag{B3}$$

$\bar{\mathcal{R}}_{a_1g';a_2g'}$ = (same for g' replacing g)\,,

$$\bar{\mathcal{R}}_{a_1g;ga_2} = \bar{\mathcal{R}}_{ga_1;a_2g} = \bar{\mathcal{R}}_{a_1g';g'a_2} = \bar{\mathcal{R}}_{g'a_1;a_2g'} = 0\,, \tag{B4}$$

$$\bar{\mathcal{R}}_{ga_1;ga_2} = -i\int_0^\infty dt\left\{\sum_{a'\neq a_1,a_2}\exp(-i\epsilon_{ga'}t)\langle F_{a_2a'}(0)F_{a'a_1}(t)\rangle + \sum_j \exp(-i\epsilon_{gj}t)\langle J_{a_2j}(0)J_{ja_1}(t)\rangle\right.$$
$$\left. + \delta_{a_1a_2}\exp(-i\epsilon_{ga_1}t)[\langle K_{a_1}(0)K_{a_1}(t)\rangle + \langle K_g(t)K_g(0)\rangle - \langle K_{a_1}(0)K_g(t)\rangle - \langle K_{a_1}(t)K_g(0)\rangle]\right\} . \quad \text{(B5)}$$

These results include all the $\bar{\mathcal{R}}$ matrix elements necessary for the calculation in Secs. IV and V. It should be noted that the different correlation functions entered in these results may correspond to different baths. Thus, correlation functions involving the operators F and K are calculated as thermal averages over states of baths of temperature T, while correlation functions involving J correspond to zero temperature baths.

APPENDIX C: SUMMARY OF RELEVANT TIME CORRELATION FUNCTIONS

Here we list the relevant time correlation functions encountered in the two intermediate levels problem and introduce a shorthand notation for their real and imaginary parts:

$$\int_0^\infty dt\exp(i\omega t)\langle F_{rs}(t)F_{sr}(0)\rangle = \Gamma^1_{rs}(\omega) + iD^1_{rs}(\omega) , \quad \text{(C1)}$$

$$\int_0^\infty dt\exp(i\omega t)\langle F_{sr}(0)F_{rs}(t)\rangle = \Gamma^2_{rs}(\omega) + iD^2_{rs}(\omega) , \quad \text{(C2)}$$

$$\int_0^\infty dt\exp(i\omega t)\langle J_{aj}(t)J_{ja}(0)\rangle = \Gamma^1_{aj}(\omega) + iD^1_{aj}(\omega) , \quad \text{(C3)}$$

$$\int_0^\infty dt\exp(i\omega t)\langle J_{ja}(0)J_{aj}(t)\rangle = \Gamma^2_{aj}(\omega) + iD^2_{aj}(\omega) , \quad \text{(C4)}$$

$$\int_0^\infty dt\exp(i\omega t)\langle K_a(t)K_b(0)\rangle = \kappa^1_{ab}(\omega) + i\eta^1_{ab}(\omega) , \quad \text{(C5)}$$

$$\int_0^\infty dt\exp(i\omega t)\langle K_a(0)K_b(t)\rangle = \kappa^2_{ab}(\omega) + i\eta^2_{ab}(\omega) , \quad \text{(C6)}$$

$$\int_0^\infty dt\exp(i\omega t)\langle J_{sj}(t)J_{jr}(0)\rangle = \gamma^1_j(\omega) + id^1_j(\omega) , \quad \text{(C7)}$$

$$\int_0^\infty dt\exp(i\omega t)\langle J_{sj}(0)J_{jr}(t)\rangle = \gamma^2_j(\omega) + id^2_j(\omega) , \quad \text{(C8)}$$

$$\int_0^\infty dt\exp(i\omega t)\langle J_{rj}(t)J_{js}(0)\rangle = \gamma^1_j(\omega) + id^1_j(\omega) , \quad \text{(C9)}$$

$$\int_0^\infty dt\exp(i\omega t)\langle J_{rj}(0)J_{js}(t)\rangle = \gamma^2_j(\omega) + id^2_j(\omega) . \quad \text{(C10)}$$

In these expressions a and b stand for r or s, and the functions Γ, D, γ, d, κ, and η are real.

