Theoret. Chim. Acta (Berl.) 40, 263–270 (1975)

The Gaussian Approximation in Molecular Radiationless Transitions

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Received July 23, 1975

The Hermite-Gaussian representation of the generating function is used to examine the form of the transition probability for a multiphonon molecular radiationless relaxation process.

Key word: Radiationless transitions

1. Introduction

Radiationless intramolecular vibronic transitions have been investigated extensively in the last few years [1–6]. Apart from their importance with respect to the problem of the relaxation of an initially excited state, these analyses are of considerable importance in connexion with molecular reaction kinetics [7, 8]. In particular, for reactions which take place in dense media (which for the typical chemist constitutes the majority situation) often it is possible to formulate a rate constant generating function [7, 8]. Such generating functions have a considerable similarity to expressions derived for the molecular radiationless relaxation phenomena. One problem which arises in connexion with molecular relaxation processes, and may be exacerbated in the molecular reacting system, is the effect of sequence congestion and individual line broadening [9–11]. Typically, this is treated by demonstrating, with one means or another, that the intrinsic lineshape is broadened, usually to a Lorentzian form. That individual Lorentz broadening may not be an important complication has been demonstrated recently by Nitzan and Jortner [12]. In general, multiphonon transitions associated with radiationless transitions exhibit Gaussian or at worst skewed Gaussian behaviour [13]. Moreover, even in the few-phonon limit the transition shape function probably exhibits a tendency to a Gaussian limit in the sense of the central limit theorem [13]. This certainly is true for neutron scattering experiments with solids, liquids, and molecules [14–16], and one expects a similar situation to apply to the reactive system.

In view of the above considerations, the purpose of this note is the examination of the form of the generating function for a molecular radiationless transition with the object of formulating a Gaussian limit for the many-phonon transition.

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Interest focuses primarily on the low temperature limit for which the radiationless transitions take place by means of tunneling below the barrier defined by the avoided crossing rule. In addition, consideration of this problem is restricted to those systems in which the frequency shifts can be considered reasonably small (in the sense of Lin's theory [1]) or vanishing.

2. Formulation of the Problem

The finite temperature transition probability for a radiationless transition is

$$w=\frac{2\pi}{\hbar Z}\sum_{i,f}\exp(-\beta E_i)|\langle i|H'|f\rangle|^2\delta(E_i-E_f)=\frac{2\pi}{\hbar}F(0) \tag{1}$$

where the transition shape factor $F(0)$ in the Condon approximation is

$$F(0)=|H'_{if}|^2G(\varepsilon_{if}) \tag{2}$$

and here H'_{if} is the electronic matrix element of the driving perturbation, ε_{if} is the energy gap separating the minima of the two vibronic states. We consider a two level representation of the electronic component of the system. Consequently, the matrix element H'_{if} involves only those electronic basis vectors associated with the two states. The function $G(\varepsilon)$ is a normalized shape function which depends upon the energy gap, and is defined by the following time integral involving the generating function $g(t)$:

$$G(\varepsilon)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,\exp(i\varepsilon t/\hbar)\,g(t) \tag{3}$$

with $g(t)$ given by

$$g(t)=\exp\left(\sum_n(\zeta_n^2/2)\{\coth(\hbar\omega_n\beta/2)(\cos\omega_n t-1)+i\sin\omega_n t\}\right) \tag{4}$$

and the sum over n is over normal modes with ζ_n the normal coordinate shift. The generating function is presented for the case in which promoting modes are not involved. When promoting modes figure in the radiationless relaxation, the generating function modifies to [1]

$$g_p(t)=g(t)\left(\sum_n(\coth(\hbar\omega_n\beta/2)+1)e^{i\omega_n t}+(\coth(\hbar\omega_n\beta/2)-1)e^{-i\omega_n t}\right) \tag{5}$$

Eqs.(4) and (5) assume no frequency shifts in the normal modes between the initial and final states. If there are non-vanishing, but nevertheless small, frequency shifts present, then according to Lin's analysis [1] a term

$$\tfrac{1}{2}i\rho_n\omega_n t\coth(\hbar\omega_n\beta/2),\qquad \rho_n=\frac{\omega_n^{(f)}-\omega_n^{(i)}}{\omega_n^{(i)}} \tag{6}$$

can be added to the gap contribution.

