EFFECTS OF VIBRATIONAL RELAXATION
ON THE OPTICAL LINESHAPES IN MOLECULAR SPECTRA

Abraham NITZAN and Joshua JORTNER

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

We derive general expressions for the time dependent optical lineshape of a molecule undergoing vibrational relaxation in a dense medium.

Recent theoretical studies [1] of vibrational relaxation of a molecule imbedded in a host medium advanced several purely stochastic or partly deterministic schemes to describe an oscillator or a system of oscillators, initially prepared in a non-equilibrium state, approaching thermal equilibrium. Experimental and theoretical studies of the coupling between radiative optical transitions and vibrational relaxation processes are of considerable interest, as they provide a direct method to monitor vibrational relaxation rates in ground and excited electronic states of molecules interacting with an external medium. The study of optical absorption or emission spectra during the course of vibrational relaxation involves a "double resonance" experiment where the molecule is prepared in a non-equilibrium vibrational distribution and subsequently undergoes an optical transition to another electronic state. Such non-equilibrium vibrational distribution in ground and in excited electronic states can be accomplished by:

(a) Infrared absorption or Raman scattering yielding a vibrationally excited ground electronic state [2], being amenable to absorption studies.

(b) Electronic relaxation from an electronically excited state of a large molecule to highly vibrationally excited states of a lower electronic configuration, which can be monitored either by absorption or by emission [3].

(c) Electronic energy transfer from the host matrix (excited optically or by ionizing radiations) to vibrationally excited states of an electronically excited configuration of the guest molecule which can be conveniently studied by emission [4] or by excited state absorption.

(d) Direct optical excitation to a reasonably high vibrational level of an excited electronic state [5].

Methods (a) and (d) result in a well defined excited state while methods (b) and (c) yield a mixture of vibrationally excited levels. Direct information concerning vibrational relaxation can be obtained from time resolved absorption and emission spectra. In a recent work, Osherov and Medvedev [6] have provided a semiclassical theory (being valid only in a non-physical high temperature limit) which approximately accounts for vibrational relaxation in the initial electronic state on the optical lineshape, by averaging the transition probability with respect to a non-equilibrium initial distribution.

In this paper we derive a general expression for the time dependent lineshape in non-equilibrium optical spectra of a molecule embedded in a dense medium. Our model system rests on the following simplifying assumptions:

(a) A two electronic level system is considered.

(b) The vibrations of the guest molecule are harmonic.

(c) The potential surfaces in the two electronic states are characterized by the same frequencies, while the origins of each (totally symmetric) modes are displaced.

(d) The medium is harmonic.

(e) The medium—molecule interaction involves coupling of a single intramolecular mode to the medium mode via nuclear coordinates.

(f) The molecular—medium coupling is recast in the rotating wave (or resonance) approximation retaining only those terms which conserve energy to the lowest order.

Our derivation which will utilize some results recently obtained by us [7], will handle the radiative interactions to second order while vibrational relaxation is handled to "infinite" order within the framework of the Wigner—Weisskopf approximation.

The total hamiltonian for the system consisting of a molecule interacting with the lattice and with the radiation field is [8]

$$H = H_0^T + H_{mL} + H_{mR} ,$$ (1)

$$H_0^T = H_0 + H_L + H_R .$$ (2)

H_0^T is the total zero order hamiltonian consisting of the molecular zero order hamiltonian H_0, the medium hamiltonian, H_L, and the radiation hamiltonian H_R. H_0 can be separated into an electronic, H_e, and a nuclear H_N parts

$$H_0 = H_e + H_N ,$$ (3)

where

$$H_e = \sum_l E_l d_l^+ d_l$$ (4)

and

$$H_N = \sum_\mu \hbar \omega_\mu a_\mu^+ a_\mu .$$ (5)

d_l^+ and d_l represent the creation and annihilation operators for the lth electronic state, while a_μ^+ and a_μ correspond to the creation and annihilation operators for the μth intramolecular (harmonic) vibration characterized by the frequency ω_μ. The lattice hamiltonian,

