Chemical Physics 24 (1977) 37–43
© North-Holland Publishing Company

ON THE IMPACT AND THE SEPARATION APPROXIMATIONS IN THE THEORY OF MULTIPHOTON INTERACTIONS WITH THERMALLY PERTURBED SYSTEMS *

Abraham NITZAN, Shaul MUKAMEL ** and Abraham BEN-REUVEN
Department of Chemistry, Tel-Aviv University, Tel Aviv, Israel

Received 30 March 1977

Criteria are provided for the factorization of thermal averages incurring in the calculation of cross-sections for several-photon processes, into products of independently averaged single-photon processes. These criteria are compared to those involved in the impact approximation for single photon spectra, and are shown to be less restrictive.

1. Introduction

The effects of thermal perturbations on single-photon spectral lineshapes, like pressure broadening in gas-phase spectroscopy and phonon effects in solid-state spectroscopy, have a long history of both experimental and theoretical research. Much less studied and understood, is the problem of thermal perturbations in processes involving several photon transitions. Huber [1] was the first to investigate this problem with regard to resonance light scattering (RSL) in gases and solids. Similar and more extended studies were made by Omont, Smith and Cooper [2] and by Hizhnyakov and Tehver [3]. More recently, Mukamel, Jortner and Ben-Reuven [4] have discussed pressure effects on time resolved RSL using the Liouville-space approach. Also Mukamel and Nitzan [5] have utilized the same approach in the discussion of RSL from a multilevel system with cross relaxation between intermediate levels. A similar problem was discussed by Kubo, Tokagawara and Hanamura [6] who extended Kubo's stochastic theory of line shapes to the problem of RSL. A Bloch-equation study of collisional effects on RSL has been made by Mukamel, Jortner and Ben-Reuven [7] and by Szöke and Courtens [8]. Recently some experimental data on collisional effects in the presence of high intensity radiation fields have been published [9]. General theoretical investigation of such problems, though still pending, is suggested [10] by a combination of the description of scattering phenomena in the density-matrix formalism [11], together with the separation approximation discussed below.

The theoretical calculation of pressure-broadened spectral line shapes in gases is usually made under either the statistical (or quasistatic) limit or the impact approximation [12]. These represent the two extreme limits where the optical process occurs on a time scale respectively much shorter, or much longer, than the time scale for the thermal motion of the perturbing medium around the optically active molecule (the duration of a collision). For this reason the impact approximation is usually valid near the line centre, whereas the quasistatic approximation holds in the far wings of the line. In the impact approximation one treats the effect of the surrounding medium on the absorbing molecule as a random succession of complete independent collisions. The problem then reduces to the calculation of a set of line-width and line-shift parameters. In the quasistatic approximation one treats the surrounding medium as an array of static configurations that inhomogeneously shift the molecular resonance frequencies†.

* One of the authors (A.N.) acknowledges support by the Commission for Basic Research, the Israel Academy of Sciences.
** Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A.

† For footnote see next page.

In solids one can still identify limits analogous to the impact and the quasistatic cases. Here the correlation time for the motion of the molecule-solid interaction plays sometimes the role of the collision time in the gas phase. Quite often neither limit is appropriate and certain lattice excitations have to be viewed as belonging to the "molecular system" rather than to the perturbing bath.

Extending the technique of the quasistatic approximation to the calculation of multiphoton transition rates (or cross sections) involves in principle no additional complication (besides that of taking a configurational average of a somewhat more complicated expression). The impact limit, however, (as well as intermediate cases) involves inelastic and quasielastic interactions of the molecule in intermediate states with the surrounding medium. Mathematically the problem can be handled by introducing another approximation – the decoupling of the thermal average (the projecting out of the medium degrees of freedom) into a product of independently-averaged terms. Each term represents an intermediate step of photon absorption or emission, assumed to occur after the surrounding medium has reached thermal equilibrium. This separation approximation is expected to hold under impact conditions but the criteria for the two approximations are not identical [13]. It is the aim of this note to establish the criteria for the separation approximation and to show that its validity may extend to regions where the impact approximation has to be modified for memory effects.