Next we utilize the following general relations involving time correlation functions of any two operators

(1):

$$\int_{-\infty}^\infty dt\exp(i\omega t)\langle B(t)A(0)\rangle = \exp(\beta\omega)\int_{-\infty}^\infty dt\exp(i\omega t)\langle A(0)B(t)\rangle , \quad \text{(C11)}$$

where $\beta = 1/k_BT$, and T is the temperature characterizing the distribution to which the average $\langle\ \rangle$ is related;

(2):

$$\langle B(t)A(0)\rangle = \langle A^\dagger(0)B^\dagger(t)\rangle^* ; \quad \text{(C12)}$$

(3):

for real operators A and B,

$$\langle B(0)A(t)\rangle = \langle A^\dagger(0)B^\dagger(t)\rangle . \quad \text{(C13)}$$

We actually used Eq. (C13) when we took the rhs of (C7) and (C9) as well as (C8) and (C10) to be equal. These identities further lead to the following relations between the different correlation functions:

$$\Gamma^2_{rs}(\omega) = \Gamma^1_{rs}(-\omega) = \Gamma^1_{rs}(\omega)\exp(-\beta\omega) , \quad \text{(C14)}$$

$$D^2_{rs}(\omega) = -D^1_{rs}(-\omega) , \quad \text{(C15)}$$

$$\Gamma^2_{aj}(\omega) = \Gamma^1_{aj}(-\omega) = \Gamma^1_{aj}(\omega)\exp(-\beta_j\omega) , \quad \text{(C16)}$$

$$D^2_{aj}(\omega) = -D^1_{aj}(-\omega) , \quad \text{(C17)}$$

$$\kappa^2_{ba}(\omega) = \kappa^1_{ab}(-\omega) = \kappa^1_{ab}(\omega)\exp(-\beta\omega) , \quad \text{(C18)}$$

$$\eta^2_{ba}(\omega) = -\eta^1_{ab}(-\omega) . \quad \text{(C19)}$$

For the "baths" seated on the molecular states j (radiative and intramolecular radiationless continua), the model employed in this paper takes $T_j = 0$ ($\beta_j = \infty$). Therefore $\Gamma^2_{aj}(\omega) = 0$.

Relations between γ^2_j and γ^1_j, d^2_j and d^1_j can also be written but turn out to be uninteresting for our purpose as only γ^1_j and d^1_j are encountered in the calculation.

To complete the definition of terms encountered in the calculation of Sec. V we introduce

$$\kappa(\omega) + i\eta(\omega) = \int_0^\infty dt\exp(-i\omega t)[\langle K_s(0)(K_s(t) - K_r(t))\rangle - \langle (K_s(t) - K_r(t))K_r(0)\rangle]$$
$$= \kappa^1_{ss} + \kappa^2_{rr} - \kappa^1_{sr} - \kappa^2_{sr} + i(\eta^1_{ss} + \eta^2_{rr} - \eta^1_{sr} - \eta^2_{sr}) \quad \text{(C20a)}$$

and its complex conjugate

$$\kappa(\omega) - i\eta(\omega) = \int_0^\infty dt\exp(i\omega t)[\langle K_r(0)(K_r(t) - K_s(t))\rangle - \langle (K_r(t) - K_s(t))K_s(0)\rangle] \quad \text{(C20b)}$$

with

$$\kappa(\omega) = \kappa^1_{ss}(\omega) + \kappa^2_{rr}(\omega) - \kappa^1_{sr}(\omega) - \kappa^2_{sr}(\omega) \quad \text{(C21a)}$$

and

$$\eta(\omega) = \eta^1_{ss}(\omega) + \eta^2_{rr}(\omega) - \eta^1_{sr}(\omega) - \eta^2_{sr}(\omega) . \quad \text{(C21b)}$$

These are the t_2-type contributions to the shift and broadening of the rs line, and contribute to the matrix elements $\bar{\mathcal{R}}_{rs,rs}$ and $\bar{\mathcal{R}}_{sr,sr}$. In the classical limit where the operators K commute, these functions take the suggestive form

$$\kappa(\omega)+i\eta(\omega)=\int_0^\infty dt\exp(-i\omega t)\times\langle(K_s(0)-K_r(0))(K_s(t)-K_r(t))\rangle \qquad (C22)$$

appearing as originated from the modulation of the energy difference $\epsilon_{rs}=\epsilon_r-\epsilon_s$ arising from elastic collisions.