$$H_L = \sum_\nu \hbar \omega_\nu b_\nu^+ b_\nu ,$$ (6)

is expressed in terms of the phonon creation operators, b_ν^+ and annihilation operators, b_ν, of the νth lattice mode characterized by the frequency ω_ν. The radiation field hamiltonian, H_R, is given in terms of the photon creation operators, f_λ^+, and annihilation operators, f_λ, and by the photon frequencies, ω_λ, for the λ photon mode

$$H_R = \sum_\lambda \hbar \omega_\lambda f_\lambda^+ f_\lambda .$$ (7)

The molecule—lattice coupling can be expressed in the general form [7]

$$H_{mL} = \hbar \sum_\mu \sum_{\{\nu\}} [G_\mu(\{\nu\}) a_\mu^+ \prod_{\{\nu\}} b_\nu + G_\mu^*(\{\nu\}) a_\mu \prod_{\{\nu\}} b_\nu^+] ,$$ (8)

where $\{\nu\}$ is the collection of medium phonons which conserve energy for the dissipation of an intermolecular phonon, i.e., $\sum_{\{\nu\}} \hbar \omega_\nu \approx \hbar \omega_\mu$ while $G_\mu(\{\nu\})$ represent the molecule—medium coupling terms. The coupling term (8) is general, including single phonon, multiphonon and phonon—vibron vibrational relaxation processes. Finally, the molecule—radiation field coupling is [8]

$$H_{mR} = \sum_{l'>l} \sum_\lambda [M_{ll'}^\lambda \exp(i\Delta_{l'} \cdot p) d_{l'}^+ d_l \exp(-i\Delta_l \cdot p) f_\lambda + \text{h.c.}] ,$$ (9)

where $M_{ll'}^\lambda$ is the electronic transition moment[†] connecting the l and l' states by the λth field mode. $p = \{p_\mu\}$ is the vector of nuclear momenta with $p_\mu = 2^{-1/2}(a_\mu^+ - a_\mu)$, while $\Delta_l = \{\Delta_{l\mu}\}$ represents the vectors of the displacements of origins of the normal modes in the lth electronic state relative to the ground state. It should be noted that as we have taken the same nuclear hamiltonian (5) for all electronic states, the interaction term (9) has to be modified by a canonical transformation so that the radiative coupling matrix elements are invariant [8].

We consider general states of the system of the type

|electronic state; intramolecular vibration; phonons; photons⟩ ,

and examine the transition from the ground electronic state g (characterized by the vibrational occupation $V_g = \{V_{g\mu}\}$, phonon occupation $V_L = \{V_\nu\}$ and radiation field occupation m_λ) to an excited state s,

$$|g, V_g, V_L, m_\lambda\rangle \rightarrow |s, V_s, V_L', m_\lambda - 1\rangle . \tag{10}$$

The time evolution of the ground state is described by

$$\exp(-i\hbar^{-1}Ht)|g, V_g, V_L, m_\lambda\rangle = \exp[-i\hbar^{-1}(H_0^T + H_{mL})t]$$

$$\times \left\{1 - i\hbar^{-1}\int_0^t \exp[i\hbar^{-1}(H_0^T + H_{mL})t]H_{mR}\exp(-i\hbar^{-1}Ht)\right\}|g, V_g, V_L, m_\lambda\rangle . \tag{11}$$

To the lowest order of the perturbation H_{mR} the total probability[††] for the process (10) is

$$\hbar^{-2}\langle g, V_g, V_L, m_\lambda|\int_0^t \exp[i\hbar^{-1}(H_0^T + H_{mL})\tau]H_{mR}^+ \exp[-i\hbar^{-1}(H_0^T + H_{mL})\tau]d\tau$$

$$\times \exp[i\hbar^{-1}(H_0^T + H_{mL})t]|S, V_s, V_L', m_\lambda - 1\rangle\langle S, V_s, V_L', m_\lambda - 1|\exp[-i\hbar^{-1}(H_0^T + H_{mL})t]$$

$$\times \int_0^t \exp[i\hbar^{-1}(H_0^T + H_{mL})\tau']H_{mR}\exp[-i\hbar^{-1}(H_0^T + H_{mL})\tau']d\tau'|g, V_g, V_L, m_\lambda\rangle . \tag{12}$$