2. The impact approximation

In the theory of pressure broadening, the generally stated criterion for the impact approximation is that the time scale for the optical interaction will be much longer than the duration of a collision. For the case of a continuous molecule-medium interaction (like for solid state systems) the "duration of a collision" is replaced by the decay time of the correlation function of the molecule-medium interaction. It is interesting to point out that the impact approximation was originally introduced in order to separate a thermal average of the time-evolution operator:

$$\langle \Delta U(t)\rangle = \langle (U(t+\Delta t, t) - 1)U(t)\rangle$$
$$\approx (\langle U(t+\Delta t, t)\rangle - 1)\langle U(t)\rangle$$

in such a way as to obtain a coarse-grained linear markoffian differential equation for $U(t)$. Arguments similar to those used in making this separation approximation have been used in treatments of stochastic effects on RSL [1,6]. This may lead to the conclusion that the separation approximation in multiphoton processes is identical to the impact approximation used in the calculation of single-photon absorption line shapes. The difference between the approximations involved is most easily seen in the Liouville-space (tetradic) Green's function formalism, [14,15,11] pertaining to the solution of the Von Neumann equation for the density operator. To outline this approach we introduce the tetradic Liouville operator (liouvillian) for the complete system (sample-plus-radiation)

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{V} = \mathcal{L}_M + \mathcal{L}_R + \mathcal{V}\,, \tag{1a}$$

where $\mathcal{L}X = \hbar^{-1}[H, X]$, with H being the corresponding hamiltonian. Here $\mathcal{L}_R$ is the free-radiation liouvillian, $\mathcal{V}$ is the interaction between the sample and the radiation field, and

$$\mathcal{L}_M = \mathcal{L}_A + \mathcal{L}_B + \mathcal{U}\,, \tag{1b}$$

where $\mathcal{L}_A$ pertains to the optically active subsystem (which we call the "molecule"), $\mathcal{L}_B$ to the rest of the sample, acting as a thermal bath, and $\mathcal{U}$ to the molecule-bath interaction.

The Green's function for the complete system (molecule + thermal bath + radiation field) may be expanded in the form ($\omega = \omega' + i0$)

$$\mathcal{G}(\omega) = (\omega - \mathcal{L})^{-1} = \mathcal{G}_0(\omega) + \mathcal{G}_0(\omega)\mathcal{V}\mathcal{G}_0(\omega)$$
$$+ \mathcal{G}_0(\omega)\mathcal{V}\mathcal{G}_0(\omega)\mathcal{V}\mathcal{G}_0(\omega) + \ldots, \tag{2}$$

where $\mathcal{G}_0(\omega) = (\omega - \mathcal{L}_0)^{-1}$.
For low-intensity incident radiations $\mathcal{G}_0(\omega)$ contains the relevant information on the absorption line shape while the term $\mathcal{G}_0(\omega)\mathcal{V}\mathcal{G}_0(\omega)\mathcal{V}\mathcal{G}_0(\omega)$ describes

† The impact approximation can be formally extended to the far wings by introducing effects of the finite duration of collisions (memory effects) in the form of frequency-dependent line-width parameters. This, however, requires the much less manageable task of obtaining off-the-energy-shell scattering amplitudes, compared to that of the impact-approximation, where only on-the-energy-shell scattering amplitudes are required.

