EXCITATION OF BENDING VIBRATIONS IN CS_2

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1. Introduction

Scientists in the USSR have proposed, on the basis of shock recovery experiments, that the shock process produces chemical reactions which cannot be explained in terms of measured pressures and calculated temperatures, and that there are "catastrophic" effects occuring in the shock front itself. Direct experiments are required to test this speculation, and optical spectroscopy appears to be a suitable tool for such experiments.

Kendall Ogilvie's experiments have shown that passage of a 5 Kb shock wave through liquid CS_2 at room temperature produces a shift of the 3700 Å absorption edge toward the red. The magnitude of the shift is about 0.11 eV, 120 Å, or 900 cm^{-1}. Static pressure measurements of CS_2 in ethanol carried out by J. Schnurr and M. Abebe of NRL show that there is very little shift in this absorption band at room temperature and 10 kilobars pressure. Measurements at near atmospheric pressure and approximately 100°C were performed by Granholm and by Ogilvie at WSU, and no significant shift was found. The calculated temperature rise for a 5 kilobar shock is about 100°C, so these two static measurements suggest that something other than pressure and temperature are involved in the shift, in agreement with conjectures from the USSR.

The absorption band discussed here arises from transitions which occur only in the bent state (CS_2 is normally linear). Moreover, as temperature in the vapor state increases, new levels become accessible from the ground state and the width of the band increases. These findings suggest that attention should be focussed on possible effects of the shock on bending deformation of the molecule.

In seeking an explanation of this apparent dynamic effect, it is natural to consider direct mechanical excitation of the CS_2 molecule by passage of the shock front. A review of theoretical and experimental evidence persuades me that the shock front passing over a particular molecule is only a few angstroms thick. This in turn suggests that the impact of the shock front on individual atoms might communicate an extraordinary amount of kinetic energy to selected vibrational modes. The material which follows represents a preliminary attempt to assess this speculation.

2. Magnitudes

Some numerical values important to this problem are given in Table 2.1. Each atom in the liquid responds to the presence of its neighbors in terms of the forces they produce on it. At equilibrium these forces are in balance because of the symmetry of the molecular distribution. Except for vibrations there is no net force on an atom, which causes it to drift in a particular direction.

As a shock approaches, this symmetry is disturbed, because the concentration of molecules is greater behind the shock than ahead of it. The result is that a force acts on the atom as the shock passes over it and for periods of time before and after which depend upon the range of forces.

Table 2.1

Numerical Values of Important Constants for CS_2

Quantity	Formula	Volume	Units
Mass of Carbon Atom	m_2	12.01	amu
		19.941×10^{-24}	g
Mass of Sulfur Atom	m_1	32.066	amu
		53.241×10^{-24}	g
Mass of CS_2 Molecule	$M = m_2 + 2m_1$	76.142	amu
		126.43×10^{-24}	amu
Separation of C and S Atoms	ℓ	1.55×10^{-8}	cm
Moment of Inertia for Bending	$I = 2m_1 m_2 \ell^2/M$	40.351×10^{-40}	gcm^2
kT for 20°C (Room Temp)	kT	404.48×10^{-16}	ergs
Rms Velocity of Free S Atom at Room Temp	$(kT/M_1)^{1/2}$	2.76	Å/psec
Rms Angular Velocity for Bending Vibration	$(kT/I)^{1/2}$	3.166	$psec^{-1}$
Frequency of Bending Vibration, ν_2	1/2	400	cm^{-1}
	ν	12	$psec^{-1}$
	ω	75.4	radians/psec
Propagation Velocity of 5Kb Shock	u_s	17	Å/psec
Particle Velocity, 5Kb Shock	u_p	2.33	Å/psec
		2.33×10^4	cm/sec
Temperature Rise 5Kb Shock	ΔT	100	°C
Boltzmann Constant	k	1.38×10^{-16}	erg/deg
Density of CS_2	ρ		
Center of Absorption Band			
Edge of Absorption Band			
Spring Constant, $H = \omega^2 I$	H	2.294×10^{-11}	ergs

Passage of the shock produces a mean particle drift velocity, u_p. In the simplest approximation the shock provides an impulse as it passes over each atom causing its velocity to measure in the direction of the shock by u_p.

Consider for a moment a free atom of mass m with velocity (u_{ox}, u_{oy}, u_{oz}) to which an impulse, $I = mu_p$, is applied in the x-direction. After the impulse is applied, the x-velocity component is $u_x = u_{ox} + u_p$. If $\vec{u}_o$ is Boltzmann distributed, mean values of the velocity components after collision are $\bar{u}^2_{ox} + u^2_p, \bar{u}^2_{oy}, \bar{u}^2_{oz}$ with $m\bar{u}^2_{ox}/2 = kT_{ox}/2$ and $m(\bar{u}^2_{ox} + u^2_p)/2 = kT_{fx}/2$ we have:

$$T_{fx} - T_{ox} = T_{fx} - T_o = mu^2_p/k$$

That is, the initial velocity distribution after impact is anisotropic and the temperature is anisotropic. For a sulfur atom with $u_p = 2.33 \times 10^4$ cm/sec,

$$T_{fx} - T_o = 210°K$$

This will relax to $T_f - T_o = 70°K$ in a time dependent on mean time between collisions. $T_{fx} - T_o$ is twice the equilibrium temperature rise for the shocked state.

A molecule imbedded in a fluid will have a more complicated response, but this simple calculation suggests that the problem is worth closer examination. It is not clear how the effects of neighboring molecules can be accounted for, but there seems to be a possibility of resonance for a single molecule. In Fig. 1 is shown a linear triatomic molecule, in bending vibration, with axis inclined at an angle, α, with respect to the x-axis.