The total probability, $P(t)$, for absorption of a λ photon during the time t is obtained by summing eq. (12) over all values of S, V_s and V_L'. When only a single final electronic state s contributes, we get

$$P(t) = \hbar^{-2}\int_0^t d\tau \int_0^t d\tau' \langle V_g, V_L|\{\exp[i\hbar^{-1}(H_L + H_N + H_{mL})\tau]\langle g, m_\lambda|H_{mR}^+|s, m_\lambda - 1\rangle$$

$$\times \exp[-i\hbar^{-1}(H_L + H_N + H_{mL})(\tau - \tau')]\langle s, m_\lambda - 1|H_{mR}|g, m_\lambda\rangle\exp[-i\hbar^{-1}(H_L + H_N + H_{mL})\tau']|V_g, V_L\rangle$$

$$\times \exp[i(\omega_\lambda - \hbar^{-1}E_{sg})(\tau - \tau')]\} , \tag{13}$$

where E_{sg} is the electronic energy gap. Making use of eq. (9) we have

---

[†] We consider symmetry allowed transitions, while for a vibronically induced transition an additional factor, p_κ, where κ is an optically promoting mode will be included in eq. (9).

[††] The treatment of radiative interactions to first order and other couplings to infinite order is formally similar to Toyozawa's study [9] of the theory of exciton line broadening. However, Toyozawa's treatment differs from ours in the following aspects: (a) He considers electronic + phonon transition, while we include intramolecular vibrations. (b) His radiative interaction does not include a vibrational part. (c) His lowest order approximation replacing $\exp(iHt)$ by $\exp(iH_Lt)$ [9,eq. (3.7)] is equivalent to a zero temperature approximation in our case.

$$P(t) = \hbar^{-2}|M^{\lambda}_{gs}|^2 m_{\lambda} \int_0^t d\tau \int_0^t d\tau' \langle V_g, V_L |\exp[-i\Delta_s \cdot p(\tau)]\ \exp[i\Delta_s \cdot p(\tau')]| V_g, V_L\rangle \exp[i(\omega_{\lambda} - \hbar^{-1}E_{sg})(\tau - \tau')] \ , \quad (14)$$

where

$$p(t) = \exp[i(H_N + H_L + H_{mL})t]\, p\, \exp[-i(H_N + H_L + H_{mL})t] \tag{14a}$$

is the nuclear momentum in the Heisenberg representation. The medium states can be assumed to be initially in thermal equilibrium. Performing the thermal average $\langle\ \rangle_T$ over the $\{V_L\}$ states, the total transition probability is

$$P(t) = 2\hbar^{-2}|M^{\lambda}_{gs}|^2 m_{\lambda} \ \mathrm{Re} \int_0^t d\tau \int_0^t d\tau'\, G(\tau,\tau')\exp[i(\omega - \hbar^{-1}E_{sg})(\tau - \tau')] \tag{15}$$

being expressed in terms of the time correlation function

$$G(\tau,\tau') = \langle\!\langle V_L | \prod_{\mu} I_{\mu}(\tau,\tau')|V_L \rangle\!\rangle_T \approx \prod_{\mu} \langle I_{\mu}\rangle_T\ , \tag{16}$$

which, in turn, is given by the auxiliary single mode function

$$I_{\mu}(\tau,\tau') = \langle V_{g\mu}|\exp[-i\Delta_{s\mu}p_{\mu}(\tau)]\ \exp[i\Delta_{s\mu}p_{\mu}(\tau')]|V_{g\mu}\rangle\ . \tag{17}$$