light scattering events. Actually, the absorption and scattering cross-sections are proportional to averages of rates which, in turn, are given by corresponding elements of the (tetradic) scattering matrix [11], $\mathcal{T}(\omega = 0) = \mathcal{V} + \mathcal{V}\mathcal{G}(\omega = 0)\mathcal{V}$. Thus, to lowest order in $\mathcal{V}$

$$\sigma_A \propto -\mathrm{i}\langle\langle gg|\mathcal{V}\langle\mathcal{G}_0(0)\rangle\mathcal{V}|gg\rangle\rangle \tag{3}$$

for absorption, and

$$\sigma_S \propto -\mathrm{i}\langle\langle g'g'|\mathcal{V}\langle\mathcal{G}_0(0)\mathcal{V}\mathcal{G}_0(0)\mathcal{V}\mathcal{G}_0(0)\rangle\mathcal{V}|gg\rangle\rangle \tag{4}$$

for scattering where $|g\rangle$ is the initial state of the molecule-radiation field system and $|g'\rangle$ is the final state. The brackets $\langle ... \rangle$ denote a thermal average. For radiation fields of higher intensity, higher-order terms of the expansion (2) should be considered. In referring to the impact approximation, we mean a well-defined procedure involved in calculating $\langle\mathcal{G}_0\rangle$ while the separation approximation invokes the decoupling of the thermal average in the form

$$\langle\mathcal{G}_0\mathcal{V}\mathcal{G}_0\mathcal{V}\mathcal{G}_0\ ...\rangle \approx \langle\mathcal{G}_0\rangle\mathcal{V}\langle\mathcal{G}_0\rangle\mathcal{V}\langle\mathcal{G}_0\rangle\ ... \tag{5}$$

The terms $\langle\mathcal{G}_0\rangle$ in eqs. (3) and (5) are averaged over the bath thermal distribution and are operators in the molecular coordinates as well as in the coordinates of the few radiation modes which actively participate in the process described. (Radiation modes which act as radiative sinks belong to the "bath" category.) Since $\mathcal{V}$ usually involves one-photon raising and lowering operators, we may anticipate the dependence of the relevant matrix elements of $\langle\mathcal{G}_0(0)\rangle$ on the radiative energies. Consider

$$g(E) \equiv (E - \mathcal{L}_M)^{-1}. \tag{6a}$$

This is a diagonal tetradic matrix element of $\mathcal{G}_0(0)$ taken in a dyadic $|n'n\rangle\rangle$ of states of the active radiation modes, to which corresponds the energy difference $E = E_n - E_{n'}$. Thus $g(E)$ is an operator reduced to the molecule-thermal bath system. The Green's functions $\langle\mathcal{G}_0(0)\rangle$, reexpressed in terms of $\langle g(E)\rangle$, are the familiar retarded Green's functions of linear-response theory,

$$\langle g(E)\rangle = \langle(E - \mathcal{L}_M)^{-1}\rangle = (E - \mathcal{L}_M - \langle\mathcal{R}(E)\rangle)^{-1}. \tag{6b}$$

Notice, however, that owing to the effect of $\mathcal{V}$ in products such as eq. (5), the value of E varies from term to term, representing different combinations of photon energies. In eq. (6a), $\mathcal{R}(E)$ is the (tetradic) level-shift operator, related to the molecule-bath interaction $\mathcal{U}$ by

$$\mathcal{R}(E) = \mathcal{U} + \mathcal{U}(1-C)(E-\mathcal{L}_M)^{-1}(1-C)\mathcal{U}, \tag{7}$$

where C is the Zwanzig projection operator representing bath averaging, defined by

$$CX\rho_B = \rho_B \mathrm{Tr}_B(X\rho_B), \tag{8}$$

Tr_B being a trace over bath states and ρ_B its equilibrium density operator. We assume here initial separability of bath and molecule density matrices (though, in principle, one can incorporate statistical correlations into the projection-operator formalism [15]).