In the following discussion attention is concentrated on the first case which is independent of promoting modes. It is a simple matter to convolute the promoting modes into the obtained result.

3. The Hermite-Gaussian Expansion

The following analysis is a modification of Sjölander's treatment [13] of the thermal neutron scattering cross-section in a Gaussian, multiphonon limit.

Write the generating function as

$$g(t)=\exp\{\gamma(t)-\gamma(0)\} \tag{7}$$

with

$$\gamma(t)=\sum_{n}(\zeta_n^2/2)\{\coth(\hbar\omega_n\beta/2)\cos\omega_n t+i\sin\omega_n t\} \tag{8}$$

and consider the following expansion

$$g(t)=e^{-\gamma(0)}\{1+\gamma(t)+\tfrac{1}{2}\gamma^2(t)+\cdots\} \tag{9}$$

Next, consider the following function $\Gamma(\varepsilon)$ defined by the integral

$$\begin{aligned}\Gamma(\varepsilon)&=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,\exp(i\varepsilon t/\hbar)(\gamma(t)/\gamma(0))\\&=\gamma^{-1}(0)\sum_{n}(E_r^{(n)}/\hbar\omega_n)\{(\langle n_n\rangle+1)\delta(\varepsilon+\hbar\omega_n)+\langle n_n\rangle\delta(\varepsilon-\hbar\omega_n)\}\end{aligned} \tag{10}$$

where $E_r^{(n)}$ is the energy associated with the normal mode displacement in the final state with respect to the initial state (half the Stokes shift energy),

$$E_r^{(n)}=\tfrac{1}{2}\hbar\omega_n\zeta_n{}^2 \tag{11}$$

and

$$\langle n_n\rangle=(e^{\hbar\omega_n\beta}-1)^{-1} \tag{12}$$

An nth order term is defined as

$$\begin{aligned}\mathscr{G}_n(\varepsilon)&=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,\exp(i\varepsilon t/\hbar)(\gamma(t)/\gamma(0))^n\\&=\int_{-\infty}^{\infty}d\varepsilon_1\ldots d\varepsilon_{n-1}\Gamma(\varepsilon-\varepsilon_1)\ldots\Gamma(\varepsilon_{n-1})\end{aligned} \tag{13}$$

Furthermore, the functions $\Gamma(\varepsilon)$ and $\mathscr{G}_n(\varepsilon)$ both are normalized

$$\int_{-\infty}^{\infty}d\varepsilon\Gamma(\varepsilon)=1\quad\text{and}\quad\int_{-\infty}^{\infty}d\varepsilon\mathscr{G}_n(\varepsilon)=1 \tag{14}$$

Therefore, the transition shape function assumes the form

$$G(\varepsilon)=e^{-\gamma(0)}\sum_{l=0}^{\infty}\frac{\gamma^l(0)}{l!\mathscr{G}}{}_l(\varepsilon) \tag{15}$$

with

$$\mathscr{G}_0(\varepsilon)=\delta(\varepsilon) \tag{16}$$

$$\mathscr{G}_1(\varepsilon)=\Gamma(\varepsilon) \tag{17}$$

$$\mathscr{G}_n(\varepsilon)=\int_{-\infty}^{\infty}d\varepsilon'\Gamma(\varepsilon-\varepsilon')\mathscr{G}_{n-1}(\varepsilon') \tag{18}$$

As long as the condition

$$|\gamma(t)| < |\gamma(0)| \qquad t \neq 0 \tag{19}$$

applies (which it will except for an Einstein solid), the following convergent expansion can be constructed

$$\gamma(t)/\gamma(0) = \sum_{v=0} (\alpha^{v}/v!)(it)^{v} \tag{20}$$

where

$$\alpha_0 = 1 \qquad \alpha_1 = \sum_n (\omega_n/\gamma(0)) \qquad \alpha_2 = \gamma^{-1}(0) \sum_n (\delta_n/2\hbar) E_r^{(n)} \coth(\tfrac{1}{2}\hbar\omega_n\beta), \text{ etc.} \tag{21}$$