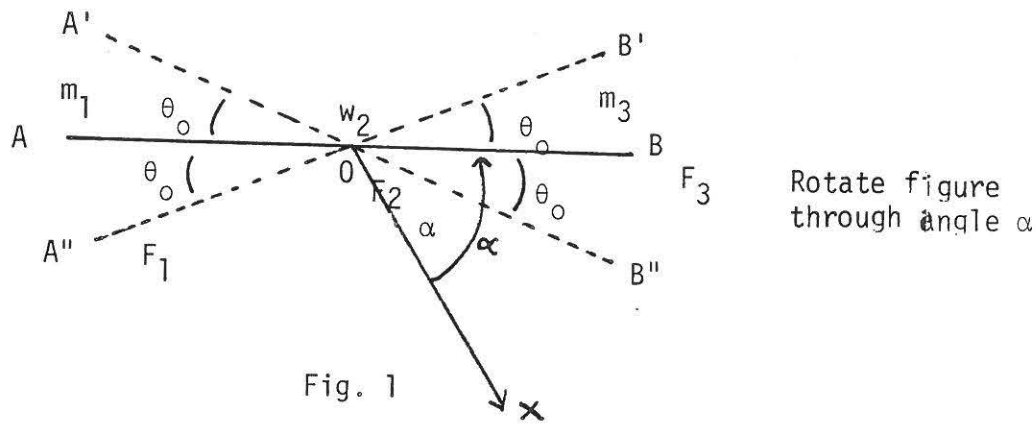


Fig. 1

Impulses acting on linear molecule

AOB is the neutral position of the molecule and A'OB', A"OB", are the extreme bent positions. Suppose a shock travelling in the x-direction passes over m_1 at time, t_1, m_2 at t_2, and m_3 at t_3. Bending is excited by striking any one of the three atoms. Action of an impulse on any one of the masses produces a combination of bending, rotation, and translation. If all three are struck simultaneously, there is only translation. If they are struck in a suitable sequence, the possibility of resonance exists.

The bending mode is of particular interest for two reasons: (i) it is only in the bent state that the 2900 - 3700 Å absorption band occurs; (ii) it is the lowest frequency mode, so velocities imparted by passage of a shock can be a larger fraction of thermal velocities than for other modes and may be expected to be more disruptive.

Suppose, for example, that a shock passes the molecule in Fig. 1 so that atom A is struck at $t = 0$, O at $t = \tau/2$ and B at $t = \tau$, where τ is the period of bending vibration. The component of velocity normal to OA produced by the impact is $u_p \sin \alpha$, of which approximately half will be contributed to bending. The corresponding angular velocity is

$$\dot{\theta}_A = u_p \sin\alpha / 2\ell$$

where ℓ = separation of C and S atoms. When the shock reaches the C-atom at O, atom A is stationary and the velocity imparted to the C-atom is approximately $2\dot{\theta}_A$. Half a period later the atom at B is struck, giving another $\dot{\theta}_A$. The net effect of the passage of the shock then is to add an amount

$$\dot{\theta} = u_p \sin\alpha / \ell$$

to the bending velocity. The corresponding average increase in vibrational kinetic energy is

$$\Delta E = I u_p^2 \sin^2\alpha / 2\ell^2 = \frac{m_1 m_2}{m_2 + 2m_1} u_p^2 \sin^2\alpha$$

$$= k\Delta T$$

$$\Delta T = 160°C \times \sin^2\alpha$$

The value of α depends on shock velocity. In the above example the time to pass over the molecule is $\tau = 1/\nu$, so

$$2\ell\cos\alpha = u_s\tau;$$

$u_s\tau/2\ell$ must be < 1 in order that a solution be possible. With the values in Table 2.1,

$$\sin^2\alpha = 0.54$$

$$\Delta T = 87°C$$

It is not evident that a Boltzmann average of the square velocity is appropriate to this problem. This subject will be taken up in a later section. Now we proceed to give a more careful treatment of the last problem.

3. Motions of the CS_2 Molecule

The CS_2 molecule is represented in Fig. 2. The neutral axis of the molecule, N'ON, is inclined at an angle α to the x-axis, which is the direction of shock propagation. The bent line, BOA, represents the molecule in the bent state, θ. The carbon atom, with mass, m_2, is at O with position $\vec{r}_2(t)$; sulfur atoms are at B and A with masses, m_1, each and positions $\vec{r}_1(t)$ and $\bar{r}_3(t)$, respectively. Define the following variables:

$$\vec{S}_1 = \overrightarrow{OB} = \vec{r}_1 - \vec{r}_2$$

$$\vec{S}_3 = \overrightarrow{OA} = \vec{r}_3 - \vec{r}_2$$

$$\vec{S} = \overrightarrow{OC} = \vec{S}_1 + \vec{S}_3 \qquad (3.1)$$

$$\vec{N} = \overrightarrow{BA} = \vec{S}_3 - \vec{S}_1 \qquad (3.2)$$

Assume that

$$|\vec{S}_1| = |\vec{S}_2| = \ell = \text{constant}; \qquad (3.3)$$

$$\vec{S} = (2\ell\sin\theta)\vec{p}$$

$$\vec{N} = (2\ell\cos\theta)\vec{n} \qquad (3.4)$$

where $\vec{n}$ and $\vec{p}$ are unit vectors in directions $\vec{S}$ and $\vec{N}$, respectively.

Assume at the outset that vibration and rotation are allowed only in the (x,y) plane, shown in Figure 2. This means that there are 4 degrees of freedom: 2 translation, 1 rotation, 1 bending vibration. Longitudinal vibrations are suppressed by the assumption that sulfur atoms are at a fixed distance from the carbon atom.

Four degrees of freedom implies 1 vector equation for motion of the center of mass and 2 scalar equations for variations of α and θ. The equations of motion are initially written in terms of the space vectors $\overline{r_1}$, $\overline{r_2}$, $\overline{r_3}$ which identify the 3 atoms. These are added to give the motion of the center of mass. By a simple transformation two mass equations are obtained: one for variations of the vector $\overrightarrow{OC}$ and a second for $\overrightarrow{BA}$.

However, these are redundant, since the motion of one determines without ambiguity the motion of the other, given the hypothesis of plane motion. Each of these vector equations gives an equation for α and one for θ. It remains to choose the two most suitable.

