Analysis of Energy Transfer for Thermally Available Vibrational Energy Levels as Measured by Photoacoustic and Infrared Emission Techniques

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An account is given of the analysis of energy relaxation processes for thermally available vibrational energy levels as measured by photoacoustic and infrared emission experiments employing intensity-modulation of the incident radiation. The main aim is to establish the effect on the observables of the distribution of the initially absorbed energy amongst the available energy modes, *i.e.*, to examine the role of translational heating. A technique using the vibrational temperatures involved is set up for the two-level problem, and developed in some detail for the more complex multi-level situation. The formulae obtained are directly related to experimental results, and should be useful to experimentalists working, in particular, with spectrophone measurements.

The investigation of molecular energy transfer for thermally available vibrational energy levels is divided into the thermodynamic and optical experimental techniques. Two of the most important optical techniques are based on infrared emission and on the photoacoustic effect. In the analysis of the results from these two techniques it is necessary to ascertain that the same relaxation rate constants are being measured; this is true both for vibrational–translational and vibrational–vibrational processes. The major problem is that associated with what Yardley and Moore [1] called "translational heating" in their laser fluorescence experiments. This phenomenon is present both for pulsed [2] and modulated [1] types of measurements, but in this note detailed analysis will be restricted to the latter, where the intensity of the radiation incident on the sample is periodically modulated. The most common measurement is that of the phase difference between the resultant signal and the incident modulated intensity; for infrared emission experiments the resultant signal is the emission from any one of the populated states, and for the photoacoustic determinations it is the pressure modulations measured in a spectrophone.

For their infrared emission experiments Yardley and Moore [1] gave a detailed treatment both for a two-level system and also for a particular example of a three-level case. They did not relate their analysis to photoacoustic measurements. Early spectrophone theory [3,4] developed an approach for the two-level system, but the multi-level case has been rather inadequately dealt with. The case of photoacoustic measurements on carbon dioxide has been treated [5] in detail but the analysis is not a general treatment and is difficult to apply to other molecules. A comprehensive paper [6] by Bauer details the relationship to normal acoustic techniques, but has the weakness that, for the experimentalist, the parameters for the multi-level problem are not easily related to observables.

Analysis of data [7,8] from the phase spectrophone has been developed for the relaxation of non-thermally available electronic states, *e.g.*, triplet states, and the purpose of this paper is to relate that previous work to the problems associated with

thermally available states. The term "translational heating" used in the laser fluorescence [1] work is, to some extent, misleading since the basis of the problem is that of the distribution of the extra energy, made available by the absorption of radiation, amongst the various available modes. However, the work of Yardley and Moore [1] on infrared emission analysis is obviously correct for the cases considered, and the relationship of their phase results to the spectrophone phase lags will be examined. An approach using vibrational temperatures will be developed and shown to be particularly useful for multi-level problems.

TWO-LEVEL SYSTEM

Although the results for a two-level system are well established both for the spectrophone phase lag [3,6] and for fluorescence measurements,[1] it is necessary to deal with the problem here in order (1) to establish terminology and to present the basis of previous approaches and (2) to establish our own approach which will use vibrational temperatures and their direct relationship to heat capacities. This latter approach will be used as a base for consideration of the multi-level problem.

(1) For each of the two levels, 0 and 1, the populations are describable as

$$N(t) = N^e + n(t) \tag{1}$$

where N^e is the equilibrium value in the absence of an exciting beam of radiation, and $n(t)$ is the time-dependent population due to the intensity modulation of the radiation.

Similarly the rate constants, $K_{10}(t)$ and $K_{01}(t)$, are given by

$$K(t) = K^e + k(t). \tag{2}$$

The time-dependence of these rate constants follows from the temperature modulation in the system which accompanies the modulated excitation as a result of the relaxation processes. Retaining only first order terms, it follows that

$$dn_1(t)/dt = I(t) - K_{10}^e n_1(t) - k_{10}(t)N_1^e + K_{01}^e n_0(t) + k_{01}(t)N_0^e \tag{3}$$

where $I(t)$ is the rate of excitation of molecules from level 0 to 1, and takes the form

$$I(t) = I^\circ + I \exp(i\omega t) \tag{4}$$

where ω is the angular frequency of the modulation.

The translational temperature $T(t) = T^e + \Delta T(t)$, with $\Delta T(t) \ll T^e$, and where $\Delta T(t)$ is the oscillatory temperature produced following the excitation process. Ignoring degeneracy factors which are readily incorporated at any stage,

$$K_{10}(t) = K_{01}(t) \exp\{E_1/kT(t)\} \tag{5}$$

with E_1 the energy gap between levels 0 and 1.

