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Commentationes

Vertical Excitation as a Transient Phenomenon

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For a particular model with two electronic states, each with two vibrations, the dipole correlation function governing electronic absorption is $e^{-i\omega_0 t}\cos\gamma t$ with spectrum $\omega_0 \pm \gamma$. The function starts as $e^{-i\omega_0 t}$ ($\gamma \ll \omega_0$), with Fourier transform peaking around ω_0 instead of $\omega_0 \pm \gamma$, and this is associated with vertical excitation. After a time $t \sim 2/\gamma$ the spectrum goes over into the normal one. As a generalization, a procedure is outlined for characterizing the state reached first after interaction with light is initiated. Finally it is suggested that one can understand aspects of internal conversion by analogy with the case of vertical excitation.

Für ein Modell mit zwei Elektronenzuständen, jeder mit zwei Schwingungen, wird die elektronische Absorption durch die Dipolkorrelationsfunktion $e^{-i\omega_0 t}\cos\gamma t$ mit dem Spektrum $\omega_0 \pm \gamma$ beschrieben. Die Funktion beginnt als $e^{-i\omega_0 t}$ ($\gamma \ll \omega_0$) mit dem Maximum der Fouriertransformierten um ω_0 statt $\omega_0 \pm \gamma$. Dies ist mit einer vertikalen Anregung verknüpft. Nach einer Zeit $t \sim 2/\gamma$ geht das Spektrum in das normale Spektrum über. Als eine Verallgemeinerung wird eine Methode ausgeführt, die den Zustand der zuerst, nach einer Wechselwirkung mit Licht, erreicht wird, beschreibt. Es wird vorgeschlagen, daß bestimmte Aspekte der inneren Konversion durch Analogie zur vertikalen Anregung zu verstehen sind.

La fonction de corrélation dipolaire gouvernant l'absorption électronique pour un modèle particulier à deux états électroniques, chacun avec deux vibrations, est $e^{-i\omega_0 t}\cos\gamma t$ avec le spectre $\omega_0 \pm \gamma$. La fonction commence comme $e^{-i\omega_0 t}(\gamma \ll w_0)$, avec une transformée de Fourier centrée autour de ω_0 au lieu de $\omega_0 \mp \gamma$; ceci est associé à l'excitation verticale. Après un temps $t \sim 2/\gamma$ le spectre devient normal. Description d'un procédé pour caractériser l'état premier atteint lorsque l'interaction avec la lumière est établie. Enfin on suggère que des aspects de la conversion interne peuvent être compris par analogie avec le cas de l'excitation verticale.

Introduction

Ordinarily the change in the nuclear potential energy function which accompanies electronic excitation calls for marked structural changes. However transfer of electronic excitation energy from one molecule to another nearby would limit the time the energy could spend on the first and if the interval should be so short as to interfere with the nuclear reorganization, one might expect, and indeed one finds some unusual effects: thus the appearance of the sharp J band with cyanine dye polymer chains and the occurrence of metallic reflection from molecular crystals composed of strong absorbers [1]. To understand effects such as these it is helpful to employ the notion of vertical excitation, according to which a molecule might first absorb light, keeping its ground state structural characteristics, before going on either to reorganize [2] or to hand its energy of excitation over to a neighbor [3].

In this note the vertical excitation plus reorganization concept by itself is explored. That is, an absorption spectrum for just a single molecule is calculated, with emphasis on the duration of the encounter between molecule and radiation. The radiation is treated classically, and is brought in via an interaction Hamiltonian which contains a stepfunction as a factor. The results are generalized, and in a final section, consideration is given to the possibility of applying the results towards the understanding of internal conversion.

The Ordinary Spectrum

We may typify the effect of vibrational reorganization through the use of a two-level model for the vibrational states within a two-level model for the electronic states. The ground state manifold will be taken to consist of the stationary-state functions

$$\psi_N\begin{pmatrix}1\\0\end{pmatrix},\quad \psi_N\begin{pmatrix}0\\1\end{pmatrix},$$

where ψ and the column vectors refer respectively to electronic and vibrational parts (we are tacitly assuming that the Born-Oppenheimer approximation is applicable and even that we may neglect the dependence of ψ on the nuclear coordinates). The excited-state manifold would be spanned by

$$\psi_V\begin{pmatrix}1\\0\end{pmatrix},\quad \psi_V\begin{pmatrix}0\\1\end{pmatrix}$$

but the stationary states would involve a mixing (unit column vectors are vibrational energy eigenfunctions corresponding to the potential energy surface for the ground state). In the extreme case there could be a spreading of vibronic intensity equally into the two transitions from $\psi_N\begin{pmatrix}1\\0\end{pmatrix}$, which transitions would then involve the following excited stationary-state functions

$$\psi_V\begin{pmatrix}1/\sqrt{2}\\1/\sqrt{2}\end{pmatrix},\quad \psi_V\begin{pmatrix}1/\sqrt{2}\\-1/\sqrt{2}\end{pmatrix}.$$