The deflection of sulfur atoms is symmetric with respect to the vector $\vec{BA} \equiv \vec{N}$, which is parallel to the neutral axis. Forces acting on the systems are

(i) external forces acting on atom j are

$$\vec{F}_j = \vec{i} m_j u_p \delta(t - x_j/u_s), \quad j = 1, 2, 3 \tag{3.5}$$

where:

u_s = shock speed

$\delta_1 \equiv \delta(t - x_s/u_s)$

This assures that the velocity of each atom will be increased by u_p as the shock passes over it. x_j is the position of the jth atom when the shock hits it.

(ii) internal forces: F_{ij} is the force acting on the jth atom due to the presence of the ith atom.

Forces acting on atom (1) are

$$\vec{F}_1 = \vec{i} m_1 u_p \delta_1 \tag{3.6a}$$

$$\vec{F}_{21} = \frac{-\vec{S}_1}{\ell} F_{21}; \; F_{21} = \text{constant} \tag{3.6b}$$

$$\vec{F}_{31} = \frac{\vec{N}}{|\vec{N}|} F_{31} \tag{3.6c}$$

F_{31} varies with separation of atoms (1) and (3).

$$|\overline{N}| = 2\ell\cos\theta \tag{3.6d}$$

so

$$\vec{F}_{31} = \frac{\vec{N}}{2\ell\cos\theta} F_{31}$$

Similarly,

$$\vec{F}_2 = \vec{i} m_2 u_p \delta_2 \tag{3.7a}$$

$$\vec{F}_{12} = \vec{S}_1 F_{12}/\ell \tag{3.7b}$$

$$\vec{F}_{32} = \vec{S}_3 F_{32}/\ell \tag{3.7c}$$

and

$$\vec{F}_3 = \vec{i} m_3 u_p \delta_3 \tag{3.8a}$$

$$\vec{F}_{23} = -\frac{\vec{S}_3}{\ell} F_{23} = \frac{-\vec{S}_3}{\ell} F_{21} \tag{3.8b}$$

$F_{23} \equiv F_{21}$ because of the symmetry of the molecule, enforced by the condition $|\overline{S}_1| = |\overline{S}_3| = \ell =$ constant.

$$\vec{F}_{13} = -\vec{N} F_{13}/2\ell\cos\theta \tag{3.8c}$$

$$\overline{F}_{21} + \overline{F}_{23} = -\frac{F_{21}\overline{S}}{\ell} \tag{3.8d}$$

The equations of motion for the three atoms are

$$m_1\ddot{\vec{r}}_1 = \overline{F}_1 + \overline{F}_{21} + \overline{F}_{31} \quad (3.9a)$$

$$m_2\ddot{\overline{r}}_2 = \overline{F}_2 + \overline{F}_{12} + \overline{F}_{32} \quad (3.9b)$$

$$m_3\ddot{\overline{r}}_3 = \overline{F}_3 + \overline{F}_{13} + \overline{F}_{23} \quad (3.9c)$$

Eqs. (3.6b), (3.6d), (3.7b), (3.7c), (3.8b), and (3.8c) represent the central force assumption, i.e.,

$$\vec{F}_{ij} = -\vec{F}_{ji}; \quad F_{ij} = F_{ji} \quad (3.10)$$

With this condition, Eqs. (3.9) can be added to give the equation of motion for the center of mass:

$$M\ddot{\overline{r}} = \overline{F}_1 + \overline{F}_2 + \overline{F}_3 \quad (3.11)$$

where

$$M \equiv m_2 + 2m_1 \quad (3.12)$$

$$\vec{r} = [m_1(\overline{r}_1 + \overline{r}_3) + m_2\overline{r}_2]/M \quad (3.13)$$

For the present purpose, Eqs. (3.9) can be simplied by introducing the vectors, $\overline{S}_1$ and $\overline{S}_3$. Then, Eqs. (3.9) yield

$$\ddot{\overline{S}}_1 = \frac{\overline{F}_1}{m_1} - \frac{\overline{F}_2}{m_2} + \frac{\overline{F}_{21}}{m_1} + \frac{\overline{F}_{31}}{m_1} - \frac{\overline{F}_{12}}{m_2} - \frac{\overline{F}_{32}}{m_2} \quad (3.14a)$$

$$\ddot{\overline{S}}_3 = \frac{\overline{F}_3}{m_1} - \frac{\overline{F}_2}{m_2} + \frac{\overline{F}_{23}}{m_1} + \frac{\overline{F}_{13}}{m_1} - \frac{\overline{F}_{12}}{m_2} - \frac{\overline{F}_{32}}{m_2} \quad (3.14b)$$

Adding Eqs. (3.14) gives an equation for $\vec{S}$:

$$\ddot{\vec{S}} = \bar{i}u_p(\delta_1 - 2\delta_2 + \delta_3) - \frac{MF_{21}}{m_1 m_2 \ell}\vec{S} \tag{3.15}$$

Substracting (3.14b) from (3.14a) gives:

$$\ddot{\vec{N}} = -\vec{i}u_p(\delta_1 - \delta_3) - \frac{\vec{N}}{m_1\ell}\left(F_{21} + \frac{F_{31}}{\cos\theta}\right) \tag{3.16}$$

Eqs. (3.11), (3.15) and (3.16) are the equations of motion of the system with new coordinates. Now reduce to scalar equations: Eq. (3.15) becomes:

$$\ddot{\alpha}\sin\theta + 2\dot{\alpha}\dot{\theta}\cos\theta = -\frac{u_p\cos\alpha}{2\ell}(\delta_1 - 2\delta_2 + \delta_3) \tag{3.17a}$$

$$\ddot{\theta}\cos\theta - \dot{\theta}^2\sin\theta - \dot{\alpha}^2\sin\theta = \frac{u_p\sin\alpha}{2\ell}(\delta_1 - 2\delta_2 + \delta_3) - \frac{MF_{21}}{m_1 m_2\ell}\sin\theta \tag{3.17b}$$

and Eq. (3.16) gives

$$\ddot{\theta}\sin\theta - \dot{\alpha}^2\cos\theta + \dot{\theta}^2\cos\theta = -\frac{u_p\cos\alpha}{2\ell}(\delta_1 - \delta_3) - \frac{\cos\theta}{m_1\ell}[F_{21} + F_{31}/\cos_\theta] \qquad (3.18a)$$

$$\ddot{\alpha}\cos\theta - 2\dot{\alpha}\dot{\theta}\sin\theta = -\frac{u_p\sin\alpha}{2\ell}(\delta_1 - \delta_3) \qquad (3.18b)$$

