Time Resolved Absorption Spectra

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A theory for the time resolved electronic absorption spectrum of a molecule undergoing collisional vibrational relaxation is proposed. Symmetry forbidden and symmetry allowed transitions are considered. Changes in absorption spectra with time for some model cases are presented. Experimental data on the triplet-triplet absorption spectrum of anthracene are interpreted in the light of the theory. A brief discussion of time resolved emission spectra, and of fluorescence from high vibrational levels is also given.

1. INTRODUCTION

Changes in the shape of the electronic spectra of aromatic molecules in the vapour phase as a function of time after excitation have recently been observed.1-3 Time resolved absorption spectra of triplet states in the vapour phase were first observed by Formosinho, Porter and West 1, 2 using nanosecond laser flash photolysis. The spectral changes observed were interpreted as being due to collisional vibrational relaxation. Recently, in the same laboratory, time resolved fluorescence spectra of vapour phase aromatic molecules have been obtained 3 by the single photon counting technique.

The observed absorbance per unit length, \( D_{ab}(\omega, t) \), as a function of light frequency \( \omega \) and time \( t \) can be written

\[
D_{ab}(\omega, t) = \sum \nu' k_{a\nu'}(\omega)X_{\nu'}(t)
\]  

(1.1)

where \( k_{a\nu'}(\omega) \) is the absorption coefficient from the single vibronic level, \( \nu' \), in the electronic state, \( a \), and \( X_{\nu'}(t) \) is the number of molecules per unit volume in the vibrational level \( \nu' \) at time \( t \). Similarly the observed emission intensity per unit volume is given by

\[
I_{ba}(\omega, t) = \sum \nu'' I_{b\nu''}(\omega)X_{b\nu''}(t).
\]  

(1.2)

Here, \( I_{b\nu''}(\omega) \) is the emission intensity distribution function for the single vibronic state \( b\nu'' \) and \( X_{b\nu''}(t) \) is defined as above. The calculation of \( D_{ab}(\omega, t) \) and \( I_{ba}(\omega, t) \) are closely related and consequently we will be mainly concerned with time resolved absorption spectra, where the total concentration \( (\Sigma_{\nu} X_{\nu}) \) remains constant in the time scale under consideration, as in the experiments of Formosinho et al.1, 2 For time resolved fluorescence spectra, or, for example, singlet–singlet absorption spectra measured on a nanosecond time scale, electronic relaxation cannot be ignored. In these cases the calculation of the \( X_{\nu}(t) \) will be considerably more complex.

It is seen from eqn (1.1) and (1.2) that the problem of describing time resolved...
spectra falls into two distinct parts: (1) that of calculating the absorption (or emission) coefficients for the individual vibronic levels involved and (2) that of calculating the time dependent populations of the individual vibronic levels.

Osherov and Medvedev have developed a semi-classical model for calculating the absorption band shape function of identical oscillators during vibrational relaxation. Nitzan and Jortner have also attempted to derive expressions for the time-dependent optical line shape of a molecule undergoing vibrational relaxation, but in their calculations only the condensed phase is considered.

We will generalise the model advocated by Osherov and Medvedev and apply it to both absorption and emission spectra.

2. THE ABSORPTION COEFFICIENT FOR SINGLE VIBRONIC STATES

The absorption coefficient of a single vibronic state \( k_{av} \) can be expressed, by a straightforward generalisation of the Einstein B-coefficient as:

\[
k_{av}(\omega) = \frac{4\pi^2 \omega}{3\hbar} \sum_{v} |R_{bv',av}^v|^2 \delta(\omega_{bv',av} - \omega).
\]  

(2.1)

In this expression the medium effect (refractive index correction) has been ignored for simplicity. \( R_{bv',av}^v \) is the transition moment between the initial state \( |av'\rangle \), (a labels the electronic state and \( v' \) its associated vibrational quantum number) and \( |bv\rangle \), where \( b \) is the final electronic state with vibrational quantum number \( v' \); \( \omega \) is the frequency of the incident light and \( \omega_{bv',av} \) the frequency of the transition \( |av'\rangle \rightarrow |bv\rangle \). Within the Born–Oppenheimer approximation \( R_{bv',av}^v \) is given by:

\[
R_{bv',av}^v = \langle \theta_{bv'} \phi_b P \phi_a \theta_{av} \rangle = \langle \theta_{bv'} | R_{ba} | \theta_{av} \rangle
\]  

(2.2)

where the \( \phi \) are electronic wave functions and \( \theta \) the products of single mode vibrational wave functions; \( P \) represents the dipole moment operator. For symmetry-allowed transitions (i.e. \( R_{ba} \) independent of the normal coordinates, \( Q \)), if there is only one vibrational mode in the molecule, we can write \( k_{av} \) as:

\[
k_{av}(\omega) = \frac{4\pi^2 \omega}{3\hbar} |R_{bav}|^2 \sum_{\nu} |\chi_{av}\chi_{bv'}\rangle)^2 \delta(\omega_{bv',av} - \omega)
\]  

