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Publication Date

1977-04-01

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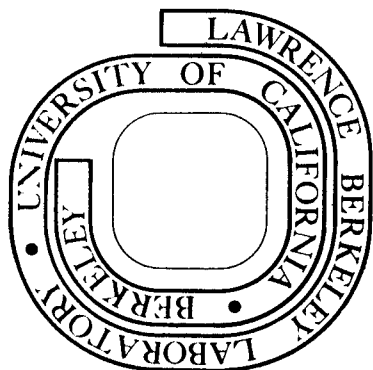C. B. Harris, R. M. Shelby, and P. A. Cornelius

April 20, 1977

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Effects of Energy Exchange on Vibrational

Dephasing Times in Raman Scattering

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Abstract

It is shown that the Raman lineshape function and/or vibrational dephasing times can reflect random frequency modulation of high frequency vibrational modes via exchange with low frequency modes. When exchange is incorporated into the vibrational correlation function, lifetimes and scattering rates between modes can be quantitatively determined from the temperature dependence of the spontaneous Raman spectrum. Finally, some experimental results on vibrational redistribution are presented which demonstrate the salient features of the theory.

The effects of molecular interactions and molecular motion are
fundamental to an understanding of vibrational relaxation and re-
distribution in liquids and solids. Until recently, most of the
information on vibrational dephasing and relaxation has come from an
analysis of the spontaneous Raman linewidth and lineshape. Since Gordon[1]
first represented the Raman lineshape as the Fourier transform of a
polarizibility autocorrelation function, investigations have concentrated
on separating the effect various relaxation pathways have on the time
decay of the correlation function. In general terms it is thought that
contributions to the vibrational part of the correlation function
decay via "inelastic scattering" events which cause relaxation or
redistribution of the excited vibrational population among other
degrees of freedom (T_1 processes) and "elastic scattering" events
which randomly modulate the vibrational phase (T_2 processes).

Recent experiments by von der Linde, Laubereau and Kaiser[2] have
separated the two contributions in the case of symmetric C-H stretching
modes in a variety of liquids. The results of their experiments on
vibrational dephasing have been interpreted essentially the same as
the spontaneous Raman lineshape function has been interpreted.
Specifically, the decay time of the vibrational correlation function
is obtained from a convolution of their laser pulse shape with an
assumed vibrational correlation function whose Fourier transform is
related to a Lorentz spontaneous Raman lineshape function. Both the
interpretation of the Raman lineshape and the deconvolution of the

vibrational dephasing time from stimulated Raman scattering assume that all phase memory is lost during the elastic scattering process or during the inelastic scattering process and thus resulting linewidths, determined by T_1 or T_2, represent the "true" decay time of the autocorrelation function.

In this letter we would like to demonstrate that the neglect of phase memory in the scattering process can in many instances lead to serious misinterpretations of the vibration correlation function for spontaneous and stimulated Raman scattering. Furthermore, we will demonstrate that the incorporation of inter or intramolecular energy exchange into the vibration correlation function allows one to extract (i) the mechanisms responsible for vibrational dephasing and relaxation when energy exchange is important (ii) a quantitative measure of the scattering times or rate constants between normal modes (iii) the lifetime in the higher energy states to which vibrational quanta are scattered, and (iv) a semi-quantitative measure of the inter or intra-molecular interaction that couples the dominant channels responsible for vibrational dephasing. The approach is valid for both spontaneous and stimulated scattering with some minor modifications. Finally, we will present some preliminary experimental results on the vibrational redistribution in the C-H stretches in 1,2,4,5-tetramethylbenzene which demonstrate the salient features of the theory.