For small θ , Eq. (3.17) gives

$$\theta\ddot{\alpha} + 2\dot{\alpha}\dot{\theta} = -\frac{u_p\cos\alpha}{2\ell}[\delta_1 - 2\delta_2 + \delta_3] \qquad (3.19a)$$

$$\ddot{\theta} + \omega^2\theta - \dot{\alpha}^2\theta = \frac{u_p\sin\alpha}{2\ell}[\delta_1 - 2\delta_2 + \delta_3] \qquad (3.19b)$$

where:

$$\omega^2 = \frac{MF_{21}}{m_1 m_2 \ell}$$

Eq. (18) becomes:

$$\theta\ddot{\theta} - \dot{\alpha}^2 + \dot{\theta}^2 = -\frac{u_p\cos\alpha}{2\ell}(\delta_1 - \delta_3) - \frac{\cos\theta}{m_1\ell}\left(F_{21} + \frac{F_{31}}{\cos\theta}\right) \qquad (3.20a)$$

$$\ddot{\alpha} - 2\theta\dot{\alpha}\dot{\theta} = -\frac{u_p\sin\alpha}{2\ell}(\delta_1 - \delta_3) \qquad (3.20b)$$

Eq. (3.19b) is the most convenient for evaluating θ; Eq. (3.20b) is most suitable for α. To the lowest order, (3.20b) becomes:

$$\ddot{\alpha} = -\frac{u_p\sin\alpha}{2\ell}(\delta_1 - \delta_3) \qquad (3.21)$$

$$\dot{\alpha}^2 = \frac{u_p\cos\alpha}{2\ell}(\delta_1 - \delta_3) \qquad (3.21a)$$

$$\ddot{\alpha} \;=\; -\frac{u_p \sin\alpha}{2\ell}\,(\delta_1 - \delta_3) \qquad (3.21b)$$

To the lowest order, (3.19a) yields:

$$\ddot{\alpha}\theta \;+\; 2\dot{\theta}\dot{\alpha} \;=\; -\frac{u_p \cos\alpha}{2\ell}\,(\delta_1 - 2\delta_2 + \delta_3) \qquad (3.22a)$$

$$\ddot{\theta} + \left(\frac{F_{21}M}{m_1 m_2 \ell} - \dot{\alpha}^2\right)\theta \;=\; \frac{u_p \sin\alpha}{2\ell}\,(\delta_1 - 2\delta_2 + \delta_3) \qquad (3.22b)$$

The most suitable equation for θ is (3.22b). For α, it is (3.21b). Eq. (3.21b) can be integrated directly. The results are

$$
\begin{array}{lll}
t < t_1, & \dot{\alpha} = 0, \; \alpha = \alpha_1 & \\
t_1 < t < t_3, & \dot{\alpha} = -u_p \sin\alpha_1/2\ell & \\
 & \alpha = \alpha_1 - u_p(t - t_1)\sin\alpha_1/2\ell & (3.23) \\
t < t, & \dot{\alpha} = -(u_p/2\ell)(\sin\alpha_1 - \sin\alpha_3) & \\
 & \alpha = \alpha_3 - (u_p/2\ell)(t - t_3)(\sin\alpha_1 - \sin\alpha_3) & \\
 & \alpha_3 = \alpha_1 - u_p(t_3 - t_1)\sin\alpha_1/2\ell &
\end{array}
$$

For $u_p = 0.1$ mm/μsec, $u_p/2\ell = 0.32$ radians/picosec, $t_3 - t_1 = 2\ell\cos\alpha_1/u_s$.

The value of the coefficient of θ in Eq. (3.22b) is just equal to ω^2 given in Table 2.1. Since $\omega = 75.4$ radian/psec and $\dot{\alpha} < 0.25$ radians/psec $\dot{\alpha}^2$ can be ignored and the spring constant is

$$k = 2\ell F_{21} = 22.94 \times 10^{-12} \text{ ergs} = 14.33 \text{ ev}.$$

Integration of Eq. (3.22b) shows that $\dot{\theta}$ increases discontinuously at t_1, t_2, and t_3 by the amounts

$$\Delta\dot{\theta}(t_1) = \Delta \equiv u_p \sin\alpha/2\ell$$

$$\Delta\dot{\theta}(t_2) = -2\Delta$$

$$\Delta\dot{\theta}(t_3) = \Delta$$

With the initial condition for $t < t_1$

$$\theta = \theta_o \cos\omega(t - t_1) + (\dot{\theta}_o/\omega)\sin\omega(t - t_1)$$

Solutions for Eq. (3.22b) are as follows:

