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VIBRATIONAL DEPHASING OF POLYATOMIC MOLECULES IN CONDENSED PHASES. II. TEMPERATURE DEPENDENCE OF RAMAN SPECTRAL LINES RESULTING FROM ENERGY EXCHANGE IN 1,2,4,5-TETRAMETHYLBENZENE

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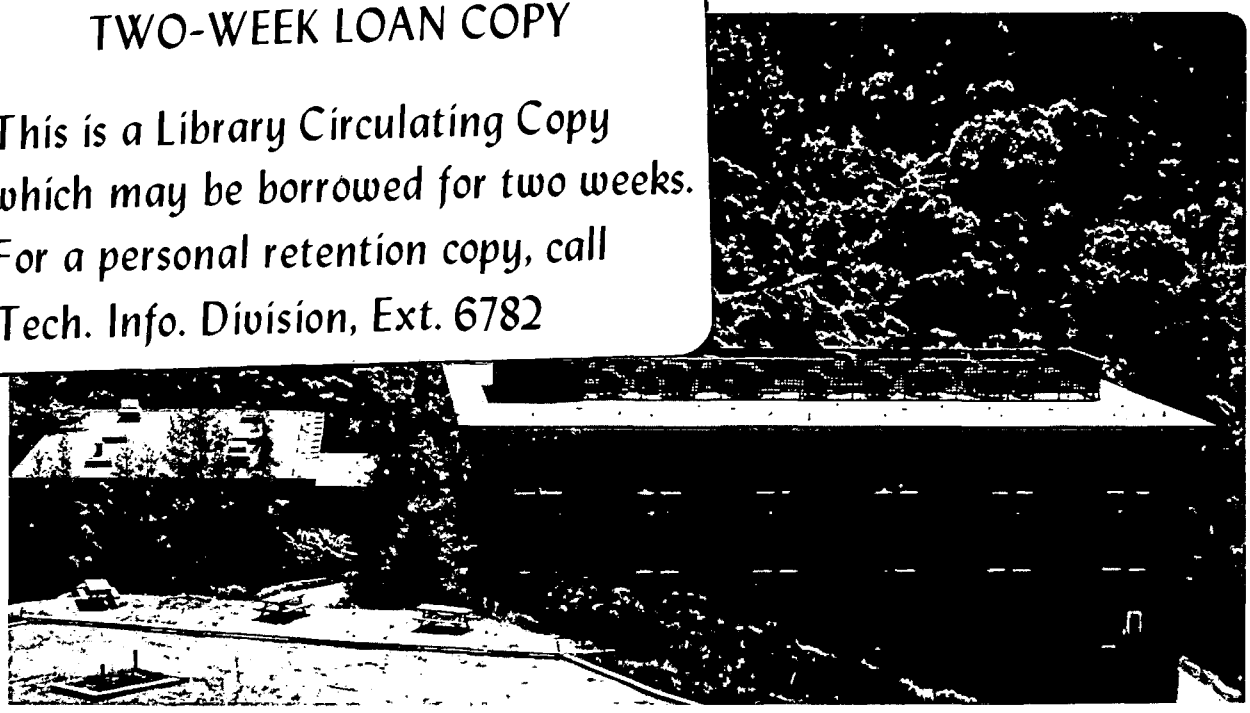

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VIBRATIONAL DEPHASING OF POLYATOMIC MOLECULES IN CONDENSED PHASES. II. TEMPERATURE DEPENDENCE OF RAMAN SPECTRAL LINES RESULTING FROM ENERGY EXCHANGE IN 1,2,4,5-TETRAMETHYLBENZENE

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ABSTRACT

In several previous publications[1,2,3] an exchange theory for vibrational dephasing was developed in which the exchange phenomenon manifests itself as a temperature-dependent line broadening and frequency shift of the Raman or infrared transitions. The Raman spectrum of 1,2,4,5-tetramethyl benzene has been found to exhibit this effect, and has been studied in detail in the C-H stretch region from 11.5°K to 300°K. This data is presented, along with an analysis using the Raman lineshape function obtained from exchange theory. The molecular parameters obtained are presented, and the results are discussed in terms of anharmonic coupling of high-energy C-H stretch modes with lower-energy methyl motions. The observations suggest that the simple model of a high-energy mode interacting with a single low-energy mode is sufficient in this case, and mechanisms are proposed to explain the observed couplings.

I. Introduction

Vibrational spectroscopy of molecules in condensed phases and its interpretation is often rendered difficult by the numerous interactions present. A large body of theoretical work currently exists which bears upon this problem. The approaches most closely related to the present discussion[1-3, 5-28] all involve the use of a stochastic description of the physical processes which influence the lineshape. Whereas much of this work has addressed questions specifically related to the problem of vibrational dynamics in condensed phases, other treatments of energy transfer and dephasing processes[7-10, 22-24, 26] are also useful to understanding vibrational spectra. In particular, theories originally developed for magnetic resonance[7-9] and extended to electronic spectroscopy[10] have been further expanded in our previous work[1-3], and here are applied to a particular problem in Raman spectroscopy.