(2.3)

where the \( \chi \) represent the one-mode vibrational wavefunctions. General expressions for the Franck–Condon factor appearing in eqn (2.3) have been derived for displaced and/or distorted harmonic oscillators. Since spectral characteristics are mainly determined by the displacement of the modes, we will neglect frequency changes in the remainder of our calculations. If we are only interested in the overall band shape of the absorption profile, we can replace the delta function in (2.3) by \( 1/\bar{\omega} \), where \( \bar{\omega} \) is the vibration frequency. After some algebra we then obtain:

\[
k_{av}(\omega) = \frac{4\pi^2 \omega}{3\hbar \bar{\omega}} |R_{ba}|^2 \exp(-S) \sum_{p,q} \frac{(-1)^p q \Gamma_{p'}(\nu' + v' - p - q)}{p!q!(\nu' - p)!(\nu' - q)!(\nu' - p)!(\nu' - q)\!}
\]  

(2.4)

Here \( S \) is related to the displacement of the normal coordinate \( Q \), i.e. the difference in equilibrium position in the final and initial electronic state:

\[
S = \frac{1}{2} \Delta^2 = \frac{1}{2} \frac{M \omega^2}{\hbar} (Q_0 - Q_0)^2.
\]  

(2.5)

Although the above treatment has the advantage of simplicity, it is difficult to apply to cases where there is more than one mode in the molecule.

We will now proceed to derive alternative expressions for these cases, and include
symmetry-forbidden transitions as well. The final results appear in eqn (2.13), (2.14) and (2.18). The reader, not interested in mathematical details may skip the remainder of this section and go on to section 3.

It has been shown generally, that the absorption coefficient of a single vibronic state can be obtained from the thermally averaged rate constant $k_{ab} (\beta, \omega)$ using the relation:

$$
k_{av'} (\omega) = \frac{1}{\delta (E - E_{av'})} \lim_{\nu \to \infty} \frac{1}{2 \pi i} \int_{-\nu}^{+\nu} \frac{d\beta}{\nu} \, e^{\beta \nu} Q_a (\beta) k_{ab} (\beta, \omega)
$$

(2.6)

where $\beta = 1/kT$ and $Q_a (\nu)$ is the partition function of the system in the electronic state $a$. For symmetry-allowed transitions $k_{ab} (\beta, \omega)$ can be expressed as:

$$
k_{ab} (\beta, \omega) = \frac{2 \pi \omega}{3 \hbar} |R_{ba}|^2 \int_{-\infty}^{+\infty} dt \exp \left[ i(t \omega_{ba} - \omega) - \sum_j \frac{1}{2} \Delta_j^2 \right] \times \right.

$$

(2.7)

Here, $\omega_{ba}$ is the electronic energy gap and $\omega_j$ the frequency of mode $j$ with displacement $\Delta_j$. The summation over $j$ covers all $N$ normal modes in the molecule. Before substituting eqn (2.7) into (2.6) we note that:

$$
\exp \left[ -\frac{1}{2} \Delta_j^2 \left( \coth \left( \frac{\beta \hbar \omega_j}{2} \right) - \operatorname{csch} \left( \frac{\beta \hbar \omega_j}{2} \right) \cos \left( \omega_j t - \frac{1}{2} \beta \hbar \omega_j \right) \right) \right] =
$$

$$
\left[ 1 - \exp \left( -\beta \hbar \omega_j \right) \right] \exp \left[ -\frac{1}{2} \Delta_j^2 \left( (1 - \exp \left( i \omega_j \right)) \right) \sum_{n_j = 0}^{v_j} \left( v_j \Delta_j^{2n_j} \right) \cos \left( \omega_j t - 1 \right)^{n_j} \exp \left( -v_j \beta \hbar \omega_j \right) \right].
$$

(2.8)

Combining eqn (2.8) with (2.7) we obtain:

$$
Q_a (\beta) k_{ab} (\beta, \omega) = \frac{2 \pi \omega}{3 \hbar} |R_{ba}|^2 \exp \left( -S \right) \int_{-\infty}^{+\infty} dt \exp \left[ i(t \omega_{ba} - \omega) + \sum_j \frac{1}{2} \Delta_j^2 \exp \left( i \omega_j \right) \right] \times
$$

$$
\sum_{n_j = 0}^{v_j} \sum_{n_j = 0}^{v_j} \left( v_j \Delta_j^{2n_j} \right) \cos \left( \omega_j t - 1 \right)^{n_j} \exp \left( -v_j \beta \hbar \omega_j \right)
$$