$t_1 < t < t_2$:

$$\theta = \theta_o \cos\omega(t - t_1) + (\dot{\theta}_1^{\dagger}/\omega)\sin\omega(t - t_1)$$

$$\dot{\theta}_1^{\dagger} = \dot{\theta}_o + \Delta$$

$t_2 < t < t_3$

$$\theta = \theta_2 \cos\omega(t - t_2) + (\dot{\theta}_2^\dagger/\omega)\sin\omega(t - t_2)$$

$$\theta_2 = \theta_o \cos\omega\Delta t + (\dot{\theta}_1^\dagger/\omega)\sin\omega\Delta t$$

$$\dot{\theta}_2^\dagger = -\omega\theta_o \sin\omega\Delta t + \dot{\theta}_1^\dagger \cos\omega\Delta t - 2\Delta$$

$$\Delta t = t_3 - t_2 \equiv t_2 - t_1 = \ell\cos\mathring{\alpha}/u_s$$

$t > t_3$

$$\theta = \theta_3 \cos\omega(t - t_3) + (\dot{\theta}_3^\dagger/\omega)\sin\omega(t - t_3)$$

$$\theta_3 = \theta_2 \cos\omega\Delta t + (\dot{\theta}_2^\dagger/\omega)\sin\omega\Delta t$$

$$\dot{\theta}_3^\dagger = -\omega\theta_2 \sin\omega\Delta t + \dot{\theta}_2^\dagger \cos\omega\Delta t + \Delta$$

$$\dot{\theta} = -\theta_3\omega\sin\omega(t - t_3) + \dot{\theta}_3^\dagger \cos\omega(t - t_3) \qquad (3.24)$$

4. Light Absorption

The experimental observation of the effect of the shock in CS_2 is that the intensity of light absorption at a given frequency in the 2900 - 3700 Å band increases and that the width of the absorption band expands toward the red. The end purpose of this calculation must then be to understand these two experimental effects. We require a suitable average over velocity and orientation of the molecules. Proceed as follows.

Let $N(\theta,\dot{\theta})d\theta d\dot{\theta}$ be the number of oscillations in the element of phase space $d\theta d\dot{\theta}$ at any instant of time. The Boltzmann distribution of N is

$$N(\theta,\dot{\theta}) = \frac{N_o}{2\pi kT}\sqrt{IH}\, e^{-H\theta^2/2kT} e^{-I\dot{\theta}^2/2kT} \qquad (4.1)$$

The plane space for the oscillator extends to $\pm\infty$ in $\dot{\theta}$, but is bounded at $\theta = \pm\,\pi/2$. However, the value of $H/2kT$ is such that $N \simeq 0$ at these limits, so integrals over θ can be extended to $\pm\infty$.

In Eq. (4.1), N_o is the total number of oscillators per unit volume. The number of oscillators in a slab of thickness dx and of unit cross section is $N_o dx$. The number in $(\theta, \theta + d\theta)$ and $(\dot{\theta}, \dot{\theta} + d\dot{\theta})$ is

$$N(\theta, \dot{\theta})d\theta d\dot{\theta}dx$$

If $\sigma(\nu,\theta)$ is the extinction cross section of an oscillator bent at an angle θ for light of frequency ν, the total cross section in the slab is

$$N(\theta, \dot{\theta})d\theta d\dot{\theta}dx \cdot \sigma(\nu,\theta)$$

Let $N(\nu)d\nu$ = number of photons with frequency in $(\nu, \nu + \nu d)$ incident per second on unit cross section.

The corresponding energy flux is

$$I(\nu)d\nu = N(\nu)h\nu d\nu \qquad (4.2)$$

Then the power removed from the incident beam by the slab is

$$-d\nu dI(\nu) = I(\nu)d\nu\cdot\sigma(\nu,\theta)N(\theta,\dot{\theta})d\theta d\dot{\theta}dx \qquad (4.3)$$

Total power removed from the beam by all oscillations is

$$-d\int I(\nu)d\nu = dx\int I(\nu)d\nu \int d\theta \int d\dot{\theta}\sigma(\nu,\theta)N(\theta,\dot{\theta})$$

Or

$$-\frac{d}{dx}\int I(\nu)d\nu = \iiint I(\nu)\sigma(\nu,\theta)N(\theta,\dot{\theta})d\nu d\theta d\dot{\theta} \qquad (4.4)$$

The effect of θ enters into the extinction process in two ways. First, the cross section $\sigma(\nu,\theta)$ at a given frequency depends upon θ through the dipole moment of the oscillator. Secondly, the position of the red edge of the pass band depends on θ. θ, in turn, depends upon $\dot{\theta}$, so all three integrals in Eq. (4.4) require consideration.

The cross-section depends upon transition probability, B, according to the formula

$$\int \sigma(\nu)d\nu = \frac{Bh\nu}{C} = \frac{8\pi^3\nu}{3hC} M^2 \qquad (4.5)$$

where M is the dipole moment of the transition and the integral extends over the width of the transition. Since σ must be symmetric in θ, we have in general, for a given frequency,

$$\sigma(\nu) = \sum_{n=0}^{\infty} \sigma_{2n}\theta^{2n}$$

The lowest order approximation is

$$\sigma(\nu) = \sigma_2 \theta^2 \qquad (4.6)$$

and we shall consider that for the present, keeping in mind that higher order terms may be equally or more important.

The second, and more difficult point has to do with variation of band edge with θ. If we consider two potentials for vibration, as in Fig 4, one for the excited electronic state with spring constant H' and one for the ground state with constant H, we have for the minimum frequency at which transitions can occur:

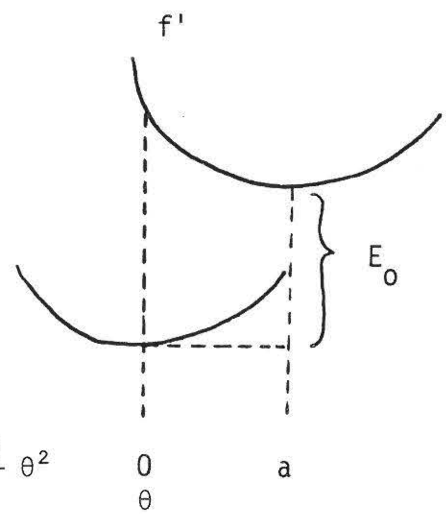


Fig. 4

"Hot" bands

$$\nu_m = \nu_o - \frac{H'a|\theta|}{h} - \frac{(H - H')}{2h}\theta^2 \qquad (4.7)$$

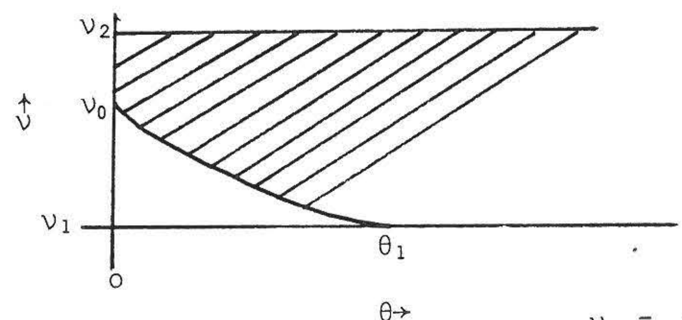
where $\nu_o = E_o/h + H'a^2/2h$ and a and E_0 have the meanings shown in figure. This expression and figure have meaning only for positive θ. The shift is assumed to be symmetric in θ.