In this formalism, the impact approximation is a simplifying assumption on $\langle\mathcal{R}(E)\rangle$ (and hence does not involve directly a decoupling of thermal averages). When the lifetime of the molecular resonance $\Gamma_0^{-1} = [-\mathrm{Im}\langle\mathcal{R}(E_0)\rangle]^{-1}$ (where E_0 is equal to the molecular resonance frequency) is much longer than that required for the decay of correlations in the molecule-bath interaction (i.e. a collision time in gas-phase spectroscopy, under binary-collision conditions), $\langle\mathcal{R}(E)\rangle$ is independent of its energy argument for energies close to resonance. For such energies, the line shape of a single isolated resonance assumes a lorentzian shape. The mathematical criterion for the validity of this approximation (and of the lorentzian form of the line shapes) is [16]

$$\frac{\Gamma_0}{(\Delta E)^2 + \Gamma_0^2} \gg \frac{1}{\Gamma_1} \qquad (\Delta E = E - E_0), \tag{9}$$

where Γ_0 is the width of the resonance and where Γ_1^{-1} is the lifetime of correlations in the molecule-bath interaction. The left-hand side of eq. (9) represents the delay time for the photon scattering off the molecule, i.e., it measures the time scale for the photon-molecule interaction (or the lifetime of their resonance state). Exactly on resonance, this is indeed Γ_0^{-1}. Eq. (9), beyond expressing a general criterion for the validity of the impact approximation, provides us with a measure of the value of ΔE, the off-resonance energy mismatch, beyond which the impact approximation is not expected to hold.

3. The separation approximation

The impact approximation has thus been identified with an assumption made for the sake of a simplified calculation of $\langle g(E)\rangle$, eq. (6). The separation approximation is defined by eq. (5). A criterion for the validity of the separation approximation may be obtained from the identities

$$CgC = C(E - \mathcal{L}_A - C\mathcal{R}C)^{-1}C\,, \qquad (10)$$

$$C\mathcal{R}C = C\mathcal{U}C + C\mathcal{R}(1-C)(E-\mathcal{L}_A-\mathcal{L}_B)^{-1}(1-C)\mathcal{U}C$$
$$\approx C\mathcal{U}C + C\mathcal{U}(1-C)\mathcal{U}C(\Delta E' + i\Gamma_1(E))^{-1}\,, \qquad (11)$$

$$Cg(1-C) = CgC\mathcal{R}(1-C)(E-\mathcal{L}_A-\mathcal{L}_B)^{-1}(1-C)$$
$$= CgC\mathcal{U}(1-C)[E-(1-C)\mathcal{L}_M(1-C)]^{-1}\,. \qquad (12)$$

The right-hand side of eq. (11) approximately represents $\langle\mathcal{R}\rangle$ as a simple "memory function"; Γ_1 is identified with the inverse correlation time of the molecule-bath interaction and $\Delta E'$ is essentially equal to ΔE. (In this simplifying description we neglect resonance structures in the memory function that may result in the appearance of satellite sidebands.)

The separation approximation, eq. (5) may be recast in the form [13]

$$Cg\mathcal{V}g\mathcal{V}\ldots C \approx CgC\mathcal{V}CgC\mathcal{V}C\ldots C\,. \qquad (13)$$

This approximation holds provided

$$F(E) \equiv |(CgC)^{-1}Cg(1-C)gC(CgC)^{-1}| \ll 1\,. \qquad (14)$$

Neglecting the trivial role of $C\mathcal{U}C$, eqs. (10)–(12) lead to the estimate

$$F(E) \sim 0\left[\frac{\langle\mathcal{U}^2\rangle}{|\Delta E + i\Gamma_1(E)|^2}\right]. \qquad (15)$$

For $E\approx E_0$ (resonance excitation) we have, taking $\Gamma_1 \equiv \Gamma_1(E_0)$,

$$F(E_0) \approx \frac{\langle\mathcal{U}^2\rangle}{\Gamma_1^2} = \frac{\langle\mathcal{U}^2\rangle/\Gamma_1}{\Gamma_1} \approx \frac{\Gamma_0}{\Gamma_1}\,, \qquad (16)$$

while for a general excitation energy we may write

$$F(E) \approx \frac{\langle\mathcal{U}^2\rangle}{\Delta E^2 + \Gamma_1^2} = \frac{\langle\mathcal{U}^2\rangle/|\Delta E + i\Gamma_1(E)|}{|\Delta E + i\Gamma_1(E)|}$$
$$\approx \frac{\Gamma_0(E)}{(\Delta E^2 + \Gamma_1^2(E))^{1/2}}\,. \qquad (17)$$