The expressions for the transition moments (the moment, μ, treated as a scalar) would be

$$\int d\tau\,\psi_N^*(1\,0)\,\mu_{\mathrm{op}}\,\psi_V\begin{pmatrix}1/\sqrt{2}\\1/\sqrt{2}\end{pmatrix}=\mu_{NV}/\sqrt{2}$$

$$\int d\tau\,\psi_N^*(1\,0)\,\mu_{\mathrm{op}}\,\psi_V\begin{pmatrix}1/\sqrt{2}\\-1/\sqrt{2}\end{pmatrix}=\mu_{NV}/\sqrt{2},$$

where μ_{NV} represents the electronic moment and the factors $1/\sqrt{2}$ stand for the Franck-Condon integrals. With these expressions squared, one-half of μ_{NV}^2 is found in each transition.

Now we number the wave functions serially, omitting the vibrationally excited ground state, and using the ground-state vibrations to define the basis

$$|0\rangle \leftrightarrow \psi_N \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |1\rangle \leftrightarrow \psi_V \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle \leftrightarrow \psi_V \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

A Hamiltonian which brings in the electronic excitation, with energy $\omega_0(\hbar = 1)$, and also the vibrational mixing accompanying this electronic excitation, with mixing parameter γ, is

$$H = \omega_0[|1\rangle\langle 1| + |2\rangle\langle 2|] + \gamma[|1\rangle\langle 2| + |2\rangle\langle 1|].$$

The levels come at 0, $\omega_0 \pm \gamma$, with eigenfunctions as postulated above. The electric moment operator is

$$\mu_{\mathrm{op}} = \mu_{NV}[|0\rangle\langle 1| + |1\rangle\langle 0|].$$

The absence of a part with $|2\rangle$ in μ comes from the choice of basis. The vertical transition $|0\rangle \to |1\rangle$, while not a transition to a stationary state, fits in with the idea of the Franck-Condon principle. Having a unit Franck-Condon integral corresponds to having no change in the nuclear wave function.

For later use and for a general orientation we first consider the steady state or long-time case. We confine our interest to the spectral function for absorption, which is proportional to the imaginary part of the complex susceptibility. This last as a Fourier transform may be considered technically as having positive and negative frequency parts, but for absorption we need use only the positive frequency part.

An expression for this part written in terms of a basis is [4]

$$\chi_+ = \sum_{rjks} c_r^* \mu_{rj} g_{jk}^+ \mu_{ks} c_s,$$

where c_r, c_s are ground state amplitudes of the r and s basis functions, μ_{rj} and μ_{ks} are electric moment matrix elements,

$$g_{jk}^+ = i\theta \langle jt | k0 \rangle_{\omega + \omega_N}.$$

$\langle jt|$ is in the Schrödinger representation and is a solution of the Schrödinger equation at the time t, whereas $|k0\rangle$ is a solution at the time zero. $\theta = \theta(t)$ is a Heaviside function. The vertical line with $\omega + \omega_N$ means a Fourier transform.

Specializing to the case of our molecular model we have

$$c_0 = 1, \quad c_1 = c_2 = 0$$

$$\mu_{01} = \langle 0|\mu|1\rangle = \mu_{NV}, \quad \mu_{02} = 0$$

$$\omega_N = 0$$

so that

$$\chi_+ = \mu_{NV}^2 g_{11}$$

$$g_{11} = i\theta\langle 1t|10\rangle|_\omega.$$

The simplicity in functional form is related to our choice of basis.

A key relation obeyed generally by the g's is

$$\omega g_{jk} = -\langle j0|k0\rangle + i\theta\langle jt|H(0)|k0\rangle|_\omega .$$

It will now be used to obtain g_{11} and hence χ_+. Thus

$$\omega g_{11} = -1 + i\theta\langle 1t|H(0)|10\rangle|_\omega$$

and

$$H(0)|10\rangle = \omega_0|10\rangle + \gamma|20\rangle$$

give

$$\omega g_{11} = -1 + \omega_0 g_{11} + \gamma g_{12} .$$

In the same way

$$\omega g_{12} = \omega_0 g_{12} + \gamma g_{11} .$$

Eliminating g_{12} we find ($x = \omega - \omega_0$)

$$g_{11} = -\frac{\omega - \omega_0}{(\omega - \omega_0)^2 - \gamma^2} = -\frac{x}{x^2 - \gamma^2} .$$