The expansion of the exponential term to give

$$\exp(E_1/kT^e)\{1 - E_1\Delta T(t)/kT_e^2\} \tag{6}$$

allows the simplification of eqn (3), yielding

$$dn_1(t)/dt = I(t) - K_{10}^e n_1(t) + K_{01}^e n_0(t) + N_1^e K_{10}^e (E_1/kT_e^2)\Delta T(t). \tag{7}$$

The validity of eqn (6) above requires that $(E_1/kT^e)[\Delta T(t)/T^e] \ll 1$; the extremely small value of $[\Delta T(t)/T^e]$ for all realistic experimental conditions assures this inequality although $(E_1/kT^e) \gg 1$ for many cases as used below [see eqn (11)]. This closely follows previous treatments [1,3] and Yardley and Moore [1] then use an energy balance equation, *viz.*

$$C_0 d[T(t)]/dt = E_1[I(t) - dn_1(t)/dt] \tag{8}$$

where C_0 is the constant volume heat capacity relevant to the combined translational and rotational modes which are assumed to be in fast equilibrium, to give the following relationships.

$$\Delta N_1(i\omega + K^e_{10} + K^e_{01}) = I + K^e_{10} A_1 \Delta T \tag{9}$$

$$\Delta T(C_0 i\omega + A_1 E_1 K^e_{10}) = E_1(K^e_{10} + K^e_{01})\Delta N_1 \tag{10}$$

where $A_1 \equiv N^e_1 E_1/kT^2_e$, and ΔN_1 and ΔT are defined by

$$n_1(t) = n^s_1 + \Delta N_1 \exp(i\omega t)$$

and

$$\Delta T(t) = \Delta T^s + \Delta T \exp(i\omega t).$$

n^s and ΔT^s are the steady state incremental values in the presence of radiation and are ignored relative to the equilibrium values in the treatment; *i.e.*, the use of high excitation power is excluded. This will be commented upon later. Yardley and Moore [1] take eqn (9) and (10) and solve for ΔN_1, thus giving eventually the phase lag ϕ suitable for infrared emission experiments. For $K_{10} \gg K_{01}$, this gives

$$\tan\phi = \omega K^{-1}_{10} + \omega^{-1}K_{10}(A_1 E_1/C_0)(1 + A_1 E_1/C_0). \tag{11}$$

For $\exp(-E_1/kT^e) \ll 1$, $A_1 E_1$ is equal to the vibrational heat capacity of level 1, C_{v_1}.

The spectrophone measures pressure changes and to use eqn (9) and (10) to derive the photoacoustic phase lag, θ, it is necessary to solve for ΔT, the amplitude of the modulating temperature change.

$$\Delta T = I[\{(i\omega + K^e_{10})(C_0 i\omega + C_{v_1} K^e_{10})/K^e_{10}E_1\} - K^e_{10}A_1]^{-1} \tag{12}$$

which leads to

$$\tan\theta = [C_0/(C_0 + C_{v_1})]\omega\tau \tag{13}$$

where $\tau = (K^e_{10} + K^e_{01})^{-1}$.

Note that in the measurement of the spectrophone phase lag there will be an additional (to θ) phase lag of $\pi/2$. This comes [7] from the need to convert a rate of pressure change into an actual pressure change.

Thus using the approach of Yardley and Moore the phase lags for fluorescence and for the spectrophone [eqn (11) and (13)] are rather different even for this simple two-level situation.

(2) A different analysis based on *vibrational* temperature will now be developed for the above problem. This will prove useful for the multi-level scheme. This approach starts off with a separation of the analysis into (i) the optical scheme with no allowance for translational heating, and (ii) the thermal part of the spectrophone cell processes. These are then combined to yield the observable phase lags. The optical scheme (i) has already been dealt with [7] for the more complex three-level scheme, and for the two-level case it gives

$$dN_1(t)/dt = I^0 + I\exp(i\omega t) - \frac{N_1(t)}{\tau} \tag{14}$$

leading, through integration, to

$$N_1(t) = \tau[I^\circ + I\exp i(\omega t - \theta_0)/(1 + \omega^2\tau^2)^{\frac{1}{2}}] \tag{15}$$

where $\tan\theta_0 = \omega\tau = \omega(K^e_{10} + K^e_{10})^{-1}$. The amplitude of the oscillatory population, in the absence of any allowance for translational heating, is then

$$\Delta N_1 = I\tau(1 + \omega^2\tau^2)^{-\frac{1}{2}}\exp(-i\theta_0) \tag{16}$$

or

$$\Delta N_1 = I\tau(1 + i\omega\tau)^{-1}. \tag{17}$$

The *thermal part* (ii), in terms of the vibrational temperature T_v, can be analysed as follows. In this the optical excitation will not explicitly be included but only the resultant oscillatory populations and *vibrational* temperature.

In general

$$N_1/N = [\exp(E_1/kT_v) + 1]^{-1} \tag{18}$$

where $N = N_0 + N_1$.