The application of exchange to vibrational dephasing and relaxation is shown in figure 1. For simplicity we assume that one channel low V' is responsible for scattering in a given temperature

range. We separate relaxation to lower states (the normal T_1 channels) from scattering between the initial state V and some other vibrational mode V'. The frequencies of the two modes that are associated with V and V' are coupled via exchange and are taken to be ω_0 and $\omega_0 + \delta\omega$ respectively. It should be noted that $\delta\omega$ can be either positive or negative depending on the nature of the inter or intramolecular coupling, and that the vibrational state V associated with the frequency $\omega_0 + \delta\omega$ is at an energy E_i <u>above</u> the initial state. The scattering rates responsible for vibrational energy exchange are given as W_+ and W_- respectively and the lifetime in V' is given simply as $\tau = (W_-)^{-1}$ as illustrated.

The effects of such scattering on the Raman spectrum can be calculated from two approaches. Exchange can be incorporated into the decay of the vibrational correlation function using Kubo[3] and Anderson[4] theory or the exchange term can be incorporated into the density matrix equations of motion for Raman scattering in a manner similar to the modified Bloch equations[5]. For spontaneous Raman scattering Kubo-Anderson theory is sufficient to realistically define the problem. In terms of the polarizibility correlation function[1,6], the intensity of scattered light with a Raman frequency ω is given by:

$$I(\omega) \sim \int_{-\infty}^{\infty} \exp(-i\omega t) <(\vec{\varepsilon}_S \cdot \overleftrightarrow{\alpha}(0) \cdot \vec{\varepsilon}_I) \quad (\vec{\varepsilon}_S \cdot \overleftrightarrow{\alpha}(t) \cdot \vec{\varepsilon}_I)>_0 <Q(0)\, Q(t)>_V \, dt$$

$$(1)$$

where the correlation function has been separated into an orientational (o) and a vibrational (v) contribution. $\alpha(t)$ is the Raman tensor for the

-4-

transition of interest, $Q(t)$ the normal coordinate, and ϵ_S and ϵ_I are the polarization vectors of the scattered and incident light.

If the interaction which is responsible for the frequency shift $\delta\omega$ does not appreciably mix different normal modes, off-diagonal elements are small and the effect of the scattering at rates W_+ and W_- can be written in terms of a time-dependent vibrational frequency $\omega_v(t)$. In this case

$$Q(t) = Q(o) \exp \left(i \int_0^t \omega_v(t') \, dt' \right) \tag{2}$$

and the correlation function is given by

$$\langle Q(o) \, Q(t) \rangle = \langle \exp \left(i \int_0^t \omega_v(t') dt' \right) \rangle \equiv \phi(t) \tag{3}$$

If the W_+ and W_- are constant in time, $\omega_v(t')$ is a Markoffian random function and $\phi(t)$ is given by[4]:

$$\phi(t) = \underline{W} \cdot \exp \left(i\omega_v + \Pi \right) \cdot \underline{1} \cdot \tag{4}$$

The matrix ω_v is diagonal and contains the possible values of $\omega_v(t)$ and

the transition matrix $\underset{\approx}{\Pi}$ incorporates the rates of transitions between these values. $\underset{\sim}{W}$ is a row vector consisting of the steady state probability distribution of $\omega_v(t)$, while $\underset{\sim}{1}$ is a column vector whose elements are all unity. Aside from other contributions to the total correlation function, the spectral lineshape is given by:

$$I(\omega) \sim \int_{-\infty}^{\infty} \exp(-i\omega t) \; \underset{\sim}{W} \cdot \exp[t(i\omega_{\underset{\approx}{v}} + \underset{\approx}{\Pi})] \cdot \underset{\sim}{1} \, dt \qquad (5)$$

$$= Re[\underset{\sim}{W} \cdot \underset{\approx}{A}^{-1} \cdot \underset{\sim}{1}]$$

where $\underset{\approx}{A} = i \, (\omega_{\underset{\approx}{v}} - \omega \underset{\approx}{I}) + \underset{\approx}{\Pi}$.