There are poles at $x = \pm\gamma$ corresponding to the lines in the spectrum at $\omega_0 \pm \gamma$. When $x = +\gamma$ the factor multiplying the pole factor of $1/x - \gamma$ is $-x/x + \gamma = -1/2$. We call this $R_{11}(\gamma)$. Also $R_{11}(-\gamma) = -x/x - \gamma = -1/2$. (The equality of the R's evidently corresponds to the spreading of intensity already found). We shall be needing the other g. It is

$$g_{12} = -\frac{\gamma}{x^2 - \gamma^2}$$

with $R_{12}(\gamma) = -1/2$ and $R_{12}(-\gamma) = +1/2$. Finally we may use the R's to write the g's as spectrally resolved

$$g_{11} = -\frac{1}{2}\frac{1}{x - \gamma} - \frac{1}{2}\frac{1}{x + \gamma}$$

$$g_{12} = -\frac{1}{2}\frac{1}{x - \gamma} + \frac{1}{2}\frac{1}{x + \gamma} .$$

For brief interaction times we shall have to work with a modification of the above procedure. The g's will contain terms which are like our present g's before the Fourier transform is taken – i.e. $\langle 1t|10\rangle$ and $\langle 1t|20\rangle$. Thus we need to invert the Fourier transforms for g_{11} and g_{12}.

To this end we observe that if $\langle j|$ is an energy eigen ψ

$$\langle jt|j0\rangle = e^{-i\omega j t}$$

and

$$i\theta\langle jt|j0)|_\omega = \frac{1}{\omega_j - \omega} .$$

More generally, if there is a sum of terms

$$\langle t|0\rangle = \sum_j R(\omega_j)e^{-i\omega_j t}$$

then

$$i\theta\langle t|0\rangle|_\omega = \sum_j \frac{R(\omega_j)}{\omega_j - \omega}.$$

Turning the argument around we have, from the spectral resolutions

$$\begin{aligned}\langle 1t|10\rangle &= \tfrac{1}{2}e^{-i(\omega_0+\gamma)t} + \tfrac{1}{2}e^{-i(\omega_0-\gamma)t}\\ &= e^{-i\omega_0 t}\cos\gamma t\\ \langle 1t|20\rangle &= \tfrac{1}{2}e^{-i(\omega_0+\gamma)t} - \tfrac{1}{2}e^{-i(\omega_0-\gamma)t}\\ &= -ie^{-i\omega_0 t}\sin\gamma t\,.\end{aligned}$$

We see that when $t > 0$ is so small that $\cos\gamma t \approx 1$ the correlation function $\langle 1t|10\rangle$ goes as $e^{-i\omega_0 t}$ (that is when $\gamma \ll \omega_0$, and this is important). The appearance of ω_0 instead of either of the frequencies $\omega_0 \pm \gamma$ foreshadows our eventual result for short times. It comes about because all the intensity in μ_{op} occurs from $|0\rangle$ to $|1\rangle$, and $\langle 1|H|1\rangle = \omega_0$; and means that the molecule has not had time to reorganize according to the γ process in the Hamiltonian.

Formalism for Transient Susceptibility

The steady state expression used above for χ_+ has as precursor the more compact relation [5]

$$\chi = i\theta\langle N-\infty|[\mu(t), \mu(0)]|N-\infty\rangle|_\omega$$

valid for the case of a system with no permanent dipole moment, where $\mu(t)$ is a Heisenberg operator referred to states of the molecule, and the ground state expectation value is being taken. To suit our present purposes the derivation of this expression has to be modified; after which we can carry the modification through to the expression involving the g's. The change selected consists of the introduction of a step function: two Heaviside functions in place of the usual one. (Alternatively, one could use a factor representing the adiabatic turning on of the perturbation $e^{\eta(t-\bar{t})}$ where η is allowed to be appreciable – in which case component spectral lines would have Lorentzian shape.)

Thus we may start with

$$H_{\text{int}} = \mu(t)E(t)$$

$$E(t) = \theta(t)fe^{i\omega t}\theta(\bar{t}-t)$$

and an expectation value for the response at the particular time $\bar{t}$

$$\langle N\bar{t}|\mu(\bar{t})|N\bar{t}\rangle\,.$$

Correspondingly the function $\theta(\bar{t}-t)$ is zero when t exceeds $\bar{t}$, which means shutting off the light the instant after the response is taken – clearly a harmless thing to do. The other (the new) Heaviside function constitutes an idealization of a sudden onset of interaction at $t=0$. We call it the switching-on of the light. Depending on which value of $\bar{t}>0$ is picked for switching the light back off, one can select from the whole range of possible time intervals.

The linear response may be found from the first terms of the S-matrix expansion for $|N\bar{t}\rangle$ as developing out of $|N-\infty\rangle$, all this in the known way. The susceptibility then works out to be

$$\chi = i\theta(s)\theta(\bar{t}-s)\langle[\mu(s),\mu(0)]\rangle|_{\omega},$$

where

$$s=\bar{t}-t.$$

(When s is then set equal to t (a new t) there results an interchange in the Heaviside functions, so that for example $\theta(s)\to\theta(t)$ refers to the original $\theta(\bar{t}-t)$.)