Since, in this case, $T(t) = T^e + \Delta T_v(t)$ and $\Delta T_v(t) \ll T^e$, it follows that

$$\exp(E_1/kT_v) = \exp(E_1/kT^e)[1 - E_1 \Delta T_v(t)/kT_e^2]. \tag{19}$$

Thus

$$N_1(t)/N = [1 + \exp(E_1/kT^e)\{1 - E_1 \Delta T_v(t)/kT_e^2\}]^{-1},$$

which, with some manipulation, gives for ΔN_1, the amplitude of the oscillatory population of level 1, under the influence of the oscillatory vibrational temperature, (with ΔT_v the amplitude of the oscillatory vibrational temperature)

$$\Delta N_1/N = \exp(-E_1/kT^e)\{1 + \exp(-E_1/kT^e)\}^{-2} E_1 \Delta T_v/kT_e^2. \tag{20}$$

If this exercise is now repeated for the same system [*i.e.*, not explicitly including the incident radiation $I(t)$] but this time describing the analysis in terms of the *translational* temperature $T(t) = T^e + \Delta T(t)$, then it is readily shown that

$$\Delta N_1/N = \exp(-E_1/kT^e)\{1 + \exp(-E_1/kT^e)\}^{-2} E_1 \Delta T/kT_e^2 \cdot (1 + i\omega\tau)^{-1} \tag{21}$$

with ΔT the amplitude of the oscillatory translational temperature, and where $\tau = (K_{10}^e + K_{01}^e)^{-1}$. Eqn (21) follows, for example, from eqn (9) with I removed.

Comparison of eqn (20) and (21) shows that

$$\Delta T_v = \Delta T(1 + i\omega\tau)^{-1} \tag{22}$$

or, in the language of eqn (15),

$$\Delta T_v = \Delta T(1 + \omega^2\tau^2)^{-\frac{1}{2}} \exp(-i\theta_0). \tag{23}$$

Taking this relationship between ΔT_v and ΔT and using it in relationship to relaxation in photoacoustic systems, the available energy, U, from the absorption of radiation is thus

$$U = C_0 \Delta T + C_{v_1} \Delta T_v \tag{24}$$

where C_0 and C_{v_1} are respectively the translational/rotational heat capacity and the vibrational heat capacity associated with level 1 in this two-level system.

From eqn (22)

$$U = \Delta T\{C_0 + C_{v_1}(1 + i\omega\tau)^{-1}\} \tag{25}$$

and the total heat capacity C^T relevant to this system is thus $C_0 + C_{v_1}(1 + i\omega\tau)^{-1}$.

Having shown that the thermal part (ii) of the photoacoustic processes is completely described by the use of the above expression for the total heat capacity, it is now necessary to combine the optical scheme (i) with the thermal analysis (ii).

The oscillatory pressure measured in the spectrophone has been shown [7] to be

$$P(\omega) = (mR/C^T)(\dot{U}/i\omega)\exp(i\omega t) \tag{26}$$

where m is the number of moles of gas in the cell, R the gas constant, and $\dot{U}$ the rate of energy release in the system, *i.e.*, the total energy release as is relevant to the optical scheme (i).

$$\Delta P = (mR/C^T)(\dot{U}/i\omega) \tag{27}$$

where ΔP is the amplitude of the oscillatory pressure.

$$\dot{U} = \Delta N_1 E_1/\tau \tag{28}$$

where ΔN_1 is given in eqn (17) as $I\tau(1+i\omega\tau)^{-1}$.

From the above it follows that

$$\Delta P = (mR/C^T)E_1 I(i\omega)^{-1}(1+i\omega\tau)^{-1} \tag{29}$$

which, in the language of eqn (15), setting $i^{-1} = \exp(-i\pi/2)$, and substituting for $C^T = C_0 + C_{v_1}(1+i\omega\tau)^{-1}$, leads to

$$\Delta P = (mRE_1 I/\omega)\exp[-i(\pi/2+\theta)]/C^T[1+\omega^2\tau^2(C_0/C^T)^2]^{\frac{1}{2}} \tag{30}$$

where

$$\tan\theta = (C_0/C^T)\omega\tau \tag{31}$$

and is exactly the same as from the previous approach expressed in eqn (13). Eqn (30), of course, also gives the amplitude information relevant to measurements on the amplitude spectrophone.

In this section, on the two-level scheme, several important points have been established:

(a) When translational heating, or the distribution of the extra absorbed energy, is taken into account, the phase lags measured by infrared emission and by the photo-acoustic method are different. Eqn (11) and (13) show this.

(b) The analysis of the effects can be divided into an optical part and a thermal part. This is very important since for any involved multi-level system, having established a chosen scheme of events, the optical part can always be explicitly stated. The thermal part, i.e., translational heating, can be incorporated *purely* in terms of heat capacity terms, with their appropriate frequency dependencies.