Eqs. (15)–(17) express the total excitation probability of an initial state characterized by the vibrational occupation $V_g = \{V_{g\mu}\}$. The absorption coefficient (or the lineshape function) is proportional to the transition probability and (apart from numerical factors) is being given by

$$L(\omega,\tau) = \frac{1}{m_{\lambda}|M^{\lambda}_{gs}|^2}\frac{dP(t)}{dt} = 2\,\mathrm{Re} \int_0^{\tau} d\tau'\, G(\tau,\tau')\ \exp[i(\omega - \hbar^{-1}E_{sg})(\tau - \tau')]\ . \tag{18}$$

Thus the calculation of the time dependent absorption coefficient reduces to the calculation of the correlation function [eq. (16)] which requires the evaluation of the vibrational creation and annihilation operators [or $p(t)$ in eq. (17)] in the Heisenberg representation. This was accomplished by us [7] utilizing the interaction (8) within the Wigner–Weisskopf approximation. Eq. (16) can be then recast in the general form:

$$G(\tau,\tau') = \exp\left(-\sum_{\mu}\tfrac{1}{2}\Delta^2_{\mu}(2\langle n_{\mu}\rangle_T + 1)\right)\exp\left(\tfrac{1}{2}\sum_{\mu}\Delta^2_{\mu}\langle n_{\mu}\rangle_T\,\{\exp(-2\gamma_{\mu}\tau) + \exp(-2\gamma_{\mu}\tau') - 2\exp[-\gamma_{\mu}(\tau+\tau')]\cos[\omega'_{\mu}(\tau-\tau')]\}\right)$$

$$\times \exp\left(\tfrac{1}{2}\sum_{\mu}\Delta^2_{\mu}(\langle n_{\mu}\rangle_T + 1)\exp[-i\omega'_{\mu}(\tau-\tau') - \gamma_{\mu}(\tau-\tau')] + \tfrac{1}{2}\sum_{\mu}\Delta^2_{\mu}\langle n_{\mu}\rangle_T\exp[i\omega'_{\mu}(\tau-\tau') - \gamma_{\mu}(\tau-\tau')]\right)$$

$$\times \prod_{\mu}\left\{(V_{g\mu})!\sum_{r=0}^{V_{g\mu}}\frac{(-1)^r}{(V_{g\mu}-r)!\,(r!)^2}\left(\frac{\Delta_{\mu}}{\sqrt{2}}\right)^{2r}\{\exp(-2\gamma_{\mu}\tau) + \exp(-2\gamma_{\mu}\tau') - 2\exp[-\gamma_{\mu}(\tau+\tau')]\cos[\omega'_{\mu}(\tau-\tau')]\}^r\right\}, \tag{19}$$

where

$$\langle n_{\mu}\rangle_T = [\exp(\beta\hbar\omega_{\mu}) - 1]^{-1}\ ; \quad \beta = (k_B T)^{-1} \tag{19a}$$

is the thermally averaged population of the μth molecular mode, while

$$\gamma_{\mu} = \pi \sum_{\{\nu\}} |G_{\mu}(\{\nu\})|^2 n(\{\nu\})\delta(\omega_{\mu} - \sum_{\nu}\omega_{\nu}) \tag{19b}$$

is the (temperature dependent) vibrational relaxation width. Finally,

$$\omega'_\mu = \omega_\mu + \delta\omega_\mu = \omega_\mu + \mathrm{PP} \sum_{\{\nu\}} \left\{ |G_\mu(\{\nu\})|^2 n(\{\nu\})/(\omega_\mu - \sum_\nu \omega_\nu) \right\}, \tag{19c}$$

where $\delta\omega_\mu$ is a (small) frequency shift, which can be neglected. In eqs. (19b) and (19c), $n(\{\nu\})$ is a function of the occupation numbers $\langle n_\nu \rangle_T$ of the modes $\{\nu\}$ [7].