The expression for χ_+ in terms of a basis is obtained the same way as before except that now both θ's have to be carried along, and make their appearance in the new g's. Thus

$$\chi_+(\bar{t}) = \sum_{rjks} c_r^* \mu_{rj} g_{jk}^+(\bar{t}) \mu_{ks} c_s,$$

where

$$g_{jk}^+(\bar{t}) = i\theta(t)\theta(\bar{t}-t)\langle jt|k0\rangle|_{\omega+\omega_N}.$$

As expected, the key relation for the g's as used in the previous section has to be modified. To obtain the new relation we differentiate a product of four functions and then integrate, $-\infty$ to $+\infty$:

$$\int_{-\infty}^{+\infty} \frac{\mathrm{d}}{\mathrm{d}t}[\theta(t)\theta(\bar{t}-t)\langle jt|k0\rangle e^{i\omega t}]\,\mathrm{d}t.$$

(Here we use ω in place of $\omega+\omega_N$ and omit the plus on the g.) Because of the θ's the bracketed expression is zero at the limits, but this is equal to

$$\begin{aligned}0 &= \delta(t)\theta(\bar{t}-t)\langle jt|k0\rangle|_{\omega} - \theta(t)\delta(\bar{t}-t)\langle jt|k0\rangle|_{\omega}\\ &\quad + \theta(t)\theta(\bar{t}-t)\frac{\mathrm{d}}{\mathrm{d}t}\langle jt|k0\rangle|_{\omega}\\ &\quad + i\omega\theta(t)\theta(\bar{t}-t)\langle jt|k0\rangle|_{\omega}\\ &= \theta(\bar{t})\langle j0|k0\rangle - \theta(\bar{t})\langle j\bar{t}|k0\rangle e^{i\omega\bar{t}}\\ &\quad + \theta(t)\theta(\bar{t}-t)(-i)\langle jt|H(0)|k0\rangle|_{\omega} + \omega g_{jk}(\bar{t}).\end{aligned}$$

The factor $\theta(\bar{t})$ may be disregarded. It simply means that unless one waits to measure the response until after the light is turned on there will be no response. Then

$$\begin{aligned}\omega g_{jk}(\bar{t}) &= -\langle j0|k0\rangle + i\theta(t)\theta(\bar{t}-t)\langle jt|H(0)|k0\rangle|_{\omega}\\ &\quad + \langle j\bar{t}|k0\rangle e^{i\omega\bar{t}}\end{aligned}$$

which is our key relation for the new g's. The first two terms on the R.H.S. are essentially the usual ones, and by themselves would allow us to construct a set of coupled equations for the $g(\bar{t})$'s in perfect analogy with the prior steady-state treatment. The third term, inhomogeneous like the first, must therefore bring in the transient behavior.

Before going on to our principal application, we consider the simplest excitation process. With two levels only and with $\omega_N = 0$ we have

$$H|10\rangle = \omega_0 |10\rangle$$

$$g^{+}_{11} = g_{11} = -\frac{1}{\omega - \omega_0} = -\frac{1}{x}$$

so that

$$\langle 1\bar{t}|10\rangle = -e^{-i\omega_0 \bar{t}}.$$

Then too

$$\chi_{+}(\bar{t}) = \mu_{01}^2 g_{11}(\bar{t}).$$

Now applying our new key relation for the $g(\bar{t})$'s

$$\omega g_{11}(\bar{t}) = -1 + \omega_0 g_{11}(\bar{t}) + e^{ix\bar{t}}$$

we obtain

$$g_{11} = \frac{-1 + e^{ix\bar{t}}}{x}.$$

Thus the shape of the absorption curve is the non-Lorentzian one

$$\mathrm{im}\, g_{11}(\bar{t}) = \frac{\sin x\bar{t}}{x}$$

as would be anticipated for a step function interaction. When $\bar{t} \to \infty$ the function goes over into $\pi\delta(x)$ (no final finite natural line width).

The Spectrum for Short Times

Now we use the key relation for the new g's to work out the absorption spectrum for the model with vibrations. As before

$$\chi_{+} = \mu_{NV}^2 g_{11}(\bar{t})$$

and then

$$\begin{aligned} \omega g_{11}(\bar{t}) = &-1 + i\theta(t)\theta(\bar{t} - t)\langle 1t|H(0)|10\rangle|_{\omega} \\ &+ \langle 1\bar{t}|10\rangle e^{i\omega\bar{t}}. \end{aligned}$$

Carrying out the operation with $H(0)$, and bringing in the result for $\langle 1t|10\rangle$ obtained above, we find

$$\begin{aligned} \omega g_{11}(\bar{t}) &= -1 + \omega_0 g_{11}(\bar{t}) + \gamma g_{12}(\bar{t}) \\ &\quad + e^{-i\omega_0\bar{t}} \cos\gamma\bar{t}\, e^{i\omega\bar{t}} \\ &= -1 + \omega_0 g_{11}(\bar{t}) + \gamma g_{12}(\bar{t}) \\ &\quad + \cos\gamma\bar{t}\, e^{ix\bar{t}}. \end{aligned}$$