In eqs. (16) and (17) we have used the fact that $\Gamma_0(E)$ measures the magnitude of $\langle\mathcal{R}\rangle$ which is essentially given by

$$\langle\mathcal{R}(E)\rangle \approx \frac{\langle\mathcal{U}^2\rangle}{\Delta E + i\Gamma_1(E)}\,. \qquad (18)$$

The mathematical criterion for the separation approximation thus becomes

$$\frac{\Gamma_0(E)}{(\Delta E^2 + \Gamma_1^2(E))^{1/2}} \ll 1\,. \qquad (19)$$

Another way of obtaining this criterion is to start from eq. (6) and take the derivative with respect to E,

$$\frac{d}{dE}\langle g(E)\rangle = \langle g(E)\rangle\left[-1 + \frac{d}{dE}\langle\mathcal{R}(E)\rangle\right]g(E)\,. \qquad (20)$$

On the other hand, from eq. (6a) we have

$$\frac{d}{dE}\langle g(E)\rangle = -\langle g(E)g(E)\rangle \qquad (21)$$

so that the approximation

$$\langle g(E)g(E)\rangle \approx \langle g(E)\rangle\langle g(E)\rangle \qquad (22)$$

holds provided

$$\frac{d}{dE}\langle\mathcal{R}(E)\rangle \ll 1\,. \qquad (23)$$

Using eq. (18) we obtain

$$\frac{d}{dE}\langle\mathcal{R}(E)\rangle \approx \frac{\langle\mathcal{U}^2\rangle}{|\Delta E + i\Gamma_1|^2} \approx \frac{\Gamma_0}{(\Delta E^2 + \Gamma_1^2)^{1/2}} \qquad (24)$$

so that the condition (23) is seen to be equivalent to eq. (19). Of course, the different terms in eq. (5) pertain to different molecular resonances, with different values of E, and therefore this is only a heuristic derivation.

In summary, the criterion for the separation approximation is given by eq. (19), while that for the impact approximation has been stated as

$$\frac{\Gamma_0(E)\Gamma_1(E)}{(\Delta E)^2 + \Gamma_0^2(E)} \gg 1\,. \qquad (25)$$

At resonance ($\Delta E \approx 0$) both criteria reduce to the better-known single condition

$$\Gamma_0(E)/\Gamma_1(E) \ll 1 \qquad (26)$$

saying that the resonance lifetime must be much longer than the correlation time for the interaction with the medium. Far from resonance, however, the impact approximation breaks down as ΔE^2 becomes much larger than $\Gamma_0\Gamma_1$, whereas the separation approximation is still valid for $|\Delta E| \gg \Gamma_0$. It may even be valid over the whole spectral range, so far as eq. (26) holds.

4. Validity estimates

4.1. Gas phase

A characteristic term in the expansion of $\langle\mathcal{R}\rangle$ for a given resonance pair $|ab\rangle\rangle$ is

$$\langle\mathcal{R}(E)\rangle \approx \left\langle \sum_j \Delta u_j \frac{1}{\Delta E + \mathrm{i}\Gamma_1} \sum_j \Delta u_j \right\rangle , \tag{27}$$

where Δu_j is the difference between the interactions of the molecule and the jth medium particle in the two levels a and b. An upper-bound estimate of eq. (27) is given under the binary-collision approximation by $\Delta u^2(r) n r^3 |\Delta E + \mathrm{i}\Gamma_1|^{-1}$, where n is the gas number density, r is the molecular diameter and $\Delta u(r)$ measures the maximal strength of the pair interaction at molecular separation. For a pressure of about one atmosphere at room temperature $\Delta u^2 n r^3 \sim 10\ \mathrm{cm}^{-2}$. Thus, $\mathrm{d}\mathcal{R}/\mathrm{d}E \sim 10(\Delta E^2 + \Gamma_1^2)^{-1}$. The maximum value $\mathrm{d}\mathcal{R}/\mathrm{d}E$ is thus $\lesssim 10/\Gamma_1^2$, which is (for the typical value $\Gamma_1 \approx 10\ \mathrm{cm}^{-1}$) of the order of 10^{-1} or less. We thus expect the separation approximation to hold over the whole spectral region for pressures up to several atmospheres at room temperature. We should particularly notice that it is expected to hold even far from resonance, where the impact approximation is no longer valid.