(c) For a discussion of thermally available levels, as above, both approaches have assumed that the radiation intensity is not too high, i.e., the equilibrium population in the absence of radiation is assumed larger than the incremental steady-state population produced by the radiation [see the expressions below eqn (10)]. For most experimental situations where a two-level analysis can be used there is no major problem here since E_1 tends to be low and the equilibrium population high. However, if an experiment requires a very high level of absorbed energy, then one can treat the problem qualitatively as follows. The population of level 1 is given by

$$N_1(t) = N_1^e + n_1^s + \Delta N_1 \exp(i\omega t) \tag{32}$$

where n_1^s, the incremental steady-state population, has been ignored previously. The translational temperature in the system can also be written as

$$T(t) = T^e + T^s + \Delta T \exp(i\omega t).$$

In a situation where $n_1^s \gg N_1^e$, ΔT can no longer be simply related to T^e, but nevertheless the extra energy made available by the absorption process has still to be distributed amongst the available modes in exactly the same way as above. This distribution will, once more, be governed by the ratio of heat capacities, C_0/C^T, but in this case this ratio is not to be calculated relevant to T^e but to $(T^e + T^s)$. Thus for this situation

$$\tan\theta = \omega\tau_m(C_0/C^T)_m \tag{33}$$

where both τ_m and $(C_0/C^T)_m$ refer to the steady-state temperature of measurement, T_m, which is equivalent to $T^e + T^s$. T_m would have to be experimentally determined or a calculation performed involving the radiation flux and the heat loss characteristics of the cell. Alternatively the measurement of $\tan\theta$ at several incident radiation

intensities, followed by an extrapolation to zero intensity, should give a θ value corresponding to T^e with the concomitant values of (C_0/C^T) and τ.

MULTI-LEVEL SYSTEM

Some care has been taken to develop expressions for the two-level case which will act as a base for the more complex situations presented by multi-level problems. The aim in this section is to provide for the experimentalist a basis of approach which will be applicable to any chosen reaction scheme, *i.e.*, to any pattern of vibrational–vibrational processes followed by the normally slower vibrational–translational step. With this in mind, and with the particular example of v_3 excitation in methane a problem on which we are currently working,[9] a start to the general problem will be made by looking at the scheme shown in fig. 1. The fact that Yardley and Moore [1] also did measurements on CH_4 allows us to compare results on the nature of the analysis with their treatment.
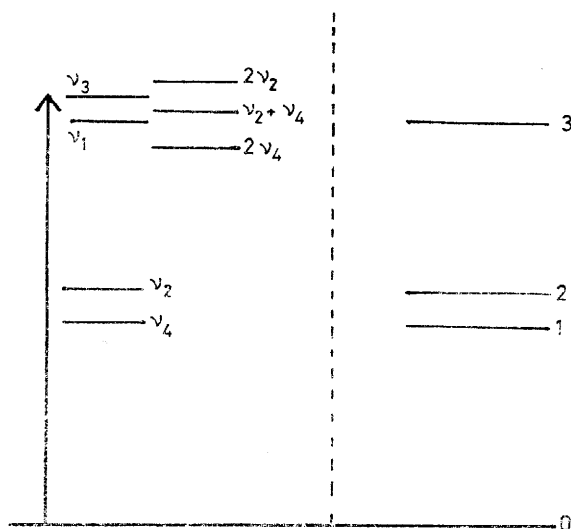

FIG. 1.—Vibrational modes of methane, with a simple labelling system (0, 1, 2, 3) adequate for analysis of photoacoustic and infrared emission measurements at low frequency and/or high pressure.

For the scheme in fig. 1, if measurements are made at either high pressure or at low frequency (ω), then the rapid V–V processes are in equilibrium and only one relaxation process to translational energy is observed. The purpose at present is not to discuss any detailed V–V pathways in CH_4 but simply to set up the photoacoustic observables for high pressure and low frequency measurements. Following absorption in v_3 the energy is very quickly degraded to the bending modes v_2 and v_4 which are in rapid equilibrium with each other. The energy flows from this coupled pair (v_2, v_4) to translational and/or rotational energy, the rotational–translational energy transfer being very fast. The relaxation time pertinent to these measurements is (v_2, v_4) to translation/rotation, *i.e.*, one relaxation time, and the question is what photoacoustic phase lag will be observed compared to the simple two-level system. For this analysis

$$N = N_0 + N_1 + N_2 \tag{34}$$

and the populations of all higher energy levels can be regarded as insignificant.

With the approach we are developing in this paper, the analysis is divided into the purely optical scheme (i) and the thermal part (ii).

OPTICAL SCHEME

The processes here are very similar to that already developed [7] for absorption into an excited singlet electronic state, decay to the lowest triplet state, and the observable relaxation time being that from the vibrationally relaxed triplet state to the ground state. The same approach can, therefore, be taken for this optical part of the analysis.

$$E_3 = H + L \tag{35}$$

where E_3 is the energy of the quantum absorbed by the v_3 state. $H + L$ is, then, the total energy available per photon absorbed, and is divided into H, the energy which is dissipated to translation much faster than the observed relaxation time, and L, the energy associated with the relatively slow relaxation step to translation. There is no need to repeat the derivation of ref. (7) which gave

$$\tan \theta_0 = \omega\tau/\{(1 + H/L) + (H/L)\omega^2\tau^2\} \tag{36}$$

where θ_0 is the photoacoustic phase lag from the optical scheme, *i.e.*, no allowance for translational heating. However, it is important for the problem now under discussion to define carefully the meaning of τ, H and L. Since it is the coupled (v_2, v_4) which relax to translation, then

$$\tau = \{[K_{10}^e/(1 + \alpha)] + K_{01}^e\}^{-1} \tag{37}$$

where α is the coefficient reflecting the relative populations of levels 1 and 2 (*i.e.*, v_2 and v_4) and is thus given by

$$\alpha = K_{12}^e/K_{21}^e. \tag{38}$$

In eqn (37) for the CH_4 example, K_{01}^e is extremely small and, to an accuracy of much better than 1 %, can be ignored.