APPENDIX D: SUMMARY OF NOTATIONS FOR WIDTHS EMPLOYED IN SEC. V

1. $\Gamma_{sj}(\equiv\sum_j\Gamma_{sj})$ and $\Gamma_{rj}(\equiv\sum_j\Gamma_{rj})$ are shorthand notations for the total widths of level s and r caused by interaction with all the zero temperature baths. When we assume $\Gamma_{sj}=\Gamma_{rj}$, Γ_j stands for both.
2. $\tilde{\Gamma}_{rs}=\Gamma_{rs}\exp(-\beta\epsilon)$, $\beta=1/k_BT$,
   $\gamma=\Gamma_{rs}+\Gamma_j$,
   $\tilde{\gamma}=\tilde{\Gamma}_{rs}+\Gamma_j$,
   $\tilde{\Gamma}_j=\Gamma_j+\frac{1}{2}\kappa$.
3. $A'=A[2(\gamma\tilde{\gamma}-\Gamma_{rs}\tilde{\Gamma}_{rs})]^{-1}$, $A=\gamma,\ \tilde{\gamma},\ \Gamma_{rs},\ \tilde{\Gamma}_{rs}$.
4. $\gamma_1=\Gamma_{rs}(\epsilon_{gs})+\Gamma_j+\kappa_r(\epsilon_{gr})$,
   $\gamma_2=\Gamma_{rs}(\epsilon_{gr})+\Gamma_j+\kappa_s(\epsilon_{gs})$,
   $\gamma_1'=\Gamma_{rs}(\epsilon_{g's})+\Gamma_j+\kappa_r(\epsilon_{g'r})$,
   $\gamma_2'=\Gamma_{rs}(\epsilon_{g'r})+\Gamma_j+\kappa_s(\epsilon_{g's})$.
5. Functions without energy arguments,
   $\Gamma_{rs}\equiv\Gamma_{rs}(\epsilon)$,
   $\kappa_a\equiv\kappa_a(0)$ $(a=r,\ s)$,
   $\Gamma_{sj}\equiv\Gamma_{sj}(\epsilon_{sj})$,
   $\Gamma_{rj}\equiv\Gamma_{rj}(\epsilon_{rj})$.
6. When we assume $\kappa_s=\kappa_r$, $\bar{\kappa}$ denotes both.

†Supported in part by the Commission for Basic Research of The Israel Academy of Sciences.