A Raman line measured in a solid or liquid contains contributions from population relaxation (T_1 processes), dephasing (T_2 processes), and inhomogeneous broadening; thus, the study of some particular interaction of interest may frequently be impeded by the presence of other effects. Experimental techniques such as stimulated Raman scattering using picosecond pulses[4,6] have been developed which allow the separation of T_1 and T_2 processes under certain conditions. Despite these successes, the picosecond laser methods are limited in their applications to only those vibrations which exhibit stimulated Raman gain.

Recently,[1,3] it was demonstrated that the temperature dependence of spontaneous Raman scattering can serve as a powerful means for investigating detailed molecular dynamics when energy exchange between

coupled vibrational modes dominates the dephasing channels. Intermolecular energy exchange manifests itself as a temperature-dependent change in linewidth and peak frequency. In an earlier publication,[2] we presented an analysis of one CH stretching mode in 1,2,4,5-tetramethyl benzene (durene), from which we were able to determine the dephasing mechanism in detail. In short, we were able to separate the lineshape into two components: a residual linewidth and peak frequency present in the low-temperature limit, plus a temperature-dependent broadening and frequency shift caused by the exchange process.

For the exchange phenomenon to be an important factor in a lineshape, several conditions must be met. For simplicity, we will assume that the lineshape to be studied is a high-frequency vibrational mode, although the discussion may readily be extended to other systems. Insofar as the vibrational motion can be regarded as a harmonic oscillator, excitations and relaxations of other vibrational modes do not affect its resonance frequency. In reality, however, the motion will contain anharmonicities which couple the given mode to other modes of the molecule. This coupling may cause significant shifts in the energy levels, in which case excitations and relaxations of the other modes will modulate the resonance frequency of the mode of interest. If we restrict the discussion to the case of two interacting modes, one of high frequency and the other of low frequency, we will have an energy level scheme described by Fig. 1.

If the energy needed to excite the low frequency mode (E_a) is on the order of kT, thermal population and depopulation of the state labelled (0,1) will occur. This will cause the resonance frequency

of the high-frequency mode to jump between two values, ω and $\omega + \delta\omega$. This physical situation can now be treated using exchange theory. The important parameters for this problem are W_+, the promotion rate for the low-frequency mode; $\delta\omega$, the frequency difference between the two transitions; and τ, the lifetime of the low-frequency mode. The dimensionless quantity $\delta\omega\tau$ allows the three exchange regimes to be distinguished: (1) $\delta\omega\tau << 1$, fast exchange; (2) $\delta\omega\tau \approx 1$, intermediate exchange; (3) $\delta\omega\tau >> 1$, slow exchange. In the slow exchange limit, the process of excitation and relaxation of the low energy mode represents complete loss of phase memory. In this case, the transition rate W_+ represents the true dephasing rate for the system and will be directly related to the linewidth. There will be two lines appearing in the spectrum, at ω and $\omega + \delta\omega$. In the fast exchange limit, the excitation and de-excitation of the low frequency mode causes negligible loss of phase memory, and therefore one will observe a single line, with an effective resonance frequency between and $\omega + \delta\omega$. The scattering rate, W_+, does not represent the dephasing rate, and the linewidth will reflect the presence of "exchange narrowing." In the intermediate regime, partial phase memory is retained in the scattering process, leading to a temperature dependence for the spectrum. As the temperature is increased, W_+ will increase and result in a broadening of the line and a shift in resonance frequency.

The usefulness of the distinction among slow, intermediate, and fast exchange arises from the fact that the quantity $\delta\omega\tau$ is easily measured experimentally from the temperature dependence of the spontaneous Raman spectrum.

In what follows, we will demonstrate that the systems which we have studied are in intermediate exchange, and that the exchange theory is sufficient to account for the observed temperature dependence of the spectrum. We will present our results for five vibrational modes in durene, and show how those results suggest a somewhat surprising scheme for the coupling of high-frequency and low-frequency vibrations in this molecule. Finally, we will discuss some possible mechanisms for this coupling.

II. Theoretical Summary

A careful treatment of the theoretical aspect of the problem has been presented elsewhere.[3] Here we will summarize the important features of that theory as they pertain to the results we have obtained. The type of system to which exchange theory is applicable can be described in terms of a three-part Hamiltonian, $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_p + \mathcal{H}_{ex}$. The zero-order Hamiltonian, $\mathcal{H}_0$, is associated with the energy levels of the molecule; $\mathcal{H}_p$, the perturbation Hamiltonian, causes shifts in energy of the levels of $\mathcal{H}_0$; and $\mathcal{H}_{ex}$ modulates the energy of the levels by imposing a time dependence on $\mathcal{H}_p$. Any formulation of exchange theory has as its goal the calculation of the autocorrelation function for the transition of interest. Although several treatments of exchange theory exist,[7-11] they share the common assumption that the exchange process can be described by a Markoffian random function of time. Under this assumption, we have shown that a treatment based on the use of coupled density matrices, and the earlier treatment of Anderson,[8] yield the same equation for the vibrational autocorrelation function:

$$\frac{Q_A(t)}{Q_A(o)} = \underset{\sim}{1} \cdot \exp t(i\omega_v + \underset{\approx}{\pi}) \cdot \underset{\sim}{W_0} \qquad (1)$$

where $\underset{\sim}{W_0}$ gives the initial population distribution, ω_v gives the transition frequencies, and $\underset{\approx}{\pi}$ is derived from the transition rates.

The form which the Hamiltonian must take in our case can be seen by again referring to Fig. 1. $\mathcal{H}_0$ will be a harmonic oscillator Hamiltonian, while $\mathcal{H}_p$ may be obtained by expanding the vibrational potential as a power series. $\mathcal{H}_p$ will be the anharmonic term in this

expansion, namely:

$$\mathcal{H}_p = \sum C_{ijk}Q_iQ_jQ_k + \sum C_{ijkl}Q_iQ_jQ_kQ_l + \ldots \tag{2}$$

where the Q's are the normal vibrational coordinates. $\mathcal{H}_p$ has the effect of shifting the levels of $\mathcal{H}_0$ and creating the frequency difference $\delta\omega$. Finally, $\mathcal{H}_{ex}$ causes transitions in the low-frequency mode, and is assumed to be a random function of time characterized by the upward transition rate W_+, and the lifetime, τ, of the upper state.

When the above parameters are inserted in Eq. (1) and the Fourier transform is taken, the following equation results for the lineshape:

$$I(\omega) = \frac{W_+(\delta\omega)^2/(1 + W_+\tau)}{[\omega'^2 - (\delta\omega/2)^2]^2 + [W_+(\omega' + \delta\omega/2) + 1/\tau(\omega' - \delta\omega/2)]^2} \tag{3}$$

where $\omega' = \omega - \omega_0 - \delta\omega/2$.

In order to describe the temperature dependence of $I(\omega)$, we assume that the low frequency mode has a constant τ over the temperature range studied, and from detailed balance W_+ is equal to $1/\tau \exp(-E_a/kT)$. E_a, the apparent "activation energy," corresponds to the energy needed to excite the low-frequency mode. That the assumption of constant τ is correct can be readily verified experimentally, as will be shown below. In Fig. 2 the resulting temperature dependence of $I(\omega)$ is shown. Several points should be borne in mind concerning this figure: (1) If τ is sufficiently short, the small second peak in the low-temperature spectrum will not be visible. (2) The assumption of constant τ will break down at high temperatures. (3) The influence

of higher harmonics will be important at higher temperatures. Because of condition 3, the characteristic narrowing phenomenon expected at high temperatures may not be experimentally observable. Nevertheless, throughout the low temperature regime, Eq. (3) will correctly describe the experimental lineshape.

Near $\omega = \omega_0$ one can obtain approximate expressions for the linewidth and peak frequency:

$$(\omega_{eff}) = \omega_0 + W_+\delta\omega / (1 + (\delta\omega)^2\tau^2) \tag{4}$$

$$T_2^{eff\ -1} = W_+(\delta\omega)^2\tau^2/(1 + (\delta\omega)^2\tau^2) + T_2'^{\ -1} \tag{5}$$

Here we have included additional, temperature-independent dephasing processes in the term $T_2'^{\ -1}$. Equations (4) and (5) are valid only in the slow to intermediate ($\delta\omega\tau \gtrsim 1$) exchange regime. These two equations predict a temperature dependence for <u>both</u> the peak frequency and the linewidth. Both of these effects should exhibit the same activation energy, E_a, provided the range of validity of the approximate expressions (4) and (5) has not been exceeded. Plots of frequency and width vs 1/T should allow the evaluation of the important quantities $\delta\omega$ and τ.

The important considerations for the experimentalist may be summarized as follows: (1) The presence of exchange is suggested by the occurrence of a broadening and a shift in frequency of a Raman line. (2) The assumption of constant τ must be verified (as will be shown below). (3) It must be established that the system is in intermediate exchange. (4) Equations (4) and (5), or alternatively Eq. (3), can be used to evaluate $\delta\omega$, τ, and E_a. From the knowledge that $\delta\omega$ arises from the

anharmonic part of the vibrational potential, it may be possible to draw conclusions as to the specific nature of the anharmonic coupling. The activation energy E_a tells which low-energy mode (or modes) of the molecule is responsible for the dephasing.

III. Experimental

The Raman spectrum of 1,2,4,5-tetramethyl benzene (see Fig. 3), or durene, was investigated in the C-H stretch region from 2850-3100 cm^{-1} A polycrystalline sample was studied over a range of temperatures 11.5°K to 300°K. In Fig. 3 we reproduce[2] the Raman spectrum at the two extreme temperatures, showing five lines which strikingly exhibit the type of behavior which makes them amenable to study by exchange theory. Additional spectra were taken at approximately 10 intermediate temperatures.

The simplest means of data analysis, and one which frequently gives satisfactory results, is to plot the log of the linewidth and frequency shift as a function of inverse temperature. Such a plot will have a slope corresponding to E_a/kT, based on Eqs. (4) and (5) and the assumption that $W_+ = 1/\tau \exp(-E_a/kT)$, while the y-intercepts in conjunction with Eqs. (4) and (5) can be used to evaluate $\delta\omega$ and τ.

The defect in this procedure is that it depends upon the validity of Eqs. (4) and (5), which are only accurate near $\omega = \omega_0$. A better method is to use the exact lineshape function given by Eq. (3), and to account for the residual low-temperature linewidth by convolution with a temperature-independent Lorentzian line. Again, we assume that the temperature dependence of the exchange lineshape function can be contained in the factor W_+. This approach results in an equation for the observed lineshape having five adjustable parameters (ω_0, $\delta\omega$, τ, E_a, and the low temperature linewidth) and two independent variables (frequency and temperature). By a least squares fitting

procedure using the experimentally observed lineshape we were able to evaluate the parameters for each of the five lines of interest. This data is presented in Table 1.

Finally, the applicability of exchange theory will be supported if it can be shown from the observed data that the transitions are in intermediate exchange, i.e., that $\delta\omega\tau \approx 1$. This can be done quite easily, since the first term in (5) divided by the second term in (4) equals $\delta\omega\tau$. This corresponds to taking the ratio of line broadening to the frequency shift for a given temperature. This quantity has been plotted as a function of temperature for all five of the transitions studied (see Fig. 4 and Reference 2), and the condition of intermediate exchange is verified in each case. In addition, Fig. 4 confirms another important assumption mentioned above, namely that τ is constant over the temperature range studied. Thus, the validity of our interpretation of these spectra is confirmed in two important respects.

Table. 1. Parameters obtained from least-squares analysis of temperature-dependent lineshape data.

	Raman Active C-H Stretch		Low Frequency Dehasing Channels			
	ω_o (cm^{-1})	Mode	Dephasing Mode	ε_i(cm^{-1})	$\delta\omega$(cm^{-1})	τ(ps)
a	2929.0	A_g, B_{1g}	B_{3g} - Torsion	194±10	+13.6	0.36
b	2957.7	A_g, B_{1g}		229±21	+10.5	0.86
c	2970.3		B_{1g}, A_g - Methyl Rock	265±6	-24.2	0.19
d	2987.3	B_{2g}, B_{3g}	B_{3g}, B_{2g} Out-of-plane Methyl Bend	341±13	-20.6	0.25
e	3027.5	A_g	B_{1g}, A_g-Methyl Rock	263±19	-21.2	0.36

IV. Results and Discussion

Although the results presented in Table 1 are interesting in their own right, it is more useful to attempt to interpret them in a way which sheds light on precisely which interactions are important dephasing mechanisms in this system. The approach which we have taken is based on a comparison of the observed activation energies (listed in Table 1) with the known low-energy vibrational spectrum of the molecule.[29] One remarkable fact emerges immediately: in four out of five cases, the activation energy matches, within experimental error, some low-energy motion of the molecule. This suggests that the simple model discussed above of a high-frequency mode coupled to a single low-frequency mode is in fact sufficient to account for the dephasing in many cases.

While the simplicity of this result is attractive, it is important to consider what mechanism might be responsible for the observed couplings, and how the single-mode selectivity might be accounted for. Unfortunately, the pursuit of this question has been hampered by the lack of a full assignment of this region of the spectrum, and therefore the conclusions to be drawn here must be regarded as less secure than other aspects of this work. Nevertheless, some assignments are well established[30] and do provide firm support for the interpretation we propose.

As was mentioned briefly in Section II, and discussed at length in the theoretical paper, the frequency difference $\delta\omega$ results from the anharmonic potential $\mathcal{H}_p$ (Eq. (2)). We have calculated the relative importance of the lower order terms in this expansion, and concluded

that terms of the form $C_{iijj}Q_i^2Q_j^2$ make the most significant contribution to $\delta\omega$. This implies two things: $\delta\omega$ may be either positive or negative; and Q_i and Q_j may have any symmetry ($Q_i^2Q_j^2$ is always totally symmetric). Any intra- or intermolecular interaction consistent with the foregoing may, in general, cause vibrational modes to couple and to exhibit a $\delta\omega$. We would like to suggest two such mechanisms which could be invoked to explain the couplings and frequency shifts which we observe.

The most obvious mechanism which would couple two vibrations is a steric interaction. An illustration of this possibility in durene is shown in Fig. 5. As the adjacent methyl groups torsion about the C-C bond, the neighboring protons closely approach one another, and would be expected to interact strongly. This would evidently affect the frequency of the methyl C-H stretching modes, thus providing the type of two-mode coupling we have outlined. An energy diagram for the torsional motion is shown in Fig. 6, the first excited torsional state being 197 cm^{-1} above the ground state. This value of 197 cm^{-1} should, according to exchange theory, manifest itself as an activation energy for the broadening and shift seen in the spectrum of the methyl C-H stretch. Our data for the C-H stretch mode at 2932 cm^{-1} is shown in Fig. 7 and analysis of this data yields an activation energy of 194 cm^{-1}, which agrees closely with the torsional frequency (197 cm^{-1}, Ref. 29). The fact that $\delta\omega$ is positive indicates that a torsional excitation increases the energy of the C-H stretch mode.

In a substituted benzene molecule, the electronegativity of the substituents strongly affects the electron density in the ring. The

vibrational frequency of a proton attached to a substituted benzene ring depends on the distribution of electron density within the ring, and hence on the nature and location of the substituents. This fact suggests a second mechanism which may be responsible for coupling the vibrational modes in durene; however, owing to the difficulty of calculating electron densities in vibrationally excited molecules, the following discussion is necessarily speculative. It is reasonable that the excitation of a vibrational mode in a molecule such as durene would significantly perturb the electron distribution in the ring. This would then affect the frequencies of other modes, and, it should be noted, could shift them to either lower or higher energies, depending on the specifics of the situation. In durene, one would expect this mechanism to manifest itself most strongly in the case of the aromatic proton stretch, since these protons are in close contact with the ring.

In Fig. 8 we show our data for the aromatic C-H stretch mode in durene (3025 cm^{-1}). Again, the temperature dependence exhibits the qualitative behavior suggestive of exchange, and a careful analysis yields a $\delta\omega$ of -21.2 cm^{-1} and an activation energy of 263 $cm^{-1} \pm 19$. This activation energy does indeed match the energy of another molecular mode, namely, the methyl rock at 282 cm^{-1}. Thus we would suggest that an excitation of the methyl rock at 282 cm^{-1} causes some change in the electron distribution in the ring, which in turn causes a shift of -21.2 cm^{-1} in the frequency of the aromatic proton stretch.

No such detailed explanations will be given for the last three modes we have analyzed, but the data is presented for the sake of

completeness in Table 1. The important point to note is that in two out of three of these additional cases, the activation energies match with low-energy methyl motions. We anticipate that, given more detailed information concerning the interactions present in this molecule, the couplings observed in these two cases could be described in terms similar to those we have discussed above. Finally, similar studies on isotopically mixed crystals should provide data which corroborates salient features of the theory as well as indicating where further development is necessary. Such experiments are currently in progress.

V. Conclusions

In this paper, we have presented an application of exchange theory to vibrational spectroscopy. That energy exchange can make an important contribution to a Raman lineshape is, of itself, a fundamentally important observation. The data presented here strongly supports our belief that exchange theory is applicable to studying the broadenings and shifts we have observed. Moreover, the use of this theory has given valuable insight into the couplings and interactions between vibrational degrees of freedom in this molecule, and a more or less complete picture of the dephasing mechanisms which are operable is emerging.

In this particular application we have observed the exchange phenomenon arising from a coupling between vibrational modes. The theory, however, is not restricted to this type of interaction; the transitions could be electronic or rotational as well. It is therefore to be expected that many spectral lines will exhibit, to a greater or lesser extent, evidence of exchange. The presence of exchange should enable, through simple experimental means, the evaluation of important molecular parameters.

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Figure Captions

Fig. 1. The four zero-order levels are shown on the left. The perturbation, $\mathcal{H}_p$ shifts the relative energy of level (1,1). This results in two transitions, at ω and $\omega + \delta\omega$. Ea, the "activation energy," is the energy difference between (0,0) and (0,1).

Fig. 2. The temperature dependence of the exchange lineshape $I(\omega)$, given by Eq. 3. The values of the parameters are: $\delta\omega = 10.0\ cm^{-1}$, $\tau = 1.25$ psec, Ea = 150 cm^{-1}. The temperatures shown are (1) 100°K, (2) 250°, (3) 1000°K.

Fig. 3. The Raman spectrum of 1,2,4,5-tetramethylbenzene at 300°K (top) and 11.5°K (bottom). The arrows indicate the direction and magnitude of the frequency shift for each line.

Fig. 4. The points represent the quantity $\delta\omega\tau$, and are obtained by dividing the line broadening by the frequency shift.

Fig. 5. These pictures illustrate the steric interaction resulting from the torsional motion of the two adjacent methyl groups. We have postulated that this steric interaction couples the torsional motion to the 2932 cm^{-1} methyl C-H stretch.

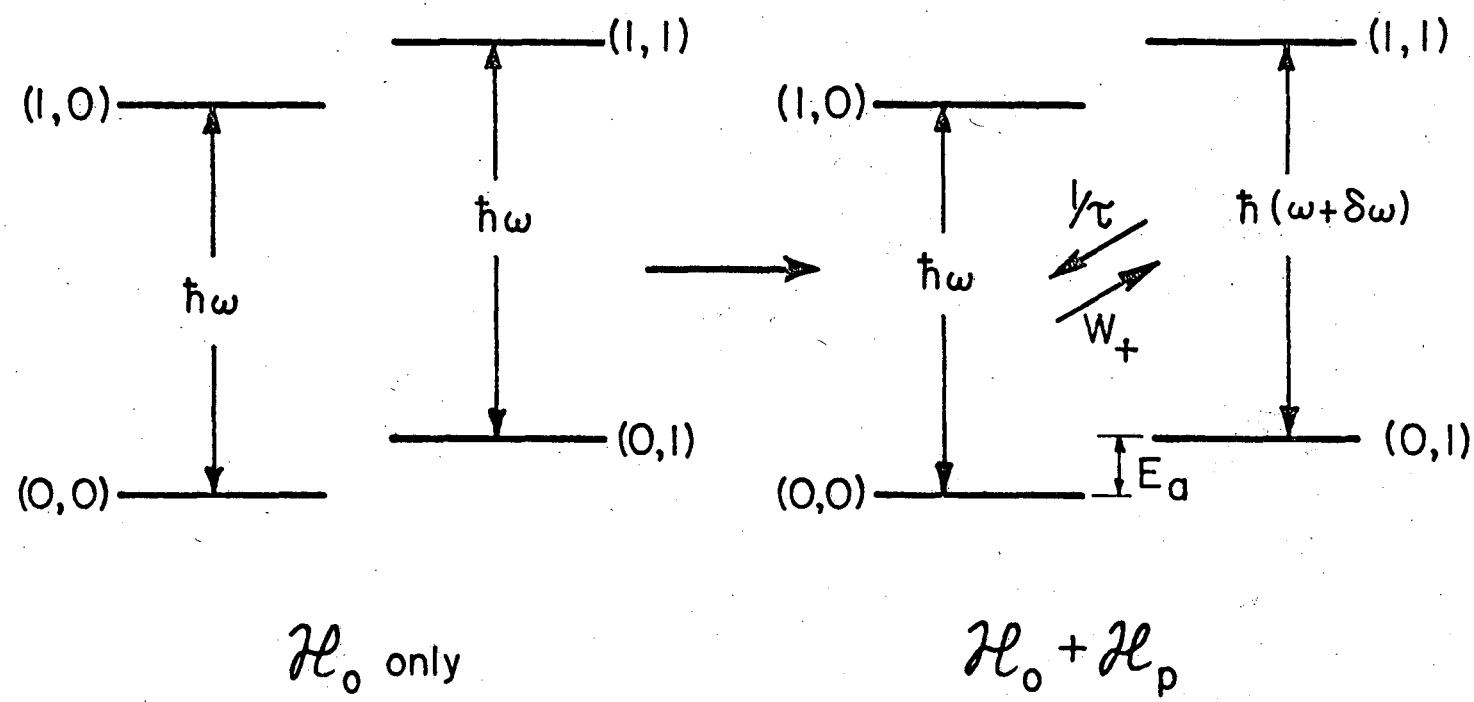
Fig. 6. Energy diagram for methyl torsion in durene. The function exhibits three-fold symmetry, and the splitting between ground and first excited state is 197 cm^{-1}. (Ref. 29)

Fig. 7. (a) Linewidth vs T for the 2932 cm^{-1} C-H stretch in durene; on the left is the raw data, to obtain the points on the right we have subtracted a temperature-independent linewidth.

The slope is approximately exponential, as predicted by our theory. (b) Frequency vs T for the same transition. Again, the data on the right was obtained by subtracting the zero-temperature peak frequency.

Fig. 8. Data for the 3025 cm^{-1} line, presented as in Fig. 7.

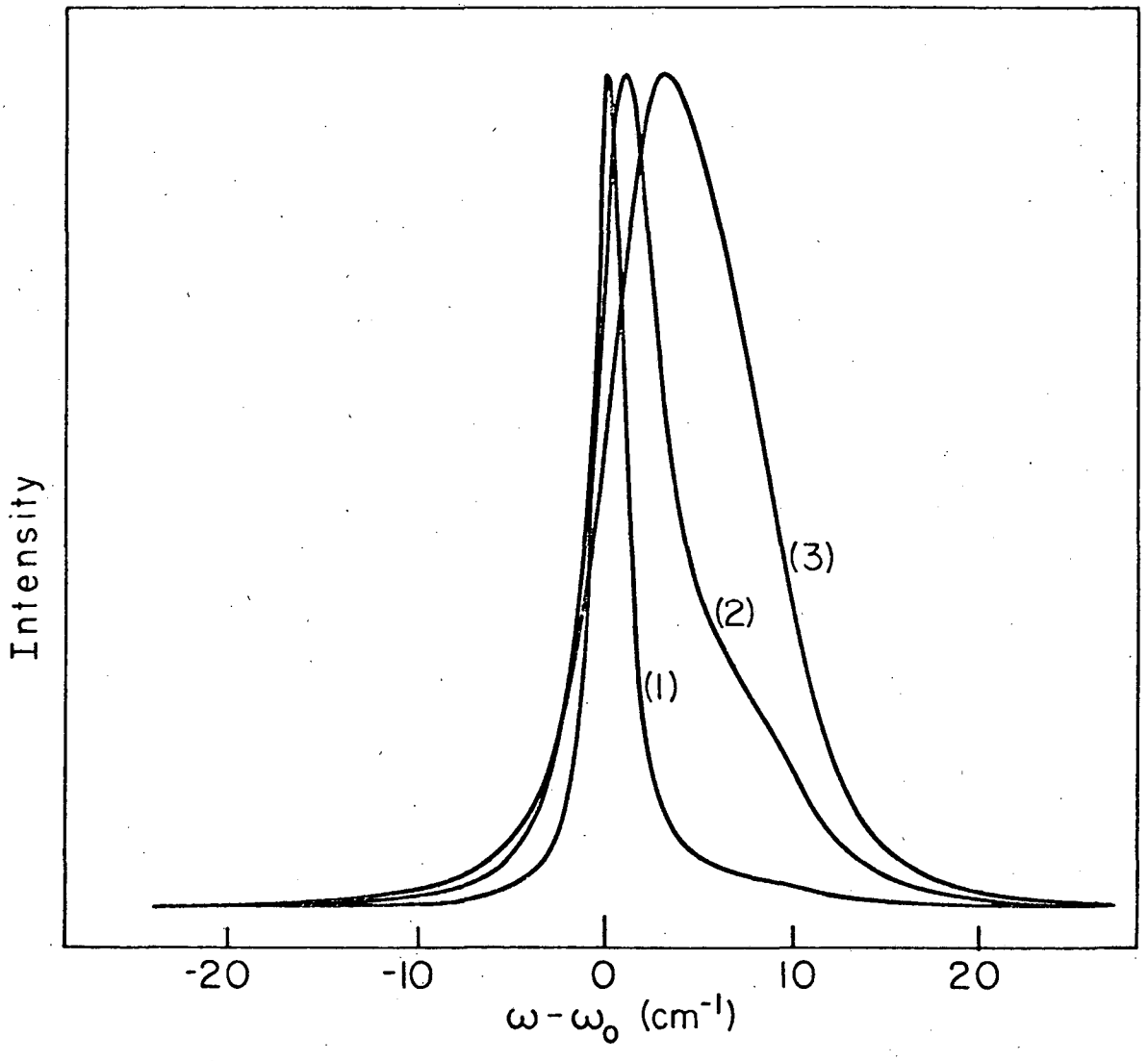
ENERGY LEVELS FOR TWO COUPLED ANHARMONIC OSCILLATORS



XBL791-5547

Figure 1

TEMPERATURE DEPENDENCE OF EXCHANGE LINESHAPE



XBL791-5548

Figure 2

SPONTANEOUS RAMAN SPECTRUM: C-H STRETCHING REGION
1, 2, 4, 5-TETRAMETHYL BENZENE (SOLID)

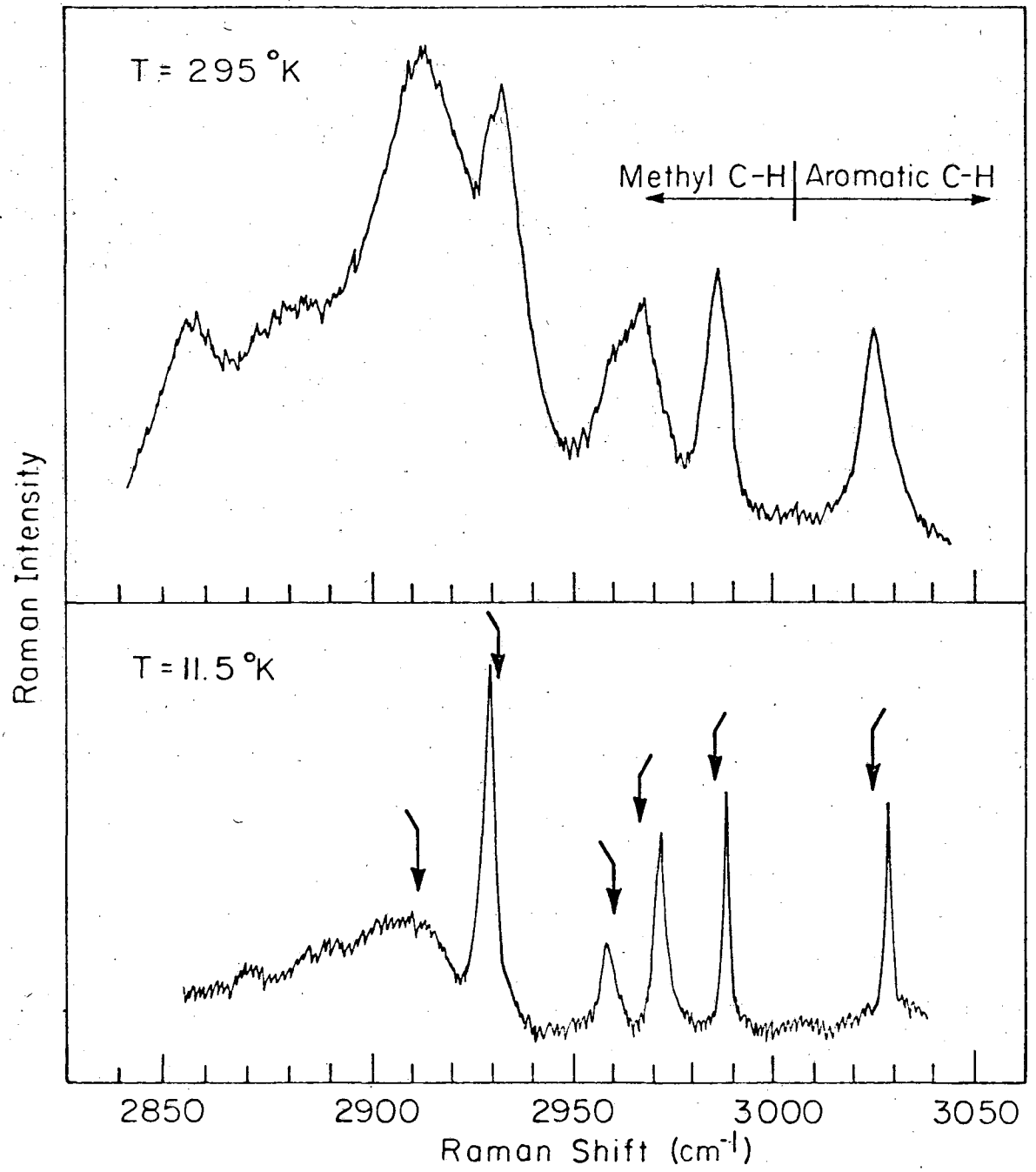


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Figure 3

RATIO OF THE TEMPERATURE DEPENDENT PORTION OF THE LINEWIDTH AND FREQUENCY SHIFT IN THE RAMAN TRANSITIONS OF TETRAMETHYLBENZENE (DURENE)

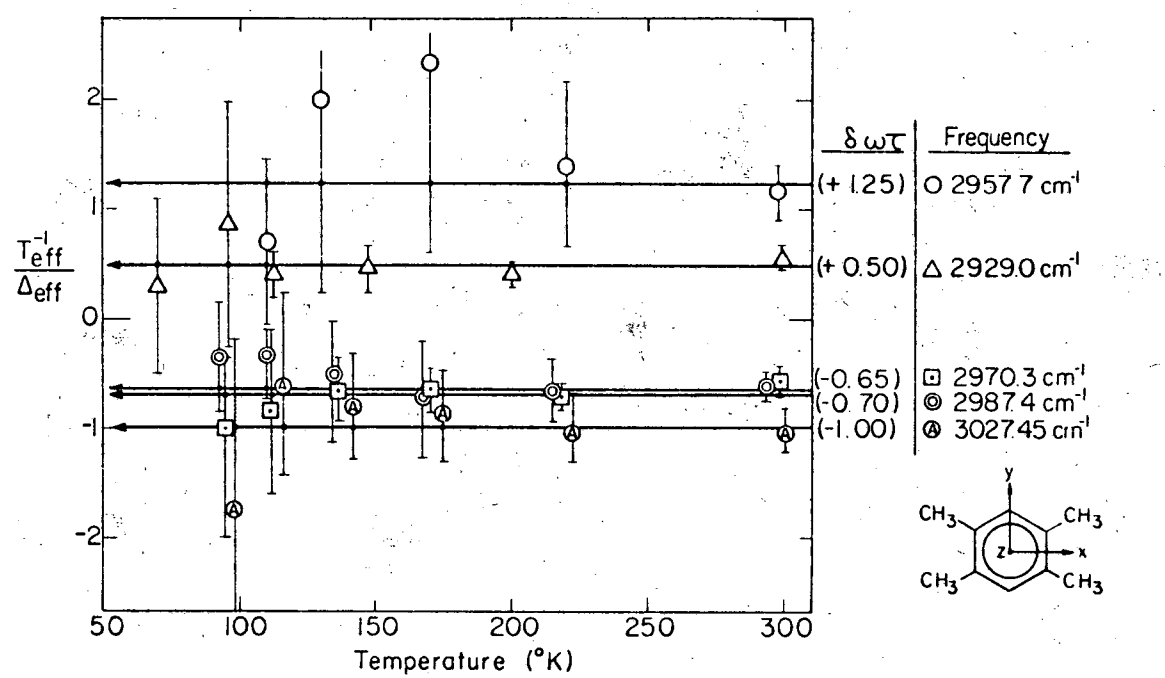

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Figure 4

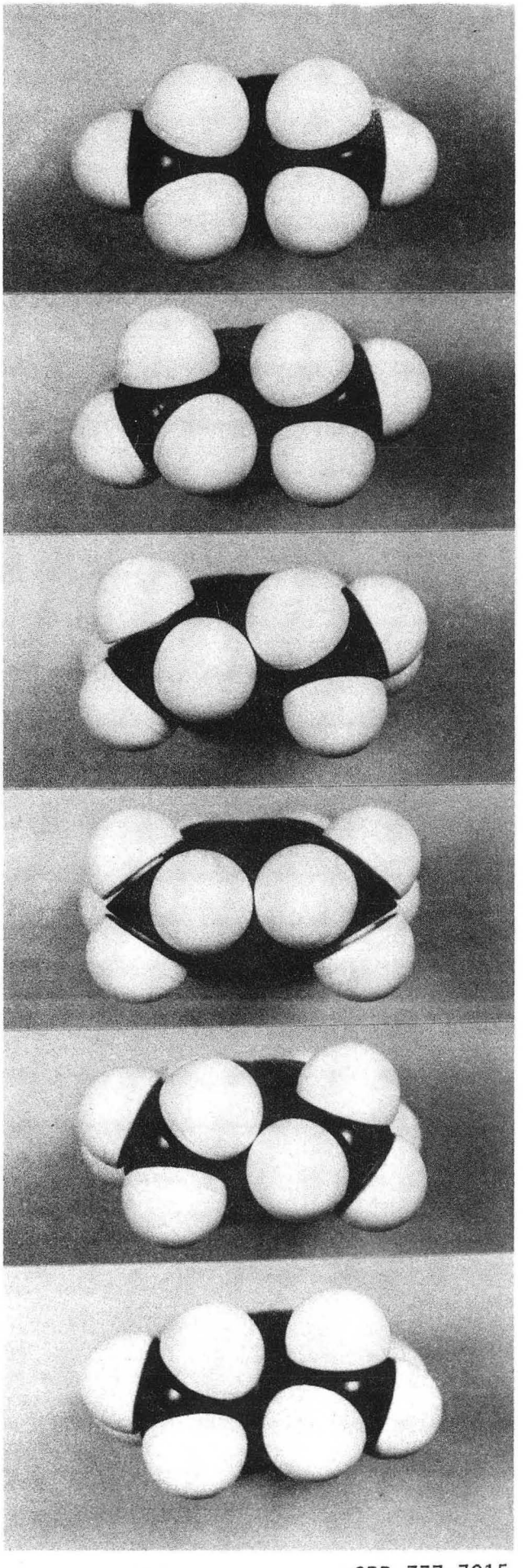

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Figure 5