$$L = [E_{10} + \alpha E_{21}/(1 + \alpha)](1 + F) \tag{39}$$

where F is the fraction (in terms of quanta) of the deactivation of v_3 to (v_2, v_4) which takes place yielding two bending quanta (v_2, v_4). The normal assumption [10] is that a process from v_3 to either one of the overtones ($2v_4$ or $2v_2$) or to the combination level $(v_2 + v_4)$, and consequently producing two bending quanta (v_2, v_4), is completely dominant; in this case $F = 1$. However, it has been suggested [9] that F is slightly < 1 and thus the general form of eqn (39) is more appropriate.

$$H = E_3 - [E_{10} + \alpha E_{21}/(1 + \alpha)](1 + F). \tag{40}$$

For this situation, then, at low frequency or high pressure with only one observed relaxation, the V–V processes being much faster, eqn (36) represents the value for $\tan \theta_0$. This formula is completely general and the use of CH_4 is only there to give it meaning by example.

THERMAL PART AND COMBINATION OF OPTICAL AND THERMAL PARTS

(*a*) The present analysis has only one observed relaxation time and is typical of almost all known cases where the upward populating of higher vibrational levels is step-wise, *e.g.*, $0 \rightarrow (1, 2) \rightarrow 3$, *etc.* It follows, therefore, from eqn (25) and the preceding discussion that the appropriate formulation of the heat capacity for this problem is

$$C^T = C_0 + C_v(1 + i\omega\tau)^{-1} \tag{41}$$

where C_v is the total vibrational heat capacity of the molecule. For high vibrational energy levels the contribution is negligible as stated in eqn (34). In eqn (41), τ is as defined in eqn (37).

In the section on the two-level system (2), the full method of combining the thermal and optical parts was described, giving the observable phase lag from a consideration of ΔP, the amplitude of the oscillatory pressure in the spectrophone [see eqn (29) and (30)]. In the present case combining eqn (41) with the analysis leading to eqn (36) gives

$$\Delta P = (mRI/\omega)[H + L(1 + i\omega\tau)^{-1}][C_0 + C_v(1 + i\omega\tau)^{-1}] \exp(-i\pi/2). \qquad (42)$$

This simplifies [see eqn (30)] to

$$\Delta P = (mRI/\omega)\left\{\frac{H^2 + [L(2H + L)]/(1 + \omega^2\tau^2)}{C_0^2 + [C_v(2C_0 + C_v)]/(1 + \omega^2\tau^2)}\right\}^{\frac{1}{2}} \exp\left[-i(\pi/2 + \theta)\right] \qquad (43)$$

where θ is the observed photoacoustic phase lag, i.e., translational heating included,

$$\tan\theta = \frac{\omega\tau[C_0/C_v - H/L]}{(1 + H/L)(1 + C_0/C_v) + (H/L)(C_0/C_v)\omega^2\tau^2}. \qquad (44)$$

This is the formulation to be used for $\tan\theta$ and it is seen to include C_0/C_v, H/L and τ. From phase measurements as a function of ω, and with a knowledge of C_0/C_v, both H/L and τ can be measured; alternatively if both phase [eqn (44)] and amplitude [eqn (43)] measurements are carried out then all three parameters C_0/C_v, H/L and τ can be experimentally determined. The value of H/L can be used to give F in eqn (39) since α can be calculated from the relative equilibrium populations of v_2 and v_4 at the temperature of measurement (i.e., from a knowledge of the energy gap E_{21} and the appropriate degeneracies).

(b) The derivation of the previous section can be questioned in respect of one aspect of the analysis; viz. in the fast equilibrium between v_2 and v_4, no allowance has been made for any change in this equilibrium due to the excess translational energy produced by the absorption process. It is necessary, therefore, to analyse this problem to determine whether any correction should be imposed on eqn (44).

$$K_{12}(t)N_1(t) = K_{21}(t)N_2(t) \qquad (45)$$

where the time-dependence of the populations and the rate constants reflects the adjustment of the equilibrium to the instantaneous gas temperature.