For the situation depicted in Fig. 1, one can show that the lineshape is given in the low power, low temperature limit by a Lorentz lineshape function:

$$I(\omega) = [1 + (\omega - \omega_e)^2 T_{eff}^2]^{-1} \qquad (6)$$

The rates for vibrational energy exchange are incorporated into the

effective frequency,

$$\omega_e = \omega_o + (\delta\omega \, W_+ \tau) / (1 + (\delta\omega)^2 \tau^2) \qquad (7)$$

and the effective relaxation time,

$$(T_{eff})^{-1} = T_1^{-1} + T_2^{-1} + W_+ (\delta\omega)^2 \tau^2 / (1 + (\delta\omega)^2 \tau^2) \qquad (8)$$

where T_1 processes to lower states and homogeneous T_2 processes associated with the vibrational state are included. Physically, vibrational energy exchange introduces two features into Raman spectra. The first is a shift of the transition frequency with temperature which reflects the time averaged contribution the upper V' state makes to the lower V state's vibrational frequency via phase memory. This is given by equation (7). The second feature is a temperature dependent line broadening that relates the rate at which the lower state V scatters to the upper state V' causing a <u>partial</u> relaxation of phase memory as given by equation (8).

It should be noted that if the vibration scatters to some state and returns to V only after a time long relative to $(\delta\omega)^{-1}$, then all phase memory is lost from scattering. The transition linewidth would be

broader in this case than in the intermediate exchange regime ($\delta\omega\tau\sim1$) and no frequency shift would result. The temperature dependent frequency shift is the characteristic feature of the spectrum, which, from an experimental point of view, is evidence for vibrational exchange between two or more normal modes. Indeed when both the temperature dependent broadening and the temperature dependent frequency shifts are analyzed, one obtains (i) W_+, which is a direct measure of the scattering rate constant from V to V'; (ii) τ, the population relaxation time in V'; (iii) E_i, the energy separation between V' and V, and (iv) $\delta\omega$, the frequency shift in V'. These quantities are otherwise difficult to obtain and reveal a considerable amount of information about vibrational redistribution and relaxation in liquids and solids.

To demonstrate these points we present the temperature dependence of the spontaneous Raman linewidth and frequency shift for one of the C-H stretching modes (2930 cm^{-1}) in solid 1,2,4,5 tetramethylbenzene in figure 2 and 3 respectively. As is illustrated in the figures, the spontaneous linewidth is observed to broaden slightly in the range 30°K to 100°K and rapidly from 100°K to room temperature. The temperature dependent broadening in the higher temperature region shows (cf. figure 2b) an exponential dependence having $E_i = 227 \pm 12$ cm^{-1}.

An analysis of the Raman frequency shift as illustrated in figure 3b also show a similar temperature dependence with $E_i = 218 \pm 45$ cm^{-1}. The presence of both the broadening and shift each having the same E_i, <u>establishes</u> that the C-H stretch is exchanging its energy with a vibrational mode 225 cm^{-1} higher and that phase memory of the upper state is retained in the scattering causing the center of the transition to shift.

The mode to which the C-H stretch is exchanging its energy is almost certainly a torsional motion of the methyl group about the carbon-methyl bond. For tetramethylbenzene, where methyl groups are adjacent, one quanta of torsion has been assigned at 190 cm^{-1}.[7] In this instance the scattering rate W_+ would be expected to depend on temperature as $W_+ = \tau^{-1} \exp(-E_i/kT)$ where $E_i \approx \omega_{torsion}$. This leads to the observed temperature dependence of the linewidth and frequency shift:

$$\Delta = [\delta\omega/(1+(\delta\omega)^2\tau^2)] \exp(-E_i/kT) \qquad (9)$$

$$(T_2^{eff})^{-1} = [(\delta\omega)^2\tau/(1+(\delta\omega)^2\tau^2)] \exp[-E_i/kT] \qquad (10)$$