(2.9)

where $S = \sum_j \Delta_j^2$. Substituting eqn (2.9) into (2.6) we obtain the exact expression for $k_{av'} (\omega)$ as:

$$
k_{av'} (\omega) = \frac{2 \pi \omega}{3 \hbar} |R_{ba}|^2 \exp \left( -S \right) \int_{-\infty}^{+\infty} dt \exp \left[ i(t \omega_{ba} - \omega) + \sum_j \frac{1}{2} \Delta_j^2 \exp \left( i \omega_j \right) \right] \times
$$

$$
\sum_{n_j = 0}^{v_j} \sum_{n_j = 0}^{v_j} \left( v_j \Delta_j^{2n_j} \right) \cos \left( \omega_j t - 1 \right)^{n_j} \exp \left( -v_j \beta \hbar \omega_j \right)
$$

(2.10)

where the set $v_j$ (the upper limits of the summation) specifies the number of quanta in each mode $j$. The integral in eqn (2.10) can be evaluated exactly, but the result is very complicated and will not be given here. If we assume that all modes have the same average frequency, $\bar{\omega}$, eqn (2.10) reduces to:

$$
k_{av'} (\omega) = \frac{2 \pi \omega}{3 \hbar} |R_{ba}|^2 \exp \left( -S \right) \int_{-\infty}^{+\infty} dt \exp \left[ i(t \omega_{ba} - \omega) + S \exp \left( i \bar{\omega} \right) \right] \times
$$

$$
\sum_{n_j = 0}^{v_j} \sum_{n_j = 0}^{v_j} \left( \cos \bar{\omega} t - 1 \right)^{n_j} \prod_{j} \frac{v_j \Delta_j^{2n_j}}{(v_j - n_j)!(n_j !)^2}
$$

(2.11)
where \( S = (N/2)\lambda^2 \) and \( n = \Sigma n_j \). Evaluating the integral exactly we obtain the absorption spectrum as a series of \( \delta \) functions:

\[
k_{av}(\omega) = \frac{4\pi^2\omega}{3c}\left| R_{ba} \right|^2 \exp (-S) \sum_{n_l=0}^{v'} \sum_{m_l=0}^{v_i} \frac{2n}{k!} \frac{(2n)!}{(2n-k)!} \times \prod_j v_j! \frac{(S/N)^{n_j}}{(v_j-n_j)(n_j)!^2} \delta \left[ \omega - \omega_{ba} - (m+n-k)\omega \right].
\]

Using the same arguments as those leading to eqn (2.4) we finally replace the \( \delta \) function by \( 1/\omega \) to obtain:

\[
k_{av}(\omega) = \frac{4\pi^2\omega}{3c\omega} \left| R_{ba} \right|^2 \exp (-S) \sum_{n_l=0}^{v'} \sum_{m_l=0}^{v_i} \frac{2n}{k!} \frac{(2n)!}{(2n-k)!} \times \frac{(2n)!}{k!(2n-k)!m!} \prod_j v_j! \frac{(S/N)^{n_j}}{(v_j-n_j)(n_j)!^2}
\]

where \( m \) is given by

\[
\frac{\omega - \omega_{ba}}{\omega} = \frac{\Delta \omega}{\omega} = m + n - k.
\]

In particular, when \( N = 1 \), eqn (2.13) reduces to

\[
k_{av}(\omega) = \frac{4\pi^2\omega}{3c\omega} \left| R_{ba} \right|^2 \exp (-S) \sum_{n_l=0}^{v'} \sum_{m_l=0}^{v_i} \frac{(2n)!}{(v-n)(v-n)!^2} \frac{(2n)!}{k!(2n-k)!m!} \prod_j v_j! \frac{(S/N)^{n_j}}{(v_j-n_j)(n_j)!^2}
\]

Next we will consider symmetry-forbidden transitions. In this case the electronic transition moment depends on the normal coordinates \( Q_i \) of one (or more) inducing modes. In general the transition moment can be written as:

\[
\mathbf{R}_{ba} = \mathbf{R}_{ba}(0) + \sum_i \left( \frac{\partial \mathbf{R}_{ba}}{\partial Q_i} \right)_0 Q_i + \ldots = \mathbf{R}_{ba}(0) + \sum_i \alpha_i Q_i
\]

where we have assumed that the inducing modes have no displacements, which will be true if these modes are non-totally symmetric. Neglecting also this frequency change between the two electronic states (or assuming this to be small) \( k_{ab}(\beta, \omega) \), the thermal average absorption coefficient can be written as:

\[
k_{av}(\beta, \omega) = \frac{2\pi \omega}{3c} \sum_j \int_{-\infty}^{+\infty} dt \left\{ n_i \exp (-it\omega_i) + (n_i + 1) \exp (it\omega_i) \right\} \times \exp \left[ it(\omega_{ba} - \omega) - \sum_j \frac{1}{2} \Delta_j^2 \left( \coth \left( \frac{1}{2} \beta \hbar \omega_j \right) - \frac{1}{2} \beta \hbar \omega_j \right) \cos \left( \frac{1}{2} \beta \hbar \omega_j \pi \right) \right]
\]