Similarly

$$\omega g_{12}(\bar{t}) = \omega_0 g_{12}(\bar{t}) + \gamma g_{11}(\bar{t}) - i \sin\gamma\bar{t}\, e^{ix\bar{t}}.$$

The solution for $g_{11}(\bar{t})$ now with the transient phenomena included is

$$g_{11}(\bar{t}) = \frac{x(-1+\cos\gamma\bar{t}\, e^{ix\bar{t}}) - i\gamma\sin\gamma\bar{t}\, e^{ix\bar{t}}}{(x+\gamma)(x-\gamma)}$$

so that

$$\operatorname{im} g_{11}(\bar{t}) = \frac{x\cos\gamma\bar{t}\sin x\bar{t} - \gamma\sin\gamma\bar{t}\cos x\bar{t}}{(x+\gamma)(x-\gamma)}.$$

With a trigonometric identity this expression simplifies to

$$\operatorname{im} g_{11}(\bar{t}) = \frac{1}{2}\,\frac{\sin(x+\gamma)\bar{t}}{x+\gamma} + \frac{1}{2}\,\frac{\sin(x-\gamma)\bar{t}}{x-\gamma}$$

an expression reminiscent of the one for the old g_{11} as spectrally resolved, only now with components which have line shapes appropriate for a step-function interaction. This last way of expressing $\operatorname{im} g_{11}(\bar{t})$ lends itself nicely to the construction of a composite absorption curve. The components scale in a simple way: thus when $\bar{t}$ is doubled we have component curves which have half the width and twice the height, and so on.

As an aid in plotting our results we may put $\bar{t}=1$ at the start. Then an interesting case results when $\gamma=\pi/2$. In this case the components have their first nodes one at the pole position of the other (see (I) in Fig. 1). This case corresponds to $\bar{t}=(\pi/4)(2/\gamma)$; that is, $\bar{t}$ in the neighborhood of $2/\gamma$ but less than $2/\gamma$. The composite absorption (solid line) has a single peak at $x=0$ ($\omega=\omega_0$) as expected for short time intervals for the interaction.

The composite curve II in the figure was obtained by adjusting the components to correspond to $\bar{t}=2$, still, of course, with $\gamma=\pi/2$. It corresponds to $\bar{t}=(\pi/2)(2/\gamma)$; that is, $\bar{t}$ in the neighborhood of $2/\gamma$ but greater than $2/\gamma$. The curve already shows a separation into two bands, one at each pole; and as $\bar{t}$ is further increased the line structure quickly sharpens.

It should be appreciated that the component curves are not unique, only the composite ones. The frequency behavior of the absorptive part of the dipole response as given by the composite curve I in Fig. 1 ought to be taken at face value as a simple distribution, peaking at ω_0. (Though with a width which necessarily embraces the range $\pm\gamma$) so that the principal harmonic component in the function being analyzed is $\omega_0=\langle 1|H|1\rangle$. Also worth noting is the abruptness of the change-over from type I to type II, in view of which one would not be very much in error to take the point of balance as $\bar{t}=2/\gamma$.

For the many-level case one could think of blurring out the absorption spectrum either by using $t<4\Delta$, $t\sim 4/\Delta$, where Δ is a representative prominent vibrational spacing, or by using $t<\Gamma$, $t\sim\Gamma$, where Γ is an appropriate measure of the width of the entire electronic band. Experimentation with components shows that the latter alternative will give a smooth envelope with overall shape governed by the magnitudes of the various Franck-Condon integrals (vertical excitation); whereas the former gives a distorted band having an imperfectly disguised

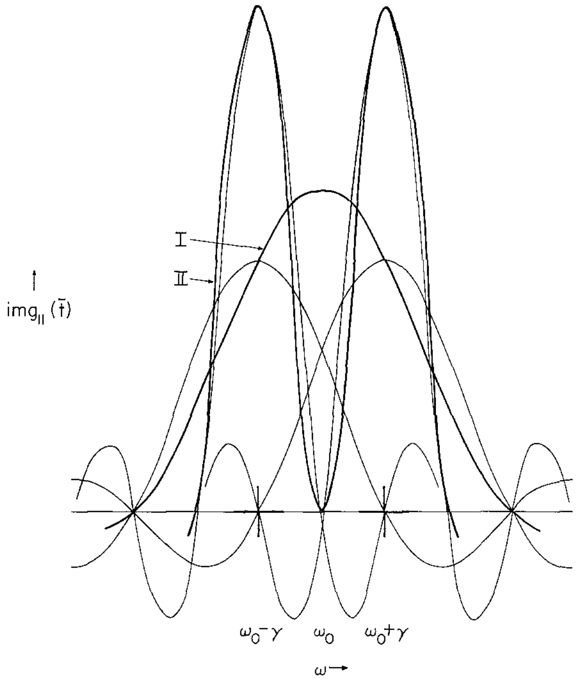

Fig. 1. Predicted absorptions for short times of interaction between light and molecule. Curve I shows spectrum for $\bar{t} < 2/\gamma (\bar{t} = (\pi/4)(2/\gamma))$ whereas curve II shows spectrum for $\bar{t} > 2/\gamma (\bar{t} = (\pi/2)(2/\gamma))$. Curves with light lines are pole components

vibrational structure. Thus γ in this note should be thought of as like Γ, in spite of the fact that literally for the two-level model it gives a vibrational interval $\Delta = 2\gamma$.