In addition, the expansion of the logarithm of the ratio $\gamma(t)/\gamma(0)$ can be constructed

$$\ln\{\gamma(t)/\gamma(0)\} = \sum_{v=0} (\kappa_v/v!)(it)^{v} \tag{22}$$

with

$$\kappa_1 = \alpha_1, \qquad \kappa_2 = \alpha_2 - \alpha_2^{1} = \Delta_0^2 = \gamma^{-2}(0) \sum_n \tfrac{1}{4}\omega_n^2 \zeta_n^2 \gamma(0) \coth(\tfrac{1}{2}\hbar\omega_n\beta) - \sum_{n,n'} \omega_n \omega_{n'}, \text{ etc.} \tag{23}$$

Thus, the function $\mathcal{G}_n(\varepsilon)$ can be expressed as

$$\mathcal{G}_n(\varepsilon) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \exp\left(i\varepsilon t/\hbar + in\kappa_1 t - \tfrac{1}{2}n\kappa_2 t^2 + n \sum_{v=3}^{\infty} (\kappa_v/v!)(it)^{v} \right) \tag{24}$$

Finally, using the expansion

$$\exp\left(n \sum_{v=3}^{\infty} (\kappa_v/v!)(it)^{v} \right) = \sum_{v=0}^{\infty} c_v^{(n)} (it)^{v} \tag{25}$$

where the $c_v^{(n)}$ are easily identified, one finds

$$\begin{aligned} \mathcal{G}_n(\varepsilon) &= \frac{1}{2\pi\hbar\sqrt{n}\Delta_0} \int_{-\infty}^{\infty} dz \sum_{v=0}^{\infty} c_v^{(n)} (iz)^{v} \exp\left(-\tfrac{1}{2}z^2 + i \frac{x_n}{\Delta_0\sqrt{n}} z \right) \\ &= \frac{2^{n/2}}{\hbar\Delta_0\sqrt{2\pi n}} \sum_{v=0}^{\infty} c_v^{(n)} \exp\left(-\frac{x_n}{2\Delta_0^2 n} \right) H_v(x/\Delta_0\sqrt{n}) \end{aligned} \tag{26}$$

where $H_m(x)$ is the mth order Hermite polynomial, and

$$x = \varepsilon/\hbar + n \sum_l \omega_l/\gamma(0) \tag{27}$$

The Hermite-Gauss expansion for the shape function reveals a skewed Gaussian shape for all transitions with $n > 0$. For $n = 0$ the series reduces to a delta function. As can be seen from the results, the degree of skewness depends on temperature, a result also anticipated by Lax [17] and by O'Rourke [18]. With respect to radiationless transitions the effect of skewness on the transition rate generally is expected to be small. The Gaussian character of the envelope about a particular n-quantum transition should determine the relaxation rate probably to within experimental error. As a consequence, it is possible to ignore skewness, and other higher order corrections, and proceed to determine a general Gaussian form for a multiphonon transition centred about a particular value of n.

We write

$$\sum_{n=0}^{\infty} \frac{\gamma^n(0)}{n!} \mathcal{G}_n(\varepsilon) = \delta(\varepsilon) + \sum_{n=1}^{\infty} \frac{\gamma^n(0)}{n!} \mathcal{G}_n(\varepsilon) \tag{28}$$

with

$$\mathcal{G}_n(\varepsilon) = \frac{1}{\hbar \Delta_0 \sqrt{2\pi n}} \exp\left(- \frac{(\varepsilon + n\Sigma_l \hbar\omega_l / \gamma(0))^2}{2nE_0^2} \right) \tag{29}$$