where \( \beta^2_i = \omega_i / \hbar \) and \( n_i = \left\{ \exp(\beta \hbar \omega_i) - 1 \right\}^{-1} \). If more than one inducing mode is present, a summation over \( i \) should be included in this expression. Repeating the procedure outlined in connection with eqn (2.6) to (2.10) we obtain for \( k_{av} \):

\[
k_{av}(\omega) = \frac{2\pi \omega}{3c} \sum_j \int_{-\infty}^{+\infty} dt \left\{ \sum_j \frac{1}{2} \Delta_j^2 \exp \left( it(\omega_{ba} - \omega) + \frac{1}{2} \Delta_j^2 \exp (it\omega_j) \right) \right\} \times \left\{ v_i \exp (-it\omega_i) + (v_i + 1) \exp (it\omega_i) \right\} \times \prod_j v_j! \Delta_j^{2n_i} \left( \cos \omega_j t - 1 \right)^{n_j}
\]

\[
\sum_{n_l=0}^{v'} \sum_{m_l=0}^{v_i} \prod_j v_j! \frac{(S/N)^{n_j}}{(v_j-n_j)(n_j)!^2}
\]

\[
\sum_{n_l=0}^{v'} \sum_{m_l=0}^{v_i} \prod_j v_j! \frac{(S/N)^{n_j}}{(v_j-n_j)(n_j)!^2}
\]
Introducing an average frequency $\bar{\omega}$ for all but the inducing modes, we finally obtain

$$
k_{av}(\omega) = \frac{4\pi^2 \omega^2 \bar{\omega}^2}{3c\hbar} \exp(-S) \left[ \sum_{n_1=0}^{v_i} \sum_{n_2=0}^{v_{i+1}} \cdots \sum_{n_N=0}^{v_N} \frac{(2n)!(1)^kS^m}{k!(2n-k)!m!} \times \prod_j \frac{\eta^j_j[(S/N)\eta^j_j]}{(v_j-n_j)![(n_j)!]^2} + \prod_j \frac{\eta^j_j[(S/N)\eta^j_j]}{(v_j-n_j)![(n_j)!]^2} \right].$$

(2.18)

Here $m'$ and $m$ have to be determined from the equations:

$$\omega - \omega_{ba} + \omega_i = (m + n - k)$$

$$\omega - \omega_{ba} - \omega_i = (m' + n - k).$$

(2.19)

### 3. THE TIME DEPENDENCE OF THE POPULATION OF SINGLE VIBRONIC LEVELS

In this section we discuss the calculation of the term $X_{v'}(t)$, the number of molecules per unit volume, in eqn (1.1). If collisional vibrational relaxation is the only process depleting the various levels $v'$, then the master equation for a harmonic oscillator for this process is given by$^{10a}$:

$$\frac{dX_{v'}}{dt} = k_c \left[ \left( v' e^{-\theta} X_{v'-1} - \{ v' + (v' + 1) e^{-\theta} \} X_{v'} + (v' + 1) X_{v'+1} \right) \right]$$

(3.1)

where $k_c$ represents the vibrational relaxation rate constant between $v' = 1$ and $v' = 0$, $\theta = \hbar \omega' / kT$ and $\omega'$ is the frequency of the mode concerned. The solution of eqn (3.1) has been given for various initial distributions by Montroll and Shuler.$^{10a}$ The solution, relevant to the present problem of time resolved absorption spectroscopy, corresponds to an initial distribution where, at $t = 0$, all molecules are in the quantum state $v'_0$. We then obtain:

$$X_{v'}(t) = X_{v'_0} \frac{(1 - e^{-\theta}) e^{-\theta \tau}}{(e^{-\theta} - e^{-\theta})} \frac{\left( e^{-\frac{\tau}{2}} - 1 \right)}{\left( e^{-\frac{\tau}{2}} - e^{-\frac{\tau}{2}} \right)} F(-v', -v'_0, 1; u^2)$$

(3.2)

where $X_{v'_0}$ represents the initial concentration of molecules in the state $v'_0$, $\tau = k_c t (1 - e^{-\theta})$, $u = \sinh (\theta/2)/\sinh (\tau/2)$ and $F(-v', -v'_0, 1; u^2)$ is the hypergeometric function. At low temperatures ($\theta = \hbar \omega / kT \gg 1$) eqn (3.2) reduces to:

$$X_{v'}(t) = X_{v'_0}(v'_0-v')!v'! (1-e^{-\tau}) v'_0-v' e^{-\tau}.$$

(3.3)