Eqs. (18) and (19) provide the final formal solution to the lineshape problem†. In order to gain further physical insight into the nature of the time dependent lineshape, let us focus attention on the zero temperature limit ($\beta \to \infty$). Furthermore, we assume that only a single vibrational mode α is initially excited, so that we start from the molecular state $|g, V_{g\alpha}, 0_{g\mu}(\mu \neq \alpha)\rangle$. The lineshape is then given by [8]

$$L(\omega,\tau) = (V_{g\alpha})! \sum_{r=0}^{V_{g\alpha}} \frac{(-1)^r}{(V_{g\alpha}-r)!\,(r!)^2} \left(\frac{\Delta_\alpha}{\sqrt{2}}\right)^{2r} \exp\left(-\tfrac{1}{2}\sum_\mu \Delta_\mu^2\right) J_r(\omega,\tau), \tag{20}$$

where

$$J_r(\omega,\tau) = \exp(-2\gamma_\alpha r\tau) \int_{-\tau}^{\tau} dx\, \exp[i\hbar^{-1}(\hbar\omega - E_{sg})x]$$

$$\times \exp\left\{\tfrac{1}{2}\sum_\mu \Delta_\mu^2 \exp(-i\omega'_\mu x - \gamma_\mu|x|)\right\} [1 + \exp(2\gamma_\alpha|x|) - 2\exp(\gamma_\alpha|x|)\cos(\omega'_\alpha x)]^r. \tag{21}$$

The (time dependent) lineshape function may be now recast as a superposition of functions which are peaked around the various transition energies. To elucidate this energy dependence we utilize the approach proposed by Lin and Bersohn [10] and by Toyozawa [9] and expand the second and third terms in $J_r(\omega)$ in power series so that the lineshape function, eq. (20) may be now rewritten in the form

$$L(\omega,\tau) = (V_{g\alpha})! \sum_{r=0}^{V_{g\alpha}} \sum_{m=0}^{r} \sum_{m'=0}^{r} \sum_{n=0}^{\infty} \frac{(-1)^{r+m+m'}}{(V_{g\alpha}-r)!\,(r!)^2} \left(\frac{\Delta_\alpha}{\sqrt{2}}\right)^{2r} \exp\left(-\tfrac{1}{2}\sum_\mu \Delta_\mu^2\right) \frac{1}{n!} \binom{r}{m}\binom{r}{m'} L(\omega,\tau;r,m,m',n), \tag{22}$$

where

$$L(\omega,\tau;r,m,m',n) = \exp(-2\gamma_\alpha r\tau) \int_{-\tau}^{\tau} dx\, \exp[i\hbar^{-1}(\hbar\omega - E_{sg})x]\, [\tfrac{1}{2}\sum_{r\mu} \Delta_\mu^2 \exp(-i\omega_\mu x - \gamma_\mu|x|)]^n$$

$$\times \exp(im\omega_\alpha x + m\gamma_\alpha|x|)\exp(-im'\omega_\alpha x + m'\gamma_\alpha|x|). \tag{23}$$

Eqs. (22) and (23) represent a superposition of terms each peaked at a photon energy $\hbar\omega$ which corresponds to the relation

$$E_{sg} - \sum_{\{n_\mu\}} n_\mu \hbar\omega_\mu - (m-m')\hbar\omega_\alpha = \hbar\omega. \tag{24}$$

Here $\{n_\mu\}$ refers to the final vibrational state in the upper electronic level $\sum_\mu n_\mu = n$, while $(m-m')$ refers to the vibrational level of the lower electronic state. For example, the term with $\{n_\mu\} = \{0_\mu\}$, $m = V_{g\alpha}$ and $m' = 0$ corresponds to the transition $V_{g\alpha} \to 0$ from the initial vibronic level to the vibrationless level of the upper electronic state. When m' assumes greater values we obtain contributions of transitions from lower vibrational levels of the initial electronic state.

† We focus attention on photon absorption, while the problem of photon emission can be handled in an analogous manner.