Generalization

If in the foregoing we had used as basis functions (see Fig. 2)

$$|a\rangle = \psi_N \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |b\rangle = \psi_V \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}, \quad |c\rangle = \psi_V \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix}$$

we should have found ($\gamma < 0$)

$$H = (\omega_0 + \gamma)\,|b\rangle\langle b| + (\omega_0 - \gamma)\,|c\rangle\langle c|$$

and

$$\mu_{\mathrm{op}} = (\mu_{NV}/\sqrt{2})\,(|a\rangle\langle b| + |b\rangle\langle a| + |a\rangle\langle c| + |c\rangle\langle a|)\,.$$

Then we would have had to use an expression for the susceptibility with two terms

$$\chi_+ = (\mu_{NV}/\sqrt{2})^2\,(g_{bb} + g_{cc})\,.$$

The component curves in Fig. 1 would have arisen not as the result of the application of a trigonometric identity to the original function obtained for $\mathrm{im}\,g_{11}$ but instead "naturally" as related to the description in terms of stationary states. The

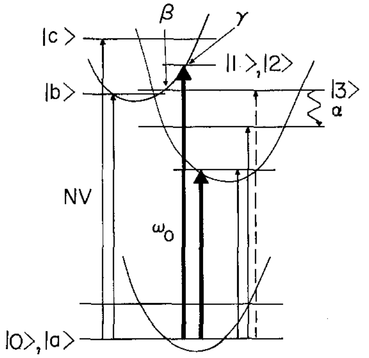

Fig. 2. Potential energy curves associated with NV and lower transition. Vertical excitation shown by heavy lines. Transition with no intensity shown by dashed line. Dissipative process (continuum of levels not depicted) by wavy line

composite curves would of course have been the same. With the basis functions $|0\rangle, |1\rangle, |2\rangle$ the characteristic constant γ, appears as an off-diagonal term in H. This corresponds manifestly to the idea of a γ process which converts $|1\rangle$ into $|2\rangle$ and which arises in an intuitively agreeable manner as we set up the equation for g_{11} namely

$$\omega g_{11} = -1 + \omega_0 g_{11} + \gamma g_{12}\,.$$

We have just seen that this process does not have to show up explicitly. Yet the correlation function will in any case turn out to be $e^{-i\omega_0 \bar{t}} \cos\gamma\bar{t}$, so that if $\gamma \ll \omega_0$ the frequency ω_0 will be the dominant one in the absorption spectrum for short times and we can say that the state $|1\rangle$ ($\langle 10|H|10\rangle = \omega_0$) occurs first; moreover these facts are independent of the basis.

Now we make the conjecture that in general if we can choose our basis set so that it contains the true ground state function, and so that χ_+ consists of one term only, call it $\mu_{01}^2 g_{11}$, then the relevant excited state basis function $|1\rangle$ will refer to the state which occurs first after the light is turned on. We have to include the proviso that the diagonal matrix element $\langle 10|H|10\rangle$, like ω_0 above, is considerably greater than the off-diagonal ones $\langle j0|H|10\rangle, j \neq 1$, like γ above.

The reasoning back of this conjecture is that when we set up the expression for g_{11} (no need to consider $g_{11}(\bar{t})$), we have to compute the Hamiltonian part

$$i\theta\langle 1|H|10\rangle|_\omega = g_{11}\langle 10|H|10\rangle + \sum_{j\neq 1} g_{j1}\langle j0|H|10\rangle$$

and, roughly speaking, for short times we may ignore the terms $j \neq 1$: which would give

$$\omega g_{11} = -1 + \omega_0 g_{11}$$

$$g_{11} = 1/\omega - \omega_0$$

and

$$\langle 1|10\rangle = e^{-i\omega_0 t}\,.$$

The Hamiltonian part of the expression for g_{11} arose because of the need to obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle 1| = -i\langle 1|H$$

under the Fourier transform. The boundary conditions are such that if we write

$$\langle 1| = c_1(t)\langle 10| + c_2(t)\langle 20| + \cdots$$

then $c_1(1) = 1$, $c_2(0) = 0, \ldots$. Now taking

$$\begin{aligned} H = {} & \langle 10|H|10\rangle|10\rangle\langle 10| + \langle 20|H|10\rangle|20\rangle\langle 10| \\ & + \langle 10|H|20\rangle|10\rangle\langle 20| + \cdots \end{aligned}$$