It should be noted that the foregoing analysis applies strictly to cases where only one mode is initially excited. If more vibrations are present in the molecule the situation is more complicated. In this investigation we will assume that each mode relaxes independently. It follows that:

$$X_{v'}(t) = \prod_j X_{v'_j}(t)$$

(3.4)

where $j$ labels the different modes. The case where vibrational energy is not only lost to the heat bath, but also transferred between the excited molecules has been considered by Davis and Wilson.$^{10b}$
If collisional vibrational relaxation is not the only process depleting the various states \(v'\), the master equation (3.1) becomes more complicated. Cases where radiative and non-radiative decay of the \(v'\) levels also occurs have recently been treated by Freed and Heller. The general form of their solutions for \(X_{v'}(t)\), however, is similar to the results obtained from eqn (3.2). Thus, although strictly speaking the use of eqn (3.2) is restricted to cases where only collisional vibrational relaxation occurs, it is expected that the results will be approximately correct for the more complicated cases, where radiative and radiationless processes take place as well.

Finally, we remark that even for intramolecular vibrational relaxation in large systems, eqn (3.1) seems to give a reasonable description of the relaxation process. It is thus expected that our results will equally well apply to time resolved spectra of condensed systems and may have a fairly wide applicability.

4. MODEL CALCULATIONS

In this section we will present some numerical applications of the formulae derived previously. In order to avoid the use of irrelevant constants we will first derive the following useful relations. From eqn (2.1) we obtain:

\[
\int k_{vv'}(\omega) \frac{d\omega}{\omega} = \frac{4\pi^2}{3ch} |R_{\text{bar}}|^2
\]

(4.1)

for symmetry-allowed transition and

\[
\int k_{vv'}(\omega) \frac{d\omega}{\omega} = \frac{4\pi^2}{3ch} \omega_{v'}^2 \frac{h}{\omega_{v'_l}^2} (v'_l + \frac{1}{2})
\]

(4.2)

for symmetry-forbidden transitions. Next we define

\[
\omega^* = \omega/\bar{\omega}
\]

\[
\Delta\omega^* = (\omega - \omega_{\text{bar}})/\bar{\omega} = m + n - k.
\]

(4.3)

Thus \(\omega^*\) measures the frequency in units of the average vibration frequency, and \(\Delta\omega^*\)

![Diagram](image-url)
FIG. 2.—Effect of an increase in the number of modes on the spectrum of oscillators with one mode excited by one quantum, all other modes with zero quanta. ..., \( S = 0.5, v_1 = 1; \ldots, S = 1.0, v_1 = 1, v'_1 = 0; \ldots, S = 1.5, v_1 = 1, v_2 = v_3 = 0; \ldots, S = 2.0, v_1 = 1, v_2 = v_3 = v'_4 = 0.\)

FIG. 3.—Effect of the number of initially excited modes on the spectrum of 4 modes with \( S = 5.0.\) ...

FIG. 4.—Time resolved spectrum for 1 mode excited initially with one quantum, \( S = 1.5, \) as a function of reduced time, \( \tau = k_d t. \ldots, \tau = 20.0; \ldots, \tau = 0.5; \ldots, \tau = 0.\)
is the energy above zero-point in terms of the number of quanta excited. For symmetry-allowed transitions we then have:

\[
\frac{k^*(\omega^*)}{\omega^*} = \frac{k_{av}(\omega)\overline{\omega}(\omega)}{\int[k_{av}(\omega)\overline{\omega}] \, d\omega} = \exp \left( -S \right) \sum_{n_1=0}^{v_1'} \ldots \sum_{n_N=0}^{v_N'} \sum_{k=0}^{2n} \frac{(-1)^k(2n)!S^m_j}{k!(2n-k)!m!} \prod_j \frac{v_j!}{(v_j'-n_j)(n_j)!^2}
\]  

(4.4)

which represents the absorption coefficient divided by the frequency as a function of the excess energy, all expressed as reduced quantities. A plot of eqn (4.4) is given in fig. 1 for one mode in different initial levels \( v' \). The case \( v'_1 = 0 \) corresponds to the "normal Franck-Condon pattern", usually observed for molecules in solution at low temperatures \( T < \hbar \omega/k \). For higher levels the spectrum is seen to be drastically changed. The occurrence of minima is due to the fact that all vibrational wavefunctions (except with \( v'_1 = 0 \)) have at least one node, so that vertical (Franck-Condon) transitions will not occur from at least this one point.

Fig. 2 illustrates the effect of increasing the number of modes \( N \) on the spectrum. Only one of the modes is excited with one quantum. The presence of unexcited modes is seen to reduce the size of the "dip" in the spectrum and also to shift the maximum to higher energy since \( S = (N/2)\Delta^2 \) is increased. Fig. 3 shows the effect of the number of initially excited modes in the spectrum. The presence of unexcited modes is seen to increase the height of the spectrum, leaving the position of the maximum unchanged. Some unexpected features are present when all four modes are excited by one quantum. We will return to this point later.