4.2. Solid phase

For an active molecule imbedded in a solid matrix a single-molecule treatment equivalent to the impact approximation is not always valid. The (approximately) Lorentzian shape of pressure-broadened isolated-resonance lines in the gas phase (neglecting Doppler effects) give place to highly asymmetric features characterized by phonon sidebands. The (essentially one-phonon) excitations giving rise to these sidebands cannot be taken as bath states but should rather be treated as belonging to the active molecular system, thus giving rise to more complex spectral shapes. A comprehensive treatment of this problem within the theory of light scattering (and other multiphoton processes is still unavailable*. However, it can be anticipated that contributions to $\mathcal{R}$ will mainly come from two types of terms: (a) terms responsible for level broadening due to multiphonon thermal relaxation processes, and (b) terms responsible for level broadening due to Raman scattering of phonons. Terms of type (a) can be estimated from theories of multiphonon vibrational relaxation and their contribution to $|\mathrm{d}\langle\mathcal{R}\rangle/\mathrm{d}E|$ can be shown to be much smaller than unity ($\sim 10^{-8\pm5}$). Terms of type (b) are practically independent of the off-resonance energy mismatch ΔE provided $\Delta E \ll \omega_\mathrm{D}$, where ω_D is the lattice Debye frequency. Thus, neither type violates the separation approximation.

* The problem is discussed, for example, by Hizhniyakov and Tehver [3], but their approach takes thermal relaxation into account in a rather qualitative fashion.

4.3. Temperature effect

As is well known from linear-response theory, $\langle\mathcal{R}\rangle$ can be represented as a Fourier transform of a time correlation function of quantities mainly involving the molecular interactions. Using general properties of such correlation function, it can be shown [5] that some contributions to $\langle\mathcal{R}\rangle$ often have the property

$$\langle\mathcal{R}(-|\Delta E|)\rangle = \langle\mathcal{R}(|\Delta E|)\rangle \exp(-\beta|\Delta E|) , \tag{28}$$

where $\beta = (k_\mathrm{B}T)^{-1}$ and ΔE is measured from a resonance center. Therefore, at low temperature $\langle\mathcal{R}\rangle$ becomes strongly energy-dependent (for $\Delta E \lesssim 0$) and the separation approximation may break down. A temperature-dependent criterion for the validity of the separation approximation is obtained from the general condition $|\mathrm{d}\langle\mathcal{R}\rangle/\mathrm{d}E| \ll 1$ in the form

$$\frac{\langle\mathcal{R}(\Delta E)\rangle}{k_\mathrm{B}T} \exp\left[-\frac{|\Delta E|}{k_\mathrm{B}T}\right] \ll 1 . \tag{29}$$

This condition may be satisfied even at rather low temperatures, since $|\langle\mathcal{R}\rangle|$ itself may then become quite small.