Eq. (5) applies only to a single electronic transition at the bending angle θ. There are many transitions which define an absorption band. The integral of cross section over a band is then a sum of integrals over individual transitions. That is,

$$\int_{\nu_m}^{\nu_2} \sigma(\nu)d\nu = \sum_{n=n_m}^{n_2} \int_{\nu_n} \sigma(\nu)d\nu \tag{4.8}$$

If transitions are sufficiently dense, the sum can be replaced by an integral. With $m(\nu)d\nu$ the number of transitions in $(\nu, \nu + d\nu)$ and $a(\nu)$ the area of each one, the effective cross section becomes $m(\nu)a(\nu)$ at ν. The density of transitions varies throughout the band, but that will be ignored here.

With σ and ν_m having the meanings indicated above, the integrals over θ and ν in Eq. (4.4) map out the ν,θ plane as shown in Fig. 5.



$$-\nu_1 = \frac{E_0}{h} - \frac{ka^2}{2h}$$

Fig. 5

Integration over the ν,θ plane.

The integral is to be taken over the shaded area.

For the inital state with oscillators in thermal equilibrium at temperature T and $I(\nu)$ constant over the absorption band, Eq. (4.4) becomes

$$-\frac{dI(\nu)}{dx}\int_{\bar{\nu}_m(T)}^{\nu_2} d\nu = Q_0$$

$$Q_o = 2N_oI(\nu)\frac{\sqrt{IH}}{2\pi kT}\int_0^\infty \theta^2 C^{-H\theta^2/2kT}\,d\theta \int_{\nu_m(\theta)}^{\nu_2} \sigma_2(\nu)d\nu \cdot \int_{-\infty}^{\infty} e^{-I\dot{\theta}^2/2hT}\,d\dot{\theta} \quad (4.9)$$

The integral over $\dot{\theta}$ is $\sqrt{2\pi kT/I}$, so Eq. (4.9) becomes, with $\sigma_2(\nu)$ = constant

$$Q_o = 2N_o\sigma_2 I(\nu)\sqrt{\frac{H}{2\pi kT}}\int_0^\infty [\nu_2 - \nu_m(\theta)]\theta^2 e^{-H\theta^2/2kT}\,d\theta \quad (4.10)$$

where ν is given by Eq. (4.7). Substitution of Eq. (4.7) into (4.10) gives

$$Q_o = N_o\sigma_2 I(\nu)(q_1 + q_2 + q_3) \quad (4.11)$$

where

$$q_1 = (\nu_2 - \nu_0)2\sqrt{\frac{H}{2\pi kT}}\int_0^\infty \theta^2 e^{-H\theta^2/2kT}\,d\theta$$

$$= (\nu_2 - \nu_0)\frac{kT}{H} \quad (4.12a)$$

$$q_2 = \frac{H'a}{h}\int_0^\infty \theta^3 e^{-H\theta^2/2kT}\,d\theta$$

$$= \frac{H'a}{h}\cdot\frac{4}{\sqrt{2\pi}}\left(\frac{kT}{H}\right)^{3/2} \quad (4.12b)$$

$$q_3 = \frac{H - H'}{2h} \int_0^\infty \theta^4 e^{-H\theta^2/2kT} \, d\theta$$

$$= \frac{3(H - H')}{2h} \cdot \left(\frac{kT}{H} \right)^2 \tag{4.12c}$$

Substitution of these into Eq. (4.11) gives

$$Q_o = N_o I(\nu)\sigma_2 \left[(\nu_2 - \nu_0) \frac{kT}{H} + \frac{H'a}{h} 2\sqrt{\frac{2}{\pi}} \left(\frac{kT}{H} \right)^{3/2} + \frac{3(H - H')}{2a} \left(\frac{kT}{H} \right)^2 \right]$$

$$= N_o I \sigma_2 \overline{\theta}^2 [\nu_2 - \overline{\nu}_m(\tau)] \tag{4.13}$$

where $\overline{\theta}^2 = kT/H$ (4.14)

$$\overline{\nu}_m(\tau) = \nu_0 - \frac{2H'a}{h} \sqrt{\frac{2kT}{\pi H}} - \frac{3(H - H')}{2h} \frac{kT}{H} \tag{4.15}$$

Differentiate Eq. (4.15) to get

$$\frac{dh\overline{\nu}_m(\tau)}{d\tau} = - \frac{H'a}{H} \sqrt{\frac{2Hk}{\pi T}} - \frac{3k}{2} \left(1 - \frac{H'}{H} \right) \tag{4.16}$$

With $H' = H/2$, suggested by Kleman's work*, and H from Table 2.1, Eq. (4.16)

---

*

becomes, for $T = 300°K$,

$$\frac{dh\bar{\nu}_m(T)}{dT} = -1.29 \times 10^{-15} a - 0.1036 \times 10^{-15} \qquad (4.17)$$

Measurements of $dh\bar{\nu}_m/dT$ are not very satisfactory. Ogilvie measured a shift of the order of 15 Å from room temperature at 400°K in one of his cells. Kleman's Table I suggests a shift of about 200 Å when temperature changes from 195 to 295°K. Ogilvie's observation gives $a = 0.032$ radians, which is less than the zero point energy deflection in the ground state. Kleman's number gives 2.077 radians, which seems extraordinarily large. Kleman's gives values of a for two transitions in the region of interest: one from 2900 to 3800 Å with $a = 0.148$ radians and a weaker transition from 3300 to 4300 Å with $a = 0.384$ radians. The first of these gives

$$\frac{dh\bar{\nu}_m}{dT} = -0.285 \times 10^{-15} \text{ ergs/deg} \qquad (4.18a)$$

$$= -1.8 \times 10^{-4} \text{ ev/deg} \quad (-0.18 \text{ ev for } 100°)$$

The second gives

$$\frac{dh\bar{\nu}_m}{dT} = -0.599 \times 10^{-15} \text{ ergs/deg} \qquad (4.18b)$$

$$= -3.74 \times 10^{-4} \text{ ev/deg}$$

For comparison, 10 Å/100 deg corresponds to -0.145×10^{-15} ergs/deg. Not even the value of Eq. (4.18b) is large enough to explain the observed shift in Shot 81-010.