The translational temperature $T(t)$ is

$$T(t) = T^e + \Delta T(t)$$

and thus from

$$K_{21}(t) = K_{12}(t) \exp[E_{21}/kT(t)] \qquad (46)$$

it follows that

$$K_{21}(t) = K_{12}(t) \exp(E_{21}/kT^e)[1 - E_{21}\Delta T(t)/kT_e^2]. \qquad (47)$$

Thus

$$N_2(t)/N_1(t) = K_{12}(t)/K_{21}(t) = \exp(-E_{21}/kT^e)/[1 - E_{21}\Delta T(t)/kT_e^2]$$

or

$$N_2(t)/N_1(t) = \alpha[1 + E_{21}\Delta T(t)/kT_e^2] \qquad (48)$$

where $\alpha = \exp(-E_{21}/kT^e)$ and is the ratio of populations at the equilibrium temperature, as before, and where $\Delta T \ll T^e$.

Note that for clarity of presentation, degeneracy factors associated with each level are being omitted. From eqn (48) it follows that

$$[N_2^e + n_2(t)] = \alpha[N_1^e + n_1(t)][1 + E_{21}\Delta T(t)/kT_e^2]$$

and thus that the required relationship of the oscillatory populations is given as

$$n_2(t) = \alpha n_1(t)[1 + A_{21}\Delta T(t)/N_2^e] + A_{21}\Delta T(t) \tag{49}$$

where N_2^e is the equilibrium population of level 2, and

$$A_{21} = N_2^e E_{21}/kT_e^2. \tag{50}$$

If $E_{21}\Delta T/kT_e^2 \ll 1$, which is the normal assumption used in previous sections, then eqn (49) simplifies to

$$n_2(t) = \alpha n_1(t) + A_{21}\Delta T(t). \tag{51}$$

With this relationship between the two oscillatory populations of levels 1 and 2 [instead of simply $n_2(t) = \alpha n_1(t)$ as is implied in the last section (a)], the overall analysis in terms of *vibrational* temperatures will now be outlined.

$$N_1(t) + N_2(t) = N_0(t)\{\exp[-E_{10}/kT_v(t)] + \exp[-E_{20}/kT_v(t)]\}. \tag{52}$$

Remembering that $T_v(t) = T_v^e + \Delta T_v(t)$, with $\Delta T_v(t) \ll T_v^e$, and defining $A_1 = N_1^e E_{10}/kT_e^2$, and $A_2 = N_2^e E_{20}/kT_e^2$, leads to

$$(\Delta N_1 + \Delta N_2)[1 + \exp(-E_{10}/kT^e)] = \Delta N_2 + A_1\Delta T_{v(1)} \tag{53}$$

where ΔN is the amplitude of $n(t)$, and $\Delta T_{v(1)}$ refers to the amplitude of the time-dependent vibrational temperature of level 1. Substituting in eqn (53) from eqn (51) in the form $\Delta N_2 = \alpha\Delta N_1 + A_{21}\Delta T$ (ΔT refers to translational temperature) yields

$$\Delta N_1\{1 + (1+\alpha)\exp(-E_{10}/kT^e)\} = A_1\Delta T_{v(1)} - A_{21}\exp(-E_{10}/kT^e)\Delta T. \tag{54}$$

In terms of the translational temperature amplitude ΔT,

$$\Delta N_1 = \{K_{10}^e A_1 - (K_{01}^e + i\omega)A_{21}\}\{(i\omega + K_{01}^e)(1+\alpha) + K_{10}^e\}^{-1}\Delta T \tag{55}$$

and combining eqn (54) and (55), after some manipulation, gives

$$\Delta T_{v(1)} = \Delta T(1 + i\omega\tau)^{-1}\{1 - i\omega\tau[A_{21}/A_1(1+\alpha) - A_{21}K_{01}^e/A_1 K_{10}^e]\}$$

which, with $K_{01}^e \ll K_{10}^e$, gives

$$\Delta T_{v(1)} = \Delta T(1 + i\omega\tau)^{-1}\{1 - i\omega\tau B\} \tag{56}$$

where

$$B = \alpha E_{21}/(1+\alpha)E_{10}.$$

Comparison of this expression with eqn (22), which was for a simple two-level scheme, say 0 and 1, shows that the presence of level 2, in fast equilibrium with level 1, does alter the $\Delta T_{v(1)}$, ΔT relationship.

Analysis along similar lines, but pertinent to the vibrational temperature of level 2, gives the following relationship

$$\Delta T_{v(2)} = \Delta T(1 + i\omega\tau)^{-1}\{1 + i\omega\tau B A_1/A_2\}. \tag{57}$$

It is interesting to note from eqn (56) and (57) that the rapid collisional processes keeping levels 1 and 2 in equilibrium results in slightly different vibrational temperatures for the two levels. This is not true of course at low values of $\omega\tau$, *i.e.*, low frequency or high pressure, where $\Delta T = \Delta T_{v(1)} = \Delta T_{v(2)}$ as expected for a system in equilibrium. At high values of $\omega\tau$, *i.e.*, at values where $\omega^2\tau^2 \gg 1$, the populations and the vibrational temperatures of levels 1 and 2 will be extremely small from the thermal processes being considered here.