we find, as $t \to 0$,

$$\langle 1|H = \langle 10|H|10\rangle\langle 10| + \langle 10|H|20\rangle\langle 20| + \cdots$$

and writing the differential equation as a difference equation ($t = \bar{t} \to 0$)

$$\begin{aligned} \langle 1\bar{t}| - \langle 10| &= -i[\langle 10|H|10\rangle\langle 10| + \langle 10|H|20\rangle\langle 20| + \cdots]\bar{t} \\ \langle 1\bar{t}| &= [1 - i(10|H|10)\bar{t}]\langle 10| + \mathrm{const}\langle 20|\bar{t} + \cdots \end{aligned}$$

so that the correlation function

$$\langle 1\bar{t}|10\rangle = 1 - i\langle 10|H|10\rangle\bar{t}\,.$$

That is, for short times, it indeed starts out the same way as $e^{-i\langle 10|H|10\rangle\bar{t}}$.

What governs the time evolution of the state reached first after the light is turned on remains to be considered. Going to a more abstract statement of the problem let us start with a set of energy eigenfunctions representing a system with no permanent dipole moment, and let us treat just one vector component. Then we should have a certain electric moment matrix, call it $\bar{\mu}$, with zeroes on the diagonal. We should like to transform a finite part of this matrix so that it has a different form, with only one non-vanishing element in the the first row (and column)

$$\mu = \begin{bmatrix} 0 & \mu_{01} & 0 & 0 & 0 & \\ \mu_{10} & 0 & \mu_{12} & \mu_{13} & \mu_{14} & \\ 0 & \mu_{21} & 0 & \mu_{23} & \mu_{24} & \cdots \end{bmatrix}.$$

We call the new part μ. The basis function for μ_{00} is to remain the same as for $\bar{\mu}_{00}$ (ground state). With the transformed matrix we should have, in the frequency range of interest

$$\chi_+ = \sum_{jk} \mu_{0j} g_{jk} \mu_{k0} = \mu_{01}^2 g_{11}$$

thus to satisfy our requirement that χ_+ consist of one term only. We now ask whether the transformation is possible.

Let us assume that the region of interest is spanned by the stationary states 1 to 3. Then the top row of $\bar{\mu}$ may be taken as

$$0 \quad \bar{\mu}_{01} \quad \bar{\mu}_{02} \quad \bar{\mu}_{03}\,.$$

Now combine the first (not the zeroth) and second energy eigenfunctions so as to give two new orthonormal functions and in such a way that the first row of a new matrix based on the combined functions has a zero in the place labelled with 2

$$0 \quad \bar{\bar{\mu}}_{01} \quad 0 \quad \bar{\mu}_{03}\,.$$

Now repeat with the new first function and the third. The result will be denoted

$$0 \quad \mu_{01} \quad 0 \quad 0\,.$$

The transformation is possible, and proceeding inductively one sees that as far as the introduction of zeroes is concerned there is no limit to the number of states which can be included.

Although it is believed that the function $|10\rangle$ is thus uniquely determined, the transformation is by no means unique, because if for $i, j > 1$

$$\langle 0|\mu_{\mathrm{op}}|i\rangle = \mu_{0i} = 0, \qquad \mu_{0j} = 0$$

then also

$$\langle 0|\mu_{\mathrm{op}}|[c_i|i\rangle + c_j|j\rangle] = 0\,.$$

The first state reached after the light is turned on would be the state $|1\rangle$ with $\mu_{01} \neq 0$. Putting aside complications from having to consider statistical weights one could say that the next state reached would be that linear combination $|k\rangle$ of the new basis functions $|2\rangle, |3\rangle, \ldots$ such that the relative degeneracy

$$|\langle 10|H|k0\rangle|^2/\langle 10|H|10\rangle - \langle k0|H|k0\rangle$$

is a maximum (like γ above which, for simplicity, was taken as connecting two perfectly degenerate states).

The relative degeneracy parameter would have to correspond to an interaction constant which is less than the main frequency, $\langle 10|H|k0\rangle \ll \langle 10|H|10\rangle$, like $\gamma \ll \omega_0$, but one readily sees that this condition is automatically achieved in practical cases. Thus for an isolated electronic transition described according to the Born-Oppenheimer approximation, the basis functions would be the set generated by multiplying the excited electronic function by ground state vibrational functions. The off-diagonal terms in the Hamiltonian needed to reconstruct the stationary state functions would be no bigger than the overall width Γ, and in most, though not all cases, this would be less than the vertical excitation frequency. Indeed if Γ were comparable with the main electronic excitation frequency one would not except the Born-Oppenheimer approximation to be valid.