5. Effect of the Shock on Light Absorption

We now proceed to calculate $\overline{\theta^2}$ and $\overline{\nu}_m$ after the shock has passed over the molecule. For this purpose we use the equations for θ and $\dot{\theta}$ (3.24) in Eq. (4.9) where the average is taken over the initial angle, θ_o, and velocity $\dot{\theta}_o$. θ now depends upon $\dot{\theta}_o$, so the integration is more difficult.

From Eq. (3.24), with $t = t_3$

$$\dot{\theta} = -\omega\theta_o \sin 2\omega\Delta t + \dot{\theta}_o \cos 2\omega\Delta t + \Delta(\cos 2\omega\Delta t - 2\cos\omega\Delta t) \tag{5.1a}$$

$$\theta = \theta_o \cos 2\omega\Delta t + \frac{\dot{\theta}_o}{\omega} \sin 2\omega\Delta t + \frac{\Delta}{\omega}(\sin 2\omega\Delta t - 2\sin\omega\Delta t) \tag{5.1b}$$

Again, assuming that $\sigma_2(\nu)$ is constant, Eq. (4.9) becomes

$$Q_o = N_o I(\nu)\sigma_2 \frac{\sqrt{IH}}{2\pi kT} \int_{-\infty}^{\infty} d\theta_o \int_{-\infty}^{\infty} \theta^2(\nu_2 - \nu_m(\theta))B(\theta_o)B(\dot{\theta}_o)d\dot{\theta}_o \tag{5.2}$$

where B(x) is the Boltzmann factor and the integration limits for θ_o are $\pm\infty$ with the explicit reflection that $\nu_m(\theta)$ is even in θ (but not in $\dot{\theta}_o$).

With $\nu_m(\theta)$ again given by Eq. (4.7), we have

$$\theta^2(\nu_2 - \nu_m) = (\nu_2 - \nu_0)\theta^2 + C\theta^2|\theta| + D\theta^4 \tag{5.3}$$

where

$$C = H'a/h, \quad D = (H - H')/2h \tag{5.4}$$

Because of the symmetry of the integrals in Eq. (5.2), only those terms in Eq. (5.3) which are even in θ_o and $\dot{\theta}_o$ will survive the integration. From Eq. (5.1b),

$$\begin{aligned} \theta^2 = {} & \theta_o^2\cos^2 2\omega\Delta t + \frac{\dot{\theta}_o^2}{\omega^2}\sin^2 2\omega\Delta t + \frac{\theta_o\dot{\theta}_o}{\omega}\sin 4\omega\Delta t \\ & + \frac{\theta_o\Delta}{\omega}(\sin 4\omega\Delta t - 4\cos 2\omega\Delta t\sin\omega\Delta t) \\ & + \frac{2\Delta\dot{\theta}_o}{\omega^2}(\sin^2 2\omega\Delta t - 2\sin 2\omega\Delta t\sin\omega\Delta t) \\ & + \frac{\Delta^2}{\omega^2}(\sin 2\omega\Delta t - 2\sin\omega\Delta t) \end{aligned} \tag{5.5}$$

Before proceeding, rewrite Eq. (2) in the form

$$Q_o = N_o I(\nu)\sigma_2(q_1 + q_2 + q_3) \tag{5.6}$$

where

$$q_1 = (\nu_2 - \nu_0)\frac{\sqrt{IH}}{2\pi kT}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\theta^2 B(\theta_o)B(\dot{\theta}_o)d\theta_o d\dot{\theta}_o \tag{5.7a}$$

$$q_2 = \frac{H'a}{h}\frac{\sqrt{IH}}{2\pi kT}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\theta^2|\theta|B(\theta_o)B(\dot{\theta}_o)d\theta_o d\dot{\theta}_o \tag{5.7b}$$

$$q_3 = \frac{H - H'}{2h}\frac{\sqrt{IH}}{2\pi kT}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\theta^4 B(\theta_o)B(\dot{\theta}_o)d\theta_o d\dot{\theta}_o \tag{5.7c}$$

We need the following integrals:

$$\frac{\sqrt{IH}}{2\pi kT}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}B(\theta_o)B(\dot{\theta}_o)d\theta_o d\dot{\theta}_o = 1 \tag{5.8a}$$

$$\frac{\sqrt{IH}}{2\pi kT}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\theta_o^2 B(\theta_o)B(\dot{\theta}_o)d\theta_o d\dot{\theta}_o =$$

$$= \frac{\sqrt{H}}{\sqrt{2\pi kT}}\int_{-\infty}^{\infty}\theta_o^2 B(\theta_o)d\theta_o = \frac{kT}{H} \tag{5.8b}$$

$$\frac{\sqrt{IH}}{2\pi kT}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\theta_o^4 B(\theta_o)B(\dot{\theta}_o)d\theta_o d\dot{\theta}_o = 3\left(\frac{kT}{H}\right)^2 \tag{5.8c}$$

$$\frac{\sqrt{IH}}{2\pi kT}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\dot{\theta}_o^2 B(\dot{\theta}_o)B(\theta_o)d\dot{\theta}_o d\theta_o = \frac{kT}{I} \tag{5.8d}$$

$$\frac{\sqrt{IH}}{2\pi kT}\int_{\infty}^{\infty}\int_{\infty}^{\infty}\dot{\theta}_o^4 B(\dot{\theta}_o)B(\theta_o)d\dot{\theta}_o d\theta_o = 3\left(\frac{kT}{I}\right)^2 \tag{5.8e}$$

$$\frac{\sqrt{IH}}{2\pi kT}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\dot{\theta}_o^2\theta_o^2 B(\theta_o)B(\dot{\theta}_o)d\theta_o d\dot{\theta}_o = \frac{(kT)^2}{IH} \tag{5.8f}$$