Eqs. (22) and (23) summarize our final result for the transient absorption rate during vibrational relaxation. We must however distinguish between the physically meaningful information and mathematical artifacts which have no bearing on the experiment. To elucidate this point we may try to isolate the contribution to the lineshape originating from a single transition. The term $\{n_\mu\} = \{0_\mu\}$, $m = r = V_{ga}$ and $m' = 0$ which corresponds to the vibronic absorption band of minimum energy, is the only term whose contribution is isolated in energy from all the other terms. This fact originates from the application of the simple model system where the frequencies are identical in the two electronic states. Selecting only this term in eqs. (20) and (22) we obtain

$$L(\omega,\tau;V_{ga},V_{ga},0,0) = \exp(-2V_{ga}\gamma_\alpha\tau)\frac{\epsilon\sin(\epsilon\tau)\exp(V_{ga}\gamma_\alpha\tau) + V_{ga}\gamma_\alpha[\cos(\epsilon\tau)\exp(V_{ga}\gamma_\alpha\tau) - 1]}{\epsilon^2 + (V_{ga}\gamma_\alpha)^2},\tag{25}$$

where

$$\epsilon = \hbar^{-1}(\hbar\omega - E_{sg} + V_{ga}\hbar\omega_\alpha).\tag{26}$$

Eq. (25) seems to yield the transient absorption lineshape for the corresponding transition. However, by virtue of the Heisenberg uncertainty principle, the required energy resolution cannot be achieved within the finite lifetime of the absorbing state. In other words, the photons absorbed during this lifetime, $\hbar(2V_{ga}\gamma_\alpha)^{-1}$ are necessarily characterized by an energy spread of $\approx 2V_{ga}\gamma_\alpha$, which is the width of the absorption line given by eq. (25). The energy dependence in eq. (25) is thus physically meaningless. The only meaningful information includes the relative total intensity of the absorption line [which, noting that

$$\int_{-\infty}^{\infty} d\omega L(\omega,\tau;r,m,m',n) = \exp(-2\gamma_\alpha r\tau)$$

for any set r, m, m', n, is given just by the corresponding coefficient in eq. (22)], its average energy location [given by eq. (26) or generally by eq. (24)] and its time evolution given for the minimum energy line by $\exp(-2V_{ga}\gamma_\alpha\tau)$, and in general as a superposition of decaying exponentials. This point has not been clearly stated by Osherov and Medvedev [6].

It must be noted that our inability to probe the internal structure of a vibrational relaxation affected lineshape is an outcome of our particular experimental situation namely, one which corresponds to a "short time" experiment whose time scale is comparable to the desired energy resolution. It by no means implies that such a probing is impossible. For example, in a long line experiment involving excitation by a wave train of well defined energy from the initial ground state into a higher vibrational level of an upper electronic state, the (time independent) lineshape may be easily probed. Simple theoretical calculation results in a lorentzian lineshape with a width given essentially by $2V\gamma$ where V is the vibrational quantum number of the excited level[†].

Finally, we consider the limiting form of our general expressions in the well known limit of thermal equilibrium in the initial molecular state. In this case the last factor in eq. (19)

$$\prod_\mu \{\langle V_{g\mu}|\exp[-\lambda_\mu^*(\tau,\tau')a_\mu^\dagger]\exp[\lambda_\mu(\tau,\tau')a_\mu]|V_{g\mu}\rangle\}\tag{27}$$

must be replaced by a thermal average which takes the form

$$\prod_\mu \exp(-|\lambda_\mu|^2\langle n_\mu\rangle_T) = \exp\left(-\sum_\mu|\lambda_\mu|^2\langle n_\mu\rangle_T\right),\tag{28}$$

with

$$\lambda_\mu(\tau,\tau') = (\Delta_\mu/\sqrt{2})[\exp(-i\omega_\mu\tau - \gamma_\mu\tau) - \exp(-i\omega_\mu\tau' - \gamma_\mu\tau')],\tag{29a}$$