This interpretation is also consistent with the observation that the only intramolecular   lattice frequencies near 200 cm^{-1} are the methyl

torsions. In addition, an interaction between the torsion and C-H
stretch is highly plausible, and similar line broadening and
frequency shifts are observed for other C-H modes in this region
(not shown). Four bands between 2920 cm^{-1} and 3000 cm^{-1} appear as
the result of the non-C_{3v} environment of the methyl groups which lifts
a two-fold degenenacy. Qualitatively speaking, the torsional motion
tends to average the environment of the three protons somewhat, and
the magnitudes and signs of the frequency shifts reflect this. Indeed,
the four bands shift toward each other with increasing temperature
but persist into the liquid phase.

Applications of equations (9) and (10) to the data in Figs. 2 and
3 allows us to determine the parameters $\delta\omega$ and τ . One finds $\delta\omega$= 14$\pm$2 cm^{-1}
and τ= 0.18 psec. These very interesting quantities would be difficult
to determine using another method. $\delta\omega$ gives the strength of the
interaction between the torsional mode and the C-H stretching mode,
and in this instance is probably due principally to intramolecular
effects. τ is a population relaxation time for the torsion which,
unlike linewidth measurements, is not obscured by contributions from
dephasing.

Finally, the scattering time $(W_+)^{-1}$ can be determined from the data.
At 30°K it is 8.7 nsec while at room temperature it is 0.54 psec.
It should be noted at this point that this mode also shows stimulated
Raman scattering at low temperature, however the dominate mode
that appears in the stimulated Raman spectrum at higher temperatures

is an A mode in C_{3v} at 2912 cm^{-1}. This A mode does not exhibit any appreciable temperature dependence and has dephasing time, T_2= 0.75 psec[8]. Presumably the A mode does not strongly couple to the torsions.

In conclusion, we feel that this formalism may find wide applicability in vibrational spectroscopy for the study of interactions between one normal mode and another and may be particularly important for conformational motions which interact with other vibrational modes through intermolecular interactions. In addition, the data demonstrates that caution must be exercised in interpreting dephasing times of even seemingly homogeneous linewidths without knowing whether or not vibrational energy exchange is important since only partial dephasing results from a single scattering event.

Figure Captions

Figure 1: Energy levels for vibrational exchange between state V and V'. A vibrational mode of frequency ω_0 and vibrational quantum number n_v interacts with some low frequency mode (quantum number n_t) such that excitation of the low frequency mode shifts the frequency by $\delta\omega$. Excitation and de-excitation occur with rates W_+ and $W_- = \tau^{-1}$.