Thus, with the definitions

$$E_0 \equiv \hbar \Delta_0 \tag{30}$$

and

$$n\Omega \equiv n \sum_l \hbar\omega_l \gamma^{-1}(0) \tag{31}$$

it is possible to express the shape function as

$$G(\varepsilon) = e^{-\gamma(0)} \left(\delta(\varepsilon) + \frac{1}{E_0} \exp(-\beta_1 x)\, F(x, z) + F_{\text{corr}} \right) \tag{32}$$

with

$$\beta_1 = \Omega^2 / 2E_0^2 = \frac{1}{\hbar^2 \Delta_0^2 \gamma(0)} (\Sigma_l \hbar\omega_l)^2 \tag{33}$$

$$F(x, z) = \sum_{n=1}^{\infty} (z^n / n!) \frac{\exp(-x^2/2n)}{(2\pi n)^{1/2}} \tag{34}$$

$$z = \gamma(0) \exp(-\tfrac{1}{2}\beta_1^2) \tag{35}$$

The term F_{corr} depends on the terms omitted in arriving at the above result. Therefore, F_{corr} depends on skewness, etc. The multiphonon transition probability is isolated as the expression

$$G_n(\varepsilon) = \frac{\exp(-\gamma(0) - \beta_1 x)\, F(x, z)}{E_0} \tag{36}$$

Values of $F(x, z)$ have been tabulated [13].

Finally, the effect of promoting modes can be incorporated into the above result by means of a convolution. The result is that the multiphonon transition centred about n is shifted to $n \pm 1$. The width of the transition E_0 remains the same.

4. Discussion

In the expression for the Gaussian limit for the radiationless transition, Eq.(32), the quantities n and E_0 define the centre of gravity and width of the transition. The effect of these terms is illustrated in the Figure. In the zero temperature limit,

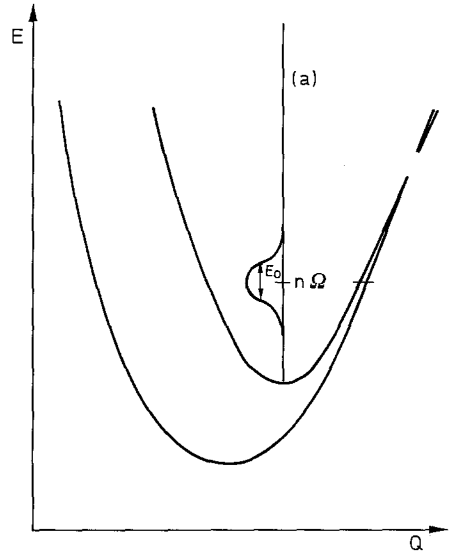

Fig. 1. The figure illustrates the statistical limit for a many-phonon transition at finite temperature. The part of the figure labelled (a) represents the relative density of phonon states involved in the transition

however, the transition width function E_0 vanishes, and each Gaussian term passes to the delta function limit. As a result, the expression for the Gaussian representation in the zero temperature limit contains the results previously derived in a number of places [5, 6]. The high temperature, multiphonon limit also is contained, it is

$$G_{ht}(\varepsilon)=(\pi\beta/\langle E_r\rangle)^{1/2}\exp\left(-\frac{(\varepsilon+\langle E_r\rangle)^2\beta}{4\langle E_r\rangle}\right) \tag{37}$$

with

$$\langle E_r\rangle=\sum_n E_r^{(n)} \tag{38}$$

If one returns to the expression for the generating function, Eq.(4), and makes the following expansion of the time argument

$$g(t)\simeq\exp\left(-\sum_n (E_r^{(n)}/\hbar\omega_n)\{\tfrac{1}{2}\omega_n^2t^2\coth(\tfrac{1}{2}\hbar\omega_n\beta)-i\omega_n t\}\right) \tag{39}$$

the integration which leads to the shape function is trivial, and yields

$$\mathcal{G}(\varepsilon)=\left(\frac{2\pi}{\sum_n \hbar\omega_n E_r^{(n)}\coth(\frac{1}{2}\hbar\omega_n\beta)}\right)^{1/2}\exp\left(-\frac{(\varepsilon+\langle E_r\rangle)^2}{2\sum_n (E_r^{(n)}\hbar\omega_n)\coth(\frac{1}{2}\hbar\omega_n\beta)}\right) \tag{40}$$