In order to compare time resolved absorption spectra we define:

\[
X^*_v(t) = \frac{X_v(t)}{X_v(0)}
\]  

(4.5)

which represents the normalised population in level \( v' \) and

\[
D(\omega^*, \tau) = \frac{D(\omega^*, \tau)}{\int[D(\omega^*, \tau)\omega^*] \, d\omega^*} = \sum_{v'} k_{av}(\omega^*)X^*_v(\tau).
\]  

(4.6)

Since for symmetry-allowed transitions \( \int k^*(\omega^*)/\omega^* \, d\omega^* \) does not depend on \( v' \) (see eqn (4.1)), \( \int[D(\omega^*, \tau)/\omega^*] \, d\omega^* \) is seen to be equal to \( \Sigma_v X^*_v(\tau) = 1 \). Thus the corresponding quantity for symmetry-forbidden transitions will be time independent only if \( X^*_v(\tau) \) does not involve the inducing mode(s); in other words, the relaxation of all other modes must be faster than that of the inducing mode(s), or the inducing mode must not be excited. Fig. 4 and 5 show the time resolved absorption spectra calculated from eqn (4.6). For simplicity we have taken the zero temperature limit of \( X^*_v(\tau) \) [eqn (3.3)] and assumed that the transition is symmetry-allowed.

The effect of an increase in temperature in the limit \( \tau \rightarrow \infty \) will be to superimpose the Boltzmann weighted spectra of all the vibrational levels. At \( \tau = 0 \) temperature will, of course, have no effect. Fig. 6 shows the relaxation of the spectra for one mode, initially in \( v'_0 = 0 \) and \( v'_0 = 1 \) respectively.

The foregoing discussion applies equally well to symmetry-forbidden transitions, if \( v'_1 = 0 \), i.e. if the inducing mode is not excited in the lower electronic state, provided we interpret \( \Delta \omega^* \) as

\[
\Delta \omega^* = (\omega - \omega_{nu} - \omega_1)/\overline{\omega}.
\]  

(4.7)

If \( v'_1 \neq 0 \) the spectrum will be composed of two overlapping broad bands, one based
on the false origin $v_i' \rightarrow v_i' + 1$ and one based on $v_i' \rightarrow v_i' - 1$ (c.f. eqn (2.18)). This behaviour is illustrated in fig. 7 and compared with the corresponding symmetry-allowed transition.

**Fig. 5.**—Time resolved spectra for 2 modes both excited initially with 1 quantum, $S = 3.0$. $\tau = 20.0$; $\cdots \cdots \cdots \cdots \tau = 0.5$; $\cdots \cdots \cdots \cdots \tau = 0$.

**Fig. 6.**—Relaxation of a single oscillator, initially in $v_o' = 0$ (a) and $v_o' = 1$ (b). $\cdots \cdots \cdots \cdots \tau = 0$, $\cdots \cdots \cdots \cdots \tau = \infty$. $\theta = \hbar \omega / kT = 1.0$ in both cases.
5. DISCUSSION

The spectra shown in fig. 1-7 represent the overall band shape of the absorption spectrum, where the frequency scale is in units of the average vibrational frequency of the molecule. Thus if \( v' = 0, \Delta \omega^* = 0 \) represents the 0-0 transition, \( \Delta \omega^* = 1 \) the 0-1 and so on. Perhaps the most noticeable effect of populating higher vibrational levels is the increase in absorption on the lower energy (red) side of the spectrum of the \( v' = 0 \) level, since transitions with a negative \( \Delta \omega^* \) (e.g. 1-0) are now possible. The values of \( S \) we have used: 0.5-1.5 per mode are consistent with the observed spectra of aromatic hydrocarbons. Strictly these remarks apply only to zero temperature, but as fig. 6 shows, the “Boltzmann” spectrum for one mode with \( S = 0.5 \) and \( \theta = h\bar{\omega}/kT = 1.0 \) (corresponding to \( T \approx 1400 \) \( \text{K} \) if \( \bar{\omega} \approx 1000 \text{ cm}^{-1} \) or \( T \approx 300 \text{ K} \) if \( \bar{\omega} = 200 \text{ cm}^{-1} \)) shows a very similar intensity distribution on the high energy side of the maximum. The major effect of temperature is again to broaden the spectrum to the red, equivalent to the introduction of hot bands into the spectrum.