Figure 2: (a) The linewidth temperature dependence contains an approximately constant contribution and a contribution above $\sim30^{\circ}K$ due to exchange. (b) The exchange contribution displays an activation energy near the methyl group torsional frequency.
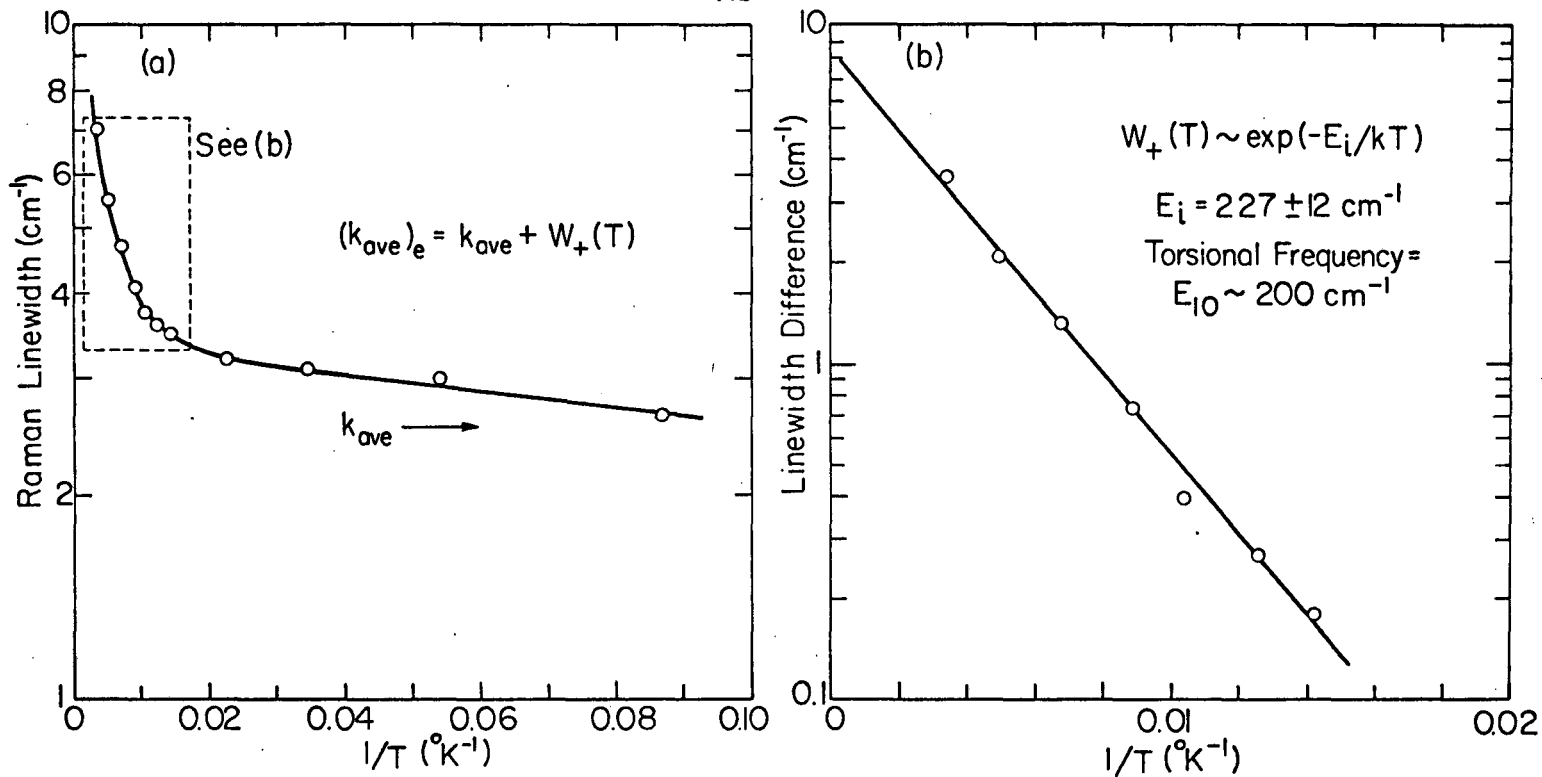