Generally, this is referred to as the strong coupling limit [3], and it is interesting to note that it corresponds to the semiclassical limit discussed by Lax [17]. Strong coupling in this case implies large magnitude coordinate shifts of the minima of the potential energy functions for the two vibronic states involved. Such situations, i.e., large coordinate shifts, are encountered frequently in connexion with radiationless transition phenomena, and in particular, in connexion with the solvent polar modes in the electron transfer reaction. The validity of the semiclassical or strong coupling limit in the high temperature range for collective system modes is undisputed. However, it would seem that considerable care must be taken with the application of this limit to molecular degrees of freedom whether in connexion with the relaxation of a molecular excited state or in connexion with the inner sphere degrees of freedom with the electron transfer reaction. As the above Gaussian limit passes correctly to the zero temperature, quantum and to the high temperature, classical limits, it seems a useful general representation, especially in cases of questionable quantal or classical character.

For polyatomic molecules the situation approaches the solid state in certain ways. That the inequality (19) is probably universally satisfied can be argued in a qualitative way. The molecular density of states becomes an almost uncountably large number for moderate excitations [20]. At this stage of the calculation the complete density of states function is of no use. However, it is possible to consider reduced density of states functions for the individual normal modes (note, the summations involved in Eq.(11) are taken over the normal modes, not over the quantum numbers within the modes). Anharmonicity, and anharmonic mixing of normal modes results in an effective broadening of each representative harmonic oscillator level in a band. Thus, associated with each normal mode must be an effective density of states function which defines the number of states in the region of the harmonically defined normal mode. These functions will be essentially continuous, and very likely nearly Gaussian. Consequently, near, but not exact, periodicity is guaranteed with the result that the inequality (19) is satisfied in general and specifically for each normal mode of the system. For molecules dissolved in liquid or solid solutions the broadening of an individual line through coupling with the continuum of medium phonons will introduce density of states functions for which a Debye cut-off must be applied to each normal mode. As a consequence, we see that not only is Eq.(19) satisfied, but in part the effect of sequence congestion can be transferred to the various quantities which enter the Gaussian representation of the shape function.

References

1. Lin,S.H.: J. Chem. Phys. **461**, 3759 (1966)
2. Fischer,S.F.: J. Chem. Phys. **53**, 3195 (1970)
3. Englman,R., Jortner,J.: Mol. Phys. **18**, 145 (1970)
4. Freed,K.F., Jortner,J.: J. Chem. Phys. **52**, 6272
5. Nitzan,A., Jortner,J.: J. Chem. Phys. **55**, 1355 (1971)
6. Nitzan,A., Jortner,J.: J. Chem. Phys. **56**, 2079 (1971)
7. Lin,S.H., Eyring,H.: Proc. Nat. Acad. Sci. U.S. **69**, 3192 (1972)
8. Dogonadze,R.R., Kuznetsov,A.M.: Chemical Reaction Kinetics in Polar Solvents, (VINITI, Moscow, 1973) (in Russian)
9. Nitzan,A., Jortner,J.: Chem. Phys. Letters **13**, 466 (1972)
10. Nitzan,A., Jortner,J.: J. Chem. Phys. **58**, 2412 (1973)
11. Schmidt,P.B.: J. Phys. B. **3**, 443 (1970)
12. Nitzan,A., Jortner,J.: Theoret. Chim. Acta (Berl.) **30**, 217 (1973)
13. Sjölander,A.: Avkiv F. Fysik **14**, 315 (1958)

14. Egelstaff,P.: Thermal neutron scattering. New York: Academic Press 1965
15. Egelstaff,P.: An introduction to the liquid state. New York: Academic Press 1967
16. Marshall,W.C., Lovesey,S.W.: Theory of thermal neutron scattering. London: Oxford University Press 1971
17. Lax,M.: J. Chem. Phys. **20**, 1752 (1952)
18. O'Rourke,R.C.: Phys. Rev. **91**, 265 (1953)
19. Holstein,T.: Am. Phys. (N.Y.) **8**, 325 (1959)
20. Christie,J.R., Craig,D.P.: Mol. Phys. **23**, 345, 353 (1972)

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