*Present Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

[1]For recent reviews, see P. P. Shorygin, Sov. Phys. Usp. 16, 99 (1973); *Light Scattering in Solids*, edited by M. Balkanski (Flammarion Sciences, Paris, 1971), W. Kiefer, Appl. Spectrosc. 28, 115 (1974); J. Behringer, in *Molecular Spectroscopy*, edited by R. F. Barrow, D. A. Long, and J. J. Miller (The Chemical Society, London, 1974), Vol. 2.
[2]D. G. Fouche and R. K. Chang, Phys. Rev. Lett. **29**, 536 (1972).
[3]R. L. St. Peters and S. D. Silverstein, Opt. Commun. **7**, 193 (1973).
[4]R. L. St. Peters, S. D. Silverstein, M. Lapp, and C. M. Penney, Phys. Rev. Lett. **30**, 191 (1973).
[5]S. D. Silverstein and R. L. St. Peters, Phys. Rev. A **9**, 2720 (1974).
[6]M. V. Klein, Phys. Rev. B **8**, 919 (1973).
[7]Y. R. Shen, Phys. Rev. B **9**, 622 (1974).
[8]P. F. Williams, D. L. Rousseau, and S. H. Dworetsky, Phys. Rev. Lett. **32**, 196 (1974).
[9]D. L. Rousseau, G. D. Patterson, and P. F. Williams, Phys. Rev. Lett. **34**, 1306 (1975).
[10]D. L. Rousseau and P. F. Williams, J. Chem. Phys. **64**, 3519 (1976).
[11]J. R. Solin and H. Merkelo, Phys. Rev. B **12**, 624 (1975).
[12]S. E. Schwartz, Phys. Rev. A **11**, 1121 (1975).
[13]J. Behringer, J. Raman Spectrosc. **2**, 275 (1974).
[14]L. S. Ditman, R. W. Gammon, and T. D. Wilkerson, Opt. Commun. **13**, 154 (1975).
[15]Y. Toyozawa (Tokyo preprint).
[16]No distinction between Raman and Rayleigh scattering is made and the discussion assumes a given initial molecular level and a given (same or different) final molecular level.
[17]D. L. Huber, Phys. Rev. **158**, 843 (1967).
[18]D. L. Huber, Phys. Rev. **170**, 418 (1968).
[19]D. L. Huber, Phys. Rev. **178**, 93 (1969).
[20]D. L. Huber, Phys. Rev. **187**, 392 (1969).
[21]A. Omont, E. W. Smith, and J. Cooper, Astrophys. J. **175**, 185 (1972).
[22]A. Omont, E. W. Smith, and J. Cooper, Astrophys. J. **182**, 283 (1973).
[23]A. Nitzan and J. Jortner, J. Chem. Phys. **57**, 2870 (1972).
[24]Chr. V. Grundherr and M. Stockburger, Chem. Phys. Lett. **22**, 253 (1973).
[25]A. Ranade and M. Stockburger, Chem. Phys. Lett. **22**, 257 (1973).
[26]J. Friedman and R. M. Hochstrasser, Chem. Phys. Lett. **32**, 414 (1975).
[27]J. Jacon, M. Berjot, and L. Bernard, C. R. Acad. Sci. (Paris) **273**, 956 (1971).
[28]D. L. Huber, Phys. Rev. B **1**, 3409 (1970).
[29]S. Mukamel and J. Jortner, J. Chem. Phys. **62**, 3609 (1975).
[30]S. Mukamel, A. Ben Reuven, and J. Jortner, Phys. Rev. A **12**, 947 (1975); J. Chem. Phys. **64**, 3971 (1976).
[31]J. Friedman and R. M. Hochstrasser, Chem. Phys. **6**, 155 (1974).
[32]J. O. Berg, C. A. Langhoff, and G. W. Robinson, Chem. Phys. Lett. **32**, 76 (1975).
[33]H. Metiu, J. Ross, and A. Nitzan, J. Chem. Phys. **63**, 1289 (1975).
[34]H. J. Kimble and L. Mandel, Opt. Commun. **14**, 167 (1975).
[35](a) For a recent review of this approach, see Ref. 43; (b) The terms "collisions" and "pressure broadening" are used here in a broad sense and include also the analogous phenomena in liquids and solids.
[36]V. Hizhnyakov and I. Tehver, Phys. Status Solidi **21**, 755 (1967).
[37]P. A. Madden and H. Wennerstrom, Mol. Phys. **31**, 1103 (1976).
[38]R. Kubo, T. Tokagawara, and E. Hanamura, OJI Seminar on Physics of Highly Excited States in Solids, Tomakomai, Japan, 1975.
[39]W. Kiefer in Ref. 1.
[40]J. M. Friedman and R. M. Hochstrasser, Chem. Phys. Lett. **33**, 225 (1975).
[41]In later sections sometimes g and g' are used to denote the molecular initial and final states plus the incoming and outgoing photons.
[42]U. Fano, Phys. Rev. **131**, 259 (1963).
[43]A. Ben Reuven, Adv. Chem. Phys. **33**, 235 (1975).
[44]A. Ben-Reuven and S. Mukamel, J. Phys. A **8**, 1313 (1975).
[45]The singularity discussed in Appendix A is no longer present owing to the sum over the bath β states.
[46]R. Zwanzig, Physica (Utrecht) **30**, 1109 (1964).
[47](a) A. Ben-Reuven and L. Klein, Phys. Rev. A **4**, 753 (1971); (b) A. Ben-Reuven, S. Mukamel, and A. Nitzan (to be published).
[48]S. Mukamel, A. Ben-Reuven, and J. Jortner (to be published).
[49]By absence of interference terms we mean, in addition to taking $\gamma_j=d_j=0$ in the general experessions, also assuming $|m_1+m_2|^2=|m_1|^2+|m_2|^2$, that is, that the two resonances are far away from each other. This, however, does not correspond to the isolated resonance case because the two resonances are interconnected by thermal relaxation.