Figure 3: The Raman frequency is shown as the function of temperature on the left. The frequency shift (on the right) displays the same activation energy as the line broadening.
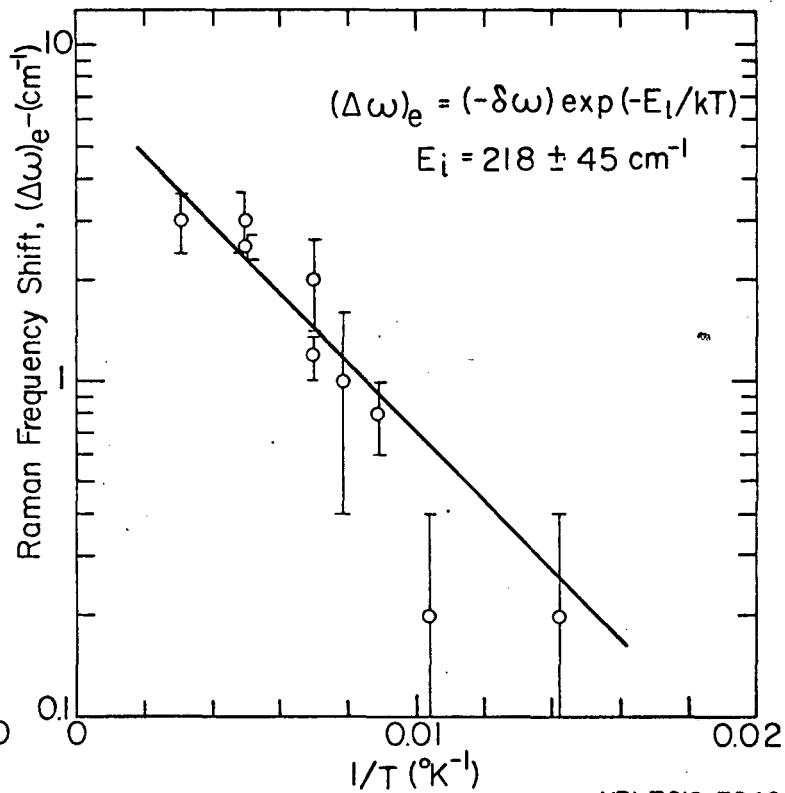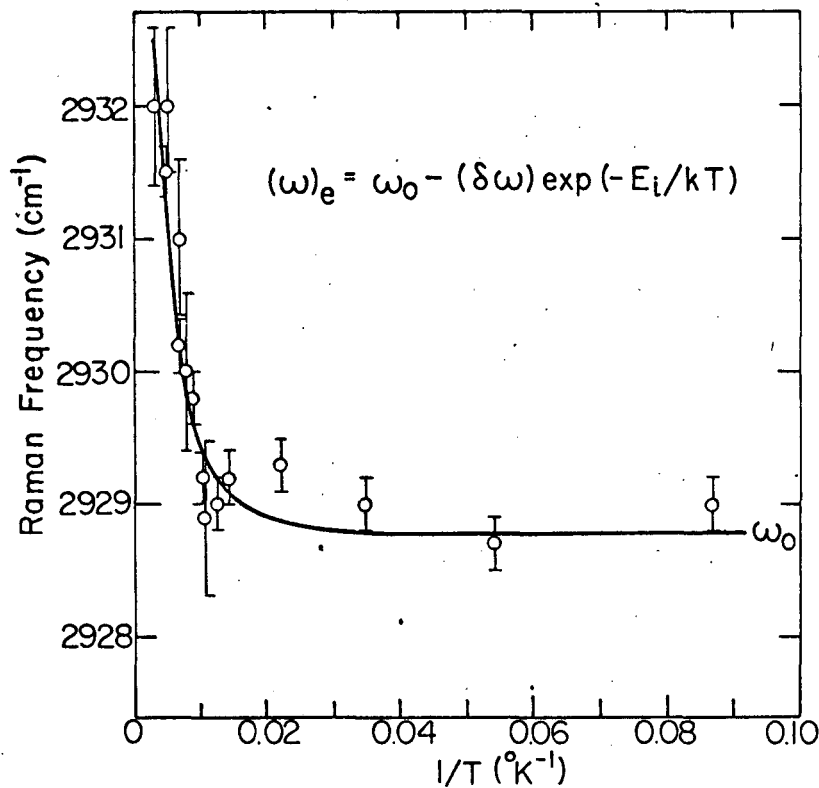
VIBRATIONAL ENERGY EXCHANGE
BETWEEN COUPLED STATES