4.4. Numerical tests

To provide a numerical test for the separation criterion we have performed computations of the absorption and scattering cross-sections for a model molecule with one excited state, coupled to a thermal bath which induces both quasielastic (T_2-type) broadening of the resonance and thermal (T_1) relaxation. The model was introduced by Huber [1] and the mathematical treatment is described in more detail in ref. [5]. We have found that the results obtained with the

Table 1

Test of unitarity in resonance light scattering in the separation approximation. (Exact quantum yields should equal unity). Calculations were done choosing the ratio of thermal broadening to radiative width Γ_r equal to 3 for $\Delta E \geqslant 0$. The thermal broadening satisfies eq. (28) for $\Delta E < 0$. Excitation energies are measured from resonance in units of the radiative width. Temperature T is measured in units of Γ_r/k_B

	Excitation energy $\Delta E/\Gamma_r$										
	−5	−4	−3	−2	−1	0	1	2	3	4	5
Quantum yield	T = 1000										
	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	T = 10										
	0.93	0.92	0.91	0.90	0.90	0.88	0.89	0.90	0.90	0.90	0.90
	T = 0.1										
	1.1	1.1	1.2	1.2	1.3	0.64	0.79	0.84	0.87	0.89	0.90

separation approximation are reliable when the criteria obtained in this work are satisfied. For example, we present in table 1 the computed total quantum yield (scattering cross-section divided by absorption cross-section) as a function of the excitation energy. This quantum yield is obtained by numerically integrating the scattering cross-section over all energies of the scattered light, including both coherent scattering and hot luminescence, and should be equal to unity in the absence of radiationless channels. For the present limited purpose we have used a simplified model where the energy-dependent contribution to $\langle \mathcal{R} \rangle$ is taken to be constant for $E > 0$, and to satisfy eq. (28) for $E < 0$. The results show that the expected unitarity property (which requires the quantum yield to be unity) is maintained in the separation approximation, provided the temperature is not too low.

5. Conclusion

In this paper we have shown that the separation approximation within the (tetradic) Green's function formalism of multiphoton processes involving thermal relaxation, is a practical method with a wide range of validity. Applications in the theory of resonance light scattering have been recently made. In particular we note that in a theory which discusses both Raman processes and fluorescence (hot luminescence) [5] the emitted light may come from levels quite distinct from the absorbing ones. Hence approximations which are valid only in the impact region are insufficient and the general validity of the separation approximation becomes crucial. It should be noted that this approximation can be very useful also in processes involving high intensity radiation fields [13].

Acknowledgement

We are grateful to Y. Ran for aiding with the computations.

References

[1] D.L. Huber, Phys. Rev. 158 (1967) 843; 170 (1968) 418; 178 (1969) 93; 187 (1969) 392.

[2] A. Omont, E.W. Smith and J. Cooper, The Astroph. J. 175 (1972) 185; 182 (1973) 283.

[3] V. Hizhnyakov and I. Tehver, Phys. Stat. Sol 21 (1967) 755.

[4] S. Mukamel, A. Ben-Reuven and J. Jortner, Phys. Rev. A12 (1975) 947.

[5] S. Mukamel and A. Nitzan, Resonance Raman Scattering from a Multilevel, Thermally Relaxing System, J. Chem. Phys. (in press).

[6] R. Kubo, T. Tokagawara and E. Hanamura, OJI Seminar on Physics of Highly Excited States in Solids, Tomakomai, Japan (1975).

[7] S. Mukamel, A. Ben-Reuven and J. Jortner, Chem. Phys. Letters 38 (1976) 394.

[8] A. Szöke and E. Courtens, Phys. Rev. Letters 34 (1975) 1053.

[9] J.L. Carlsten and A. Szöke, Phys. Rev. Letters 36 (1975) 667.

[10] A. Ben-Reuven, J. Jortner and S. Mukamel, Resonant Two-Photon Spectra, to be published.

[11] A. Ben-Reuven and S. Mukamel, J. Phys. A, 8 (1975) 1313.
[12] M. Baranger, in: Atomic and molecular processes, ed. D.R. Bates, (Academic Press, New York, 1962).
[13] A. Ben-Reuven and L. Klein, Phys. Rev. A4 (1971) 753.
[14] U. Fano, Phys. Rev. 131 (1963) 259.
[15] A. Ben-Reuven, Adv. Chem. Phys. 33 (1975) 235.
[16] E.P. Wigner, Phys. Rev. 98 (1955) 145;
F.T. Smith, Phys. Rev. 118 (1960) 349.