It is convenient to introduce coefficients:

$$\begin{aligned}
a_1 &= \cos^2 2\omega\Delta t \\
a_2 &= \sin^2 2\omega\Delta t/\omega^2 \\
a_3 &= \sin 4\omega\Delta t/\omega \\
a_4 &= \Delta(\sin 4\omega\Delta t - 4\cos 2\omega\Delta t \sin\omega\Delta t)/\omega \\
a_5 &= 2\Delta(\sin^2 2\omega\Delta t - 2\sin 2\omega\Delta t \sin\omega\Delta t)/\omega^2 \\
a_6 &= \Delta^2(\sin 2\omega\Delta t - 2\sin\omega\Delta t)^2/\omega^2
\end{aligned} \tag{5.9}$$

Then, Eq. (5.5) can be written

$$\theta^2 = a_1\theta_o^2 + a_2\dot{\theta}_o^2 + a_3\theta_o\dot{\theta}_o + a_4\theta_o + a_5\dot{\theta}_o + a_6 \tag{5.10}$$

Note the following relations:

$$\begin{aligned}
a_1 + \omega^2 a_2 &= 1 \\
a_4^2 + \omega^2 a_5^2 &= 4a_6 \\
a_3^2 &= 4a_1 a_2 \\
\omega^2 &= H/I : \quad \frac{1}{I} = \frac{\omega^2}{H}
\end{aligned}$$

Then, applying Eq. (5.8)

$$q_1 = (\nu_2 - \nu_0)\left(a_1\frac{kT}{H} + a_2\frac{kT}{I} + a_6\right)$$

$$I = H/\omega^2 \text{ and } a_1 + a_2\omega^2 = 1, \text{ so this becomes}$$

$$q_1 = (\nu_2 - \nu_0)\left(\frac{kT}{H} + a_6\right) \tag{5.11}$$

q_3 is obtained by integrating even terms of θ^4, obtained by squaring Eq. (5.10):

$$q_3 = \frac{H - H'}{2h}\left[3\left(\frac{kT}{H}\right)^2 + 6a_6\frac{kT}{H} + a_6^2\right]$$

$$= \frac{H - H'}{2h}\left[3\left(\frac{kT}{H} + a_6\right)^2 - 2a_6^2\right] \tag{5.12}$$

Evaluation of q_2, Eq. (5.7b) is hard because $|\theta|$ is an irrational function of θ_o and $\dot{\theta}_o$. It will be treated in a very approximate manner here. According to the theorem of the mean for integrals, q_2 can be written

$$q_2 = \frac{H'a}{h}\frac{\sqrt{IH}}{2\pi kT}\,\overline{|\theta|}\int_{\infty}^{\infty}\int_{\infty}^{\infty}\theta^2 B(\theta_o)B(\dot{\theta}_o)d\theta_o d\dot{\theta}_o \tag{5.13}$$

Since $|\theta|$ is non-vanishing at $\theta_o = \theta_o = \theta$, its presence under the integral increases the value of the integrand in the neighborhood of the origin proportionately more than at some distance from the origin. This suggests, then, that if $|\overline{\theta}|$ is taken to be the square root of $\overline{\theta^2}$, q_2 will be overestimated slightly. This value will be assumed for the sake of simplicity. Then,

$$q_2 = \frac{N'a}{h} \left(\overline{\overline{\theta^2}}\right)^{3/2}$$

$$= \frac{H'a}{h} \left(\frac{kT}{H} + a_6 \right)^{3/2} \qquad (5.14a)$$

When Eq. (14) with $a_6 = 0$ is compared with Eq. (4.12b), it is apparent that q_2 is underestimated. This error can be remedied in the limits $a_6 = 0$ and $T = 0$ by taking q_2 to be

$$q_2 = \frac{H'a}{h} \left(d\,\frac{kT}{H} + a_6 \right)^{3/2} \qquad (5.14b)$$

where $d = \dfrac{4}{\sqrt{2\pi}} \simeq 1.366$.

Collecting results we have

$$Q_0 = N_0 I(\nu) \sigma_2 (q_1 + q_2 + q_3) \qquad ($$

where

$$q_1 = (\nu_2 - \nu_0)\left(\frac{kT}{H} + a_6\right) \qquad ($$

$$q_2 = \frac{H'a}{h}\left(d\,\frac{kT}{H} + a_6\right)^{3/2} \qquad ($$

$$q_3 = \frac{H - H'}{2h}\left[3\left(\frac{kT}{H} + a\right)^2 - 2a_6^2\right] \qquad ($$

where

$$d = 4/\sqrt{2\pi} \sim 1.366$$

with

$$\bar{\theta}^2 = \left(\frac{kT}{H} + a_6\right) = \bar{\theta}_o^2(1 + Ha_6/kT) \qquad ($$

Eq. (6) can be written

$$Q_o = N_o I(\nu)\bar{\theta}^2[\nu_2 - \bar{\nu}_m]$$

where

$$\nu_m = \nu_o - \frac{H'a}{h}\left(d\,\frac{kT}{h} + a_6\right)^{3/2}\left(\frac{kT}{H} + a_6\right)^{-1}$$
$$- \frac{H - H'}{2h}\left[3\left(\frac{kT}{H} + a_6\right) - 2a_6^2\left(\frac{kT}{H} + a_6\right)^{-1}\right] \qquad ($$