By analogy with the previous treatment [eqn (22)-(25)] the total heat capacity for this system of levels 0, 1 and 2 can be written

$$C^T = C_0 + C_{v(1)}(1+i\omega\tau)^{-1}(1-i\omega\tau B) + C_{v(2)}(1+i\omega\tau)^{-1}(1+i\omega\tau BA_1/A_2). \quad (58)$$

Since $C_{v(1)} = E_{10}A_1$ and $C_{v(2)} = E_{20}A_2$, it follows that

$$C^T = C_0 + (1+i\omega\tau)^{-1}\{C_v + i\omega\tau\gamma\} \quad (59)$$

where the total vibrational heat capacity C_v, for this system, equals $C_{v(1)} + C_{v(2)}$, and where $\gamma = BA_1E_{21}$.

Thus the effect of allowing for the translational temperature increment on the equilibrium between levels 1 and 2 is seen by comparison of eqn (59) and (41).

Solving for $\tan\theta$, for comparison with eqn (44), gives

$$\tan\theta = \frac{\omega\tau\left\{\left(\dfrac{C_0}{C_v}+\dfrac{\gamma}{C_v}\right)-\dfrac{H}{L}\left(1-\dfrac{\gamma}{C_v}\right)\right\}}{\left(1+\dfrac{H}{L}\right)\left(1+\dfrac{C_0}{C_v}\right)+\omega^2\tau^2\dfrac{H}{L}\left(\dfrac{C_0}{C_v}+\dfrac{\gamma}{C_v}\right)}. \quad (60)$$

Are the terms in γ of any quantitative significance?

From the definitions of B and A_1, and by using $C_{v(1)} = E_{10}A_1$ and $C_{v(2)} = E_{20}A_2$,

$$\gamma/C_v = \alpha E_{21}^2/(1+\alpha)(E_1^2+\alpha E_2^2). \quad (61)$$

For the CH_4 example, $\alpha = 0.22$, $E_{21} = 227$ cm^{-1}, $E_{10} = 1306$ cm^{-1} and $E_{20} = 1533$ cm^{-1}, and thus $\gamma/C_v = 0.0042$. In eqn (60), then, the γ correction is seen to be completely insignificant.

In the general situation for photoacoustic measurements on any molecule it is also apparent that γ/C_v will not appreciably affect the relaxation results. This can be seen as follows:

(a) As $E_{21} \to 0$, $\alpha \to 1$, and $\gamma/C_v \to 0$, and

(b) as E_{21} gets large, $\alpha \to 0$ and $\gamma/C_v \to 0$.

Eqn (44) is thus suitable for accurate analysis of any problem of this type in the phase spectrophone, and eqn (43) gives the concomitant expression for the amplitude spectrophone.

COMPARISON WITH YARDLEY AND MOORE [1]

So far in this section on multi-level systems only the approach developed in this paper using vibrational temperatures (see earlier for the two-level basis of this approach) has been studied. The optical part and the thermal part plus combination have been discussed above.

It is important at this stage to compare the above results with the analysis given by Yardley and Moore [1] for a particular case, *viz.* the case of CH_4 as given in fig. 1, with $N_3 = 0$, but with the assumption that all photons absorbed into ν_3 produce two bending quanta (ν_2, ν_4). This assumption is that $F = 1$ in eqn (39), and the analysis is not performed, therefore, in terms of H and L but in terms of the relevant CH_4 energy gaps. Their purpose was to examine the phase lag observed in infrared emission from level 1, *i.e.*, the ν_4 mode, and for comparison with our analysis it is necessary to take their basic equations and apply them to the photoacoustic observables. Their analysis is in terms purely of translational temperature increments ·

Their basic equations [see eqn (32) and (33) in ref. (1)] are

$$\Delta N_1\{(i\omega + K_{01}^e)(1+\alpha) + K_{10}^e\} = 2I + (K_{10}^e A_1 - i\omega A_{21})\Delta T \tag{62}$$

and

$$C_0 \Delta T = IE_3/i\omega - E_1 \Delta N_1 - E_2(\alpha \Delta N_1 + A_{21}\Delta T) \tag{63}$$

where changes have been made to correspond to our terminology. The rationale of these equations is obvious from the processes described in the present work. Solving eqn (62) and (63) for ΔT gives

$$\Delta T/I = \{E_3 + i\omega\tau(E_3 - E_b)\}/i\omega[C_0 + C_{v(1)} + C_{v(2)} + i\omega\tau\{C_0 + E_{21}A_{21}/(1+\alpha)\}] \tag{64}$$

where $E_b = 2(E_{10} + \alpha E_{20})/(1+\alpha)$, and the other symbols have their previous meaning. This leads to an expression for $\tan\theta$, the photoacoustic phase lag, of

$$\tan\theta = \frac{\omega\tau\{E_b(C_0 + C_v) - E_3 C_v + E_{21}A_{21}E_3/(1+\alpha)\}}{E_3(C_0 + C_v) + \omega^2\tau^2(E_3 - E_b)(C_0 + E_{21}A_{21}/\{1+\alpha\})}. \tag{65}$$

If this is expressed in the terminology of H and L, remembering that Yardley and Moore are assuming that $F = 1$, then *exact* agreement is obtained with eqn (60).