† Similar result has been obtained by Schmidt [11].

$$|\lambda_\mu(\tau,\tau')|^2 = \tfrac{1}{2}\Delta_\mu^2 \{\exp(-2\gamma_\mu\tau) + \exp(-2\gamma_\mu\tau') - 2\exp[-\gamma_\mu(\tau+\tau')]\cos[\omega'_\mu(\tau-\tau')]\} \ . \tag{29b}$$

If the medium is at a temperature T_L while the molecule corresponds to a thermal average at a temperature T_m we obtain

$$G(\tau,\tau') = \exp\left\{\sum_\mu \tfrac{1}{2}\Delta_\mu^2(2\langle n_\mu\rangle_{T_L} + 1)\right\}\exp\left\{\sum_\mu (\langle n_\mu\rangle_{T_L} - \langle n_\mu\rangle_{T_m})|\lambda_\mu|^2\right\}$$

$$\times \exp\left\{\tfrac{1}{2}\sum_\mu \Delta_\mu^2(\langle n_\mu\rangle_{T_L} + 1)\exp[-i\omega'_\mu(\tau-\tau') - \gamma_\mu(\tau \ \tau')] + \tfrac{1}{2}\sum_\mu \Delta_\mu^2\langle n_\mu\rangle_{T_L}\exp[i\omega'_\mu(\tau-\tau') - \gamma_\mu(\tau-\tau')]\right\} \ . \tag{30}$$

In the usual case, when $T_L = T_m$ we get just the result which corresponds to the fast vibrational relaxation case. In this event, $G(\tau,\tau') = G(\tau - \tau')$ and $L(\omega)$ is independent of time.

Eq. (30) provides the well known result for thermally averaged lineshape except for the inclusion of the imaginary components in the molecular frequencies, accounting for vibrational relaxation. The absorption lineshape is a superposition of lorentzians, the 0–0 line being a delta function while the width of the $V'_\alpha \to V''_\alpha$ transition is $(V'_\alpha + V''_\alpha)\gamma_\alpha$, corresponding to the vibrational relaxation widths in the initial and final states. The relative intensities of the bands are given by the conventional Franck–Condon factors.

References

[1] B. Ya Zeldovich, A.M. Perelomov and V.S. Popov, Soviet Phys. JETP 28 (1969) 308;
E.W. Montroll and K.E. Shuler, J. Chem. Phys. 26 (1957) 454;
I. Oppenheim, K.E. Shuler and G.H. Weiss, Advan. Mol. Relaxation Processes 1 (1967–68) 13;
J.M. Schurr, Intern. J. Quantum Chem. 5 (1971) 239.

[2] F. DeMartini and J. Ducuing, Phys. Rev. Letters 17 (1966) 117.

[3] E. Drent and J. Kommandeur, Chem. Phys. Letters 8 (1971) 303;
S.J. Formosinho, G. Porter and M.A. West, Chem. Phys. Letters 6 (1970) 7.

[4] D.S. Tinti and G.W. Robinson, J. Chem. Phys. 49 (1968) 3229.

[5] C.J. Werkhoven, P.A. Geldof, M.F.M. Post, J. Langelaar, R.P.H. Rettschnick and J.D.W. van Voorst, Chem. Phys. Letters 9 (1971) 6.

[6] V.O. Osherov and E.S. Medvedev, Chem. Phys. Letters 8 (1971) 550.

[7] A. Nitzan and J. Jortner, Mol. Phys., to be published.

[8] A. Nitzan and J. Jortner, J. Chem. Phys., to be published

[9] Y. Toyozawa, Progr. Theoret. Phys. 20 (1958) 53.

[10] S.H. Lin, J. Chem. Phys. 44 (1966) 3759;
S.H. Lin and R. Bersohn, J. Chem. Phys. 48 (1968) 2732.

[11] P.P. Schmidt, J. Phys. B 3 (1970) 443.