Postscript on Internal Conversion

For the calculation of transition probabilities the traditional procedure is to connect eigenstates of an unperturbed Hamiltonian by means of the perturbing term. Sometimes it is not so obvious how to divide the full Hamiltonian into perturbed and unperturbed parts – that is, how to describe the states: initial and final, and correspondingly, how to see what causes the transition. A case in point is the radiationless transition from the ground vibrational level of, say, the second excited singlet to an accidentally degenerate vibronic state belonging to the first excited singlet (see Fig. 2). It is perhaps natural to have misgivings about this or that explanation of such processes along the following lines: if the pertinent states in the region of the degeneracy are eigenstates of the full molecular Hamiltonian, stationary states, then there should be no mixing, and no opportunity to describe radiationless transitions.

The foregoing treatment of vertical excitation gives us a clue as to how to proceed, because there we started with what can be regarded as a full Hamiltonian without the conventional division into unperturbed and perturbed parts, and yet we found a time dependent process, the nuclear reorganization, with characteristic constant $\sim\gamma$. What made this possible was that the prepared state, the one formed first after the light was turned on, was not a stationary state. To understand internal conversion we may in effect follow the evolution of such a prepared state yet a step further [6]. Typically (for simple molecules) we encounter a new state, call it $|3\rangle$, which is accidentally degenerate with and interacts with one of the vibronic states say the one $(1/\sqrt{2})\,[|1\rangle+|2\rangle]$ or $|b\rangle$, with energy $\omega_0+\gamma$. Then we should have as the Hamiltonian

$$\begin{aligned}H=&\,\omega_0[|1\rangle\langle 1|+|2\rangle\langle 2|]+(\omega_0+\gamma)\,|3\rangle\langle 3|\\&+\gamma[|1\rangle\langle 2|+|2\rangle\langle 1|]\\&+\beta\{(1/\sqrt{2})\,[|1\rangle+|2\rangle]\,\langle 3|+|3\rangle\,(1/\sqrt{2})\,[\langle 1|+\langle 2|]\}\,.\end{aligned}$$

Whereas the reorganization constant $\gamma\sim10^{14}$, β, the constant for internal conversion is usually estimated to be somewhere in the neighborhood of 10^9. The two processes are well separated. It is not unrealistic here to take the electric moment operator still as

$$\mu_{\text{op}}=\mu_{NV}[|0\rangle\langle 1|+|1\rangle\langle 0|]$$

neither with terms involving $|2\rangle$ nor with terms involving $|3\rangle$, the new level. This corresponds to the situation which we describe intuitively as no overlap of intensity between the two electronic absorption bands, and would allow us to go ahead using just g_{11}, as before, for the susceptibility function. The state reached first is therefore $|1\rangle$. The unfolding of this state goes initially according to the γ process, because (referring to the previous section) $|2\rangle$ is the only state degenerate with $|1\rangle$. The further unfolding can be followed. If we are interested in the frequency region around $\omega_+=\omega_0+\gamma$ (and considering that $\gamma\gg\beta$) we may proceed more directly by introducing a change in notation. We take $(|10\rangle\leftrightarrow|a0\rangle)$

$$\mu_{\text{op}}=(\mu_{NV}/\sqrt{2})\,(|a\rangle\ \langle b|+|b\rangle\langle a|)$$

that is, without any contribution from $|3\rangle$ just as the original μ_{op} had no contribution from $|2\rangle$, and

$$\begin{aligned}H=&\,(\omega_0+\gamma)\,(|b\rangle\langle b|+|3\rangle\langle 3|)\\&+\beta(|b\rangle\langle 3|+|3\rangle\langle b|)\,.\end{aligned}$$

The "first" state reached is $|b\rangle$ and the develpment of $|b\rangle$ is governed by β. That $|3\rangle$ can be identified with a vibronic level belonging to a distinct potential energy surface is perhaps not always the case. If it should prove to be the case then we see that β is a matrix element over the terms needed to round out the Hamiltonian of the Born-Oppenheimer approximation.

The susceptibility this time is $\chi_+ = (\mu_{NV}^2/2)g_{bb}$. The Green's function, as spectrally resolved, is

$$g_{bb} = -\frac{1}{2}\frac{1}{\omega-(\omega_+ + \beta)} - \frac{1}{2}\frac{1}{\omega-(\omega_+ - \beta)}$$

so that the absorption spectrum in the region of ω_+, in perfect analogy with the work on vertical excitation, is governed by the Fourier transform of the correlation function, namely

$$e^{-i\omega_+\bar{t}}\cos\beta\bar{t}\,.$$

When $t<2/\beta$ (but $\bar{t}\gg 2/\gamma$) we have simply a broad absorption at ω_+. When $\bar{t}>2/\beta$ the splitting materializes. The first zero of the correlation function as modulated by $\cos\beta\bar{t}$ corresponds to the first passage of the excitation over into $|3\rangle$. Thus we can use β as a characteristic constant. What is more, if for some reason when the excitation passes over to $|3\rangle$ it cannot get back (the α process in Fig. 2) then $1/\beta$ will serve to determine the lifetime of the state at ω_+ [7]; also the width, which would encompass the region $\omega_+ \pm \beta$ much in the same way that curve I in Fig. 1 covers the region $\omega_0 \pm \gamma$.

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