W_+ = Scattering rate from V

τ = Lifetime in V'

$n_v = 0, n_t = 1$

$n_v = 0, n_t = 0$ —Ground State
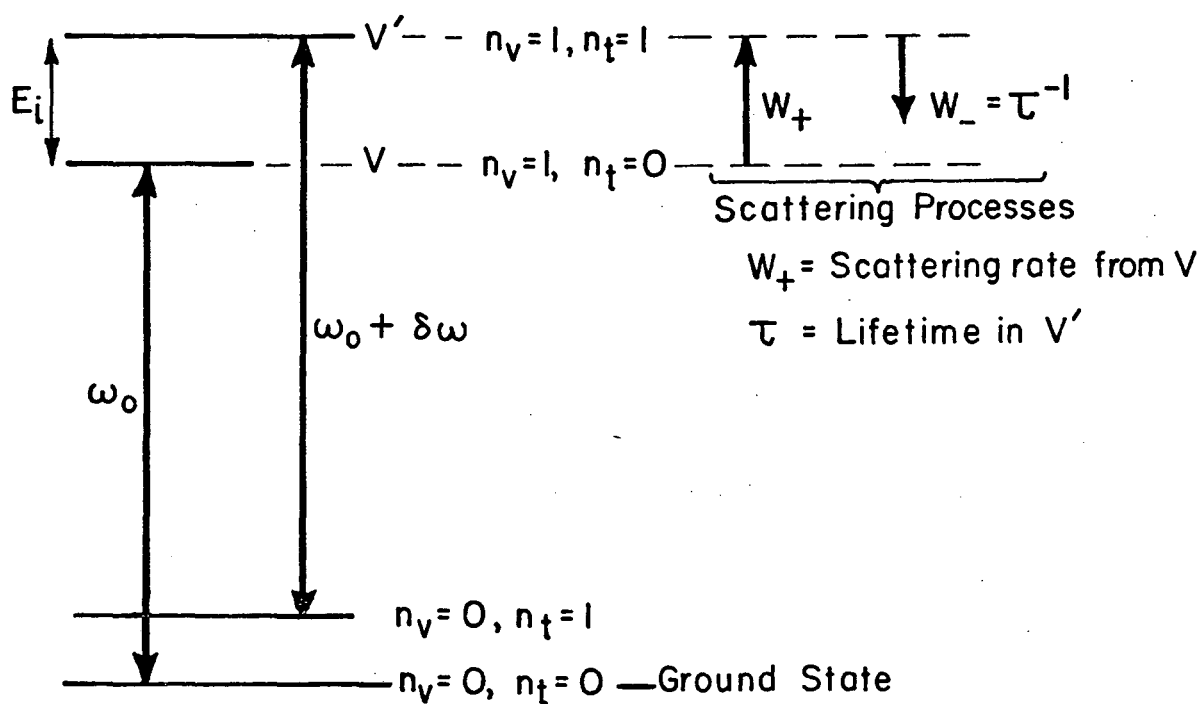
XBL 774-5291

TEMPERATURE DEPENDANCE OF RAMAN LINEWIDTH FOR THE DURENE METHYL C-H STRETCH
(ω_{vib} = 2932 cm^{-1})

(a)

See (b)

$(k_{ave})_e = k_{ave} + W_+(T)$

$k_{ave} \longrightarrow$

Raman Linewidth (cm^{-1})

1/T (°K^{-1})

(b)

$W_+(T) \sim \exp(-E_i/kT)$

$E_i = 227 \pm 12$ cm^{-1}

Torsional Frequency =
$E_{10} \sim 200$ cm^{-1}

Linewidth Difference (cm^{-1})

1/T (°K^{-1})

XBL 7612-7945

TEMPERATURE DEPENDENT RAMAN FREQUENCY SHIFT FOR THE DURENE METHYL C-H STRETCH
(ω_{vib} = 2932 cm^{-1})

$$(\omega)_e = \omega_0 - (\delta\omega)\exp(-E_i/kT)$$

$$(\Delta\omega)_e = (-\delta\omega)\exp(-E_i/kT)$$

$$E_i = 218 \pm 45 \text{ cm}^{-1}$$

XBL7612-7946

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8. As measured using the method of Ref. 2.

UJ , J ɹ / . J / ., ɔ