The time resolved spectra of fig. 4 and 5 demonstrate one important feature, from an experimental point of view. The relaxation of the initial spectrum to the equilibrium spectrum is very rapid on a \( \tau \) scale. Indeed for \( \tau = 5 \) the spectrum is indistinguishable from the fully relaxed spectrum shown (calculated at \( \tau = 20 \)). At low temperatures \( \tau = k_c t \), where \( k_c \) is the vibrational relaxation rate constant between \( v' = 1 \) and \( v' = 0 \) and \( t \) is the time. For time resolved absorption studies the practical time resolution is at present \( ca. 30 \text{ ns} \), thus \( k_c = 5/t \) must be less than \( ca. 2 \times 10^8 \text{ s}^{-1} \) in order for changes in the spectrum to be experimentally observable. This means that reasonably low pressure gas phase experiments and slow electronic relaxation are required to study the effects of vibrational relaxation on absorption and emission spectra by conventional techniques. Picosecond laser techniques should make it possible to study these effects in solution however, since for a \( k = 10^{11} \text{ s}^{-1} \) a time resolution of \( < 50 \text{ ps} \) is required.

Fig. 8 shows the unrelaxed and relaxed triplet-triplet absorption spectra of anthracene obtained by Formosinho, Porter and West using laser flash photolysis. Here with a pressure of \( ca. 2 \text{ Torr} \) of methane the relaxation is complete in \( ca. 2 \mu s \), placing a lower limit of \( 2.5 \times 10^6 \text{ s}^{-1} \) on \( k \).
The absorption spectra of aromatic molecules in both their singlet and triplet states give rise to a series of broad (500-1000 cm⁻¹) bands separated by approximately 1400 cm⁻¹ which are considered to be progressions in the totally symmetric carbon-carbon stretching modes. In the case of anthracene T₁→T₃ absorption, the vapour phase spectrum shows two bands with relative intensities similar to the solution values i.e. 1 : 0.34 (liquid paraffin). The band separation is 1420 cm⁻¹ consistent with the idea that the bands are the first two members of a totally symmetric C–C progression with a displacement (S) of 0.35. Fig. 8 shows only the first (most intense) band of this spectrum. The most likely cause of the large half width (500 cm⁻¹) of the 0–0 band observed by Formosinho et al. is sequence broadening as the temperature (200°C) is well above the value suggested by Byrne and Ross which would be sufficient to wash out all observable structure by this effect. It should be noted that due to the introduction of an average frequency, the theory of section 2 cannot be applied to the calculation of the absorption coefficient of a vibrational band (see Appendix).

To decide on the vibrational distribution in the initially formed triplet state, it is at present necessary to rely on theoretical predictions. Calculations based on the model of Heller et al. show that the most probable final state is one with the same number of quanta in the totally symmetric C–C modes as the initial state. The electronic energy gap is taken up by the higher frequency C–H vibrations.

Upon excitation at 347 nm anthracene is prepared in the S₁ state with one quantum of C–C stretch. Thus, the initially formed triplet state will have 1 quantum of C–C stretch excited, with the rest of the energy in C–H modes (4 quanta of C–H will be sufficient to take up the rest of the energy.) The pressure is sufficiently low (2 Torr) for collisions during the singlet lifetime (5 ns) to be effectively ignored. So, within the framework of the above model, the effects observed by Formosinho et al. can be considered to be caused by the 1–1 band relaxing into the 0–0 band. The relative heights for the relaxed and unrelaxed triplet states are 1 : 0.44. The ratio of the 0–0...
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to the 1-1 band for an $S$ of 0.35 (obtained from the relaxed spectrum) is $1:0.43$, in support of our explanation.

So far the discussion has been concerned with absorption spectra for allowed transitions. As was remarked in section 4, little modification is required for symmetry-forbidden absorptions. The spectra calculated from eqn (2.18) are normalised to $2\nu + 1$; the symmetry-forbidden spectra in fig. 7 have been divided by this factor (= 3 in this case) to facilitate comparison with the allowed spectra. We will now go on to consider emission spectra (eqn (1.2)).

The emission intensity distribution function $I(\omega)$ for a single vibronic state $b\nu^*$ is given by

$$I_{b\nu^*}(\omega) = \frac{4\pi c^3}{3\hbar^3} \sum_{\nu'} |R_{b\nu'^*\nu^*}|^2 \delta(\omega_{b\nu'^*\nu^*} - \omega). \quad (5.1)$$

If eqn (5.1) is compared with eqn (2.1) it will be seen that they are identical apart from a factor of $c^2/\omega^3$. In other words the results for absorption spectra can easily be translated to emission spectra. Indeed the plots of $k_{b\nu^*}/\omega^*\Delta\omega^*$ against $\Delta\omega^*$ in fig. 1-3 can be translated into fluorescence spectra by simply taking the mirror image about the $n-n(A\omega^* = 0)$ transition of the absorption spectra. Recently several papers \cite{21-23} have been published describing the “$S_2$” fluorescence of pyrene vapour. Parmenter \cite{24} has suggested that this emission may be normal $S_1$ fluorescence from high vibrational levels, and indeed if the spectrum given by Deinum et al.\cite{23} is compared with the mirror image of the spectrum in fig. 3 where all four modes are excited with one quantum, a marked similarity is seen. Both spectra exhibit a shoulder and a weak band on the high energy side of the spectrum. Thus our calculations seem to support Parmenter’s explanation.