This agreement of the approaches for this example is useful confirmation of the general approach used earlier, and highlights the different phase lags measured in the two techniques, infrared emission and the photoacoustic pressure modulations. According to Yardley and Moore the phase lag ϕ, relevant to ν_4 emission, is given to a good approximation as

$$\tan\phi = \omega\tau + (\omega\tau)^{-1}[A_1 E_3(1+\alpha)/2C_0][1 + A_1(E_1 + \alpha E_2)/C_0]. \tag{66}$$

GENERAL MULTI-LEVEL SOLUTIONS

(a) Single Relaxation

For most molecules the total vibrational heat capacity relaxes to translational energy with one rate-determining relaxation time. In terms of molecular energy levels this means that fast V–V energy transfer in the higher vibrational modes results in the population of the lowest excited level which couples relatively slowly to translational energy. For this situation, no matter how many vibrational levels are involved, the heat capacity is

$$C^T = C_0 + C_v(1 + i\omega\tau)^{-1}$$

where C_v is the total vibrational heat capacity and τ is the relaxation time of the coupling to translational motion.

Thus our earlier analysis for three levels with its proof that second-order terms (*i.e.*, the γ terms) are insignificant will apply to any number of vibrational levels; the observed photoacoustic phase lag will be as given in eqn (44) for high pressure or low frequency measurements.

(b) Double Relaxation

For a few molecules ultrasonic measurements have noted that the total vibrational heat capacity does not relax to translation with one relaxation time. Two separate relaxations are involved. This is readily incorporated into the thermal part of the photoacoustic analysis as

$$C^T = C_0 + C_{v(a)}(1 + i\omega\tau_a)^{-1} + C_{v(b)}(1 + i\omega\tau_b)^{-1}. \tag{67}$$

The optical part is calculable[7] for as many relaxations as is necessary. In practice, to fully analyse for an unknown ratio $C_{v(a)}/C_{v(b)}$, both phase and amplitude information would be needed.

(c) Low pressure or high frequency measurements

If the region of measurement is such that ω^{-1} is comparable with the rate constants for V–V transfer, then several processes will add to yield a resultant phase lag. The thermal part of the analysis at these high frequencies or low pressures will, in general, be accounted for by simply replacing C^T with C_0 and will thus have no frequency dependence. The particular optical scheme appropriate to the system will thus account fully for the observed phase lags. In order to indicate the method a simple scheme of three levels is shown in fig. 2. The measurements are at a high enough
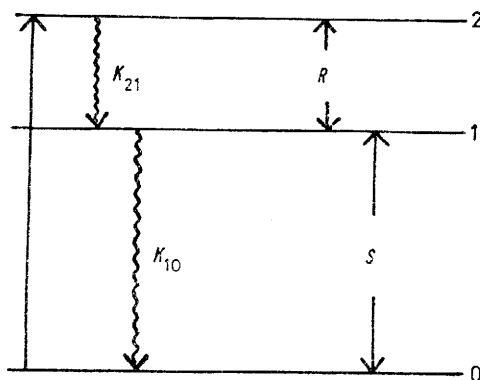

FIG. 2.—Extremely simple example of a relaxation mechanism with both the $2 \rightarrow 1$ and $1 \rightarrow 0$ processes contributing to observed phase lags.

frequency to have the 2-1 process contribute to the phase lag. Two components, one arising from each excited state, contribute to the total signal. These can be considered as two vectors, each with a defined amplitude and phase, and can be added vectorially to give the observed resultant. For the example in fig. 2, and in a frequency region where $C^T{}_{\xi} = C_0$, the amplitude of the pressure modulation in the spectrophone is given by

$$\Delta P = (mRI/\omega C_0)(1+\omega^2\tau_2^2)^{-\frac{1}{2}}[R^2+(1+\omega^2\tau_1^2)(2RS+S^2)]^{\frac{1}{2}} \exp\left[-i(\pi/2+\theta)\right] \qquad (68)$$

where $\tau_2 = K_{21}^{-1}$ and $\tau_1 = K_{10}^{-1}$.

$$\tan\theta = \frac{R\sin\phi_2 + S\cos\phi_1 \sin(\phi_2+\phi_1)}{R\cos\phi_2 + S\cos\phi_1 \cos(\phi_2+\phi_1)} \qquad (69)$$

with $\tan\phi_2 = \omega\tau_2$, $\tan\phi_1 = \omega\tau_1$, $\cos\phi_2 = (1+\omega^2\tau_2^2)^{-\frac{1}{2}}$, $\sin\phi_2 = \omega\,\tau_2/(1+\omega^2\tau_2^2)^{\frac{1}{2}}$.

An appropriate frequency scan will enable analysis in terms of τ_1 and τ_2. More complex V–V patterns are amenable to this straightforward vector addition method, the important point for this paper being that the thermal part of the analysis reduces to a constant (i.e., C_0) for low pressure or high frequency measurements when V–V processes are contributing to the observed phase-lags.

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(PAPER 8/1028)