For the calculation of time resolved emission spectra, the major problem will be the calculation of the time dependent populations of the individuals levels, since both radiative and non-radiative decay rates in general depend on $\nu'$. However, if no significance is attached to the area under the emission spectrum, the qualitative changes in spectral shape will be amenable to the kind of approach given in this paper. Experiments of this kind are in progress with naphthalene vapour.

APPENDIX

LINESHAPE CAUSED BY SEQUENCE-CONGESTION

It is evident that the expressions for the absorption coefficients of single vibronic levels in section 2 cannot be applied to the vibrational bands in time resolved spectra. If the vibrational band under consideration is represented by the transition $v_{\nu'}^{opt} \rightarrow v_{\nu}^{opt}$ and $\{v_{\nu}'\}$ and $\{v_{\nu}''\}$ denote the vibrational quantum numbers of all other modes in the initial and final electronic states, respectively, then the absorption coefficient of the single vibronic level for that particular vibrational band is given by:

$$k_{b\nu'}(v_{\nu'}^{opt} \rightarrow v_{\nu}^{opt}) = \frac{4\pi^2 c}{3\hbar} \sum_{\nu''} |\langle v_{\nu'}^{opt} | v_{\nu}^{opt} \rangle|^2 \sum_{v_{\nu}''} |\langle v_{\nu}'' | v_{\nu}'' \rangle|^2 \delta(\omega_{b\nu'^*\nu^*} - \omega) \quad (A1)$$

for symmetry allowed transitions. Eqn (A1) shows that the normal modes in $\{v_{\nu}'\}$ and $\{v_{\nu}''\}$ determine the band shape by sequence congestion. If these modes have a frequency shift between the two electronic states this transition will actually give rise to many closely spaced lines, the spacing depending on the frequency shift of each of the modes. The most important modes will be the low frequency ($h\nu \approx 500$ cm$^{-1}$) vibrations. Generally these modes are non-totally symmetric and can thus have no displacement. This implies that in absorption only the transitions $v' \rightarrow v''$, $v'' \pm 2n$ can take place. Inspection of the relevant Franck–Condon factors for these transitions shows that, even for large frequency shifts, the only important transitions will be $v' \rightarrow v''$, which have Franck–Condon factors of almost unity.
We here derive an approximate formula for the band shape determined entirely by sequence congestion. For this purpose, we use the case of the absorption coefficient at thermal equilibrium as an illustration.

Replacing the low frequency modes by one $N$-fold degenerate oscillator, the normalised absorption coefficient for allowed transitions at thermal equilibrium is given by:

$$k^\beta_{ab}(\omega, \omega) = \sum_{v'v''} P_{av'}|\langle v'|v'' \rangle|^2 \delta[\omega - \omega_{ba} - (v'' + \frac{1}{2}N)\omega'' + (v' + \frac{1}{2}N)\omega']$$  \hspace{1cm} (A2)

where $P_{av'}$ is the Boltzmann factor for the initial electronic state:

$$P_{av'} = \frac{1}{Q_a} \frac{(v'+N-1)!}{v'!(N-1)!} \exp (-\beta h \omega v')$$  \hspace{1cm} (A3)

and $Q_a$ is the partition function. Replacing the $\delta$ function by $1/|\omega'' - \omega'|$, the spacing of the sequence bands, and using the observation that $|\langle v'|v'' \rangle|^2 \approx \delta_{v',v''}$ we obtain:

$$k^\beta_{ab}(\omega, \omega) = \frac{1}{(\omega'' - \omega)(\omega' + N - 1)!} \frac{(v' + N - 1)!}{Q_a} \exp (-\beta h \omega v'')$$  \hspace{1cm} (A4)

where $\omega$ is given by

$$\omega = \omega_{ba} - (N/2)(\omega' - \omega') + v''(\omega'' - \omega').$$  \hspace{1cm} (A5)

These relations imply that the spectrum will consist of the envelope of a series of lines, separated by $|\omega'' - \omega'|$, whose heights are given by eqn (A4). If $\omega'' < \omega'$, which is the most common case, the spectrum will be broadened toward lower energies, below the "true" 0–0 band at $\omega = \omega_{ba} - (N/2)(\omega'' - \omega')$.

Eqn (A4) is illustrated in fig. 9 for three different values of $\beta h \omega'$. As is expected, the spectrum becomes broader at higher temperatures. Both the general appearance and the
half width (~8(\omega''-\omega')\approx800\text{ cm}^{-1}) of these spectra are in agreement with the spectra discussed by Byrne and Ross.\textsuperscript{18}

The case of symmetry forbidden transitions can be discussed similarly and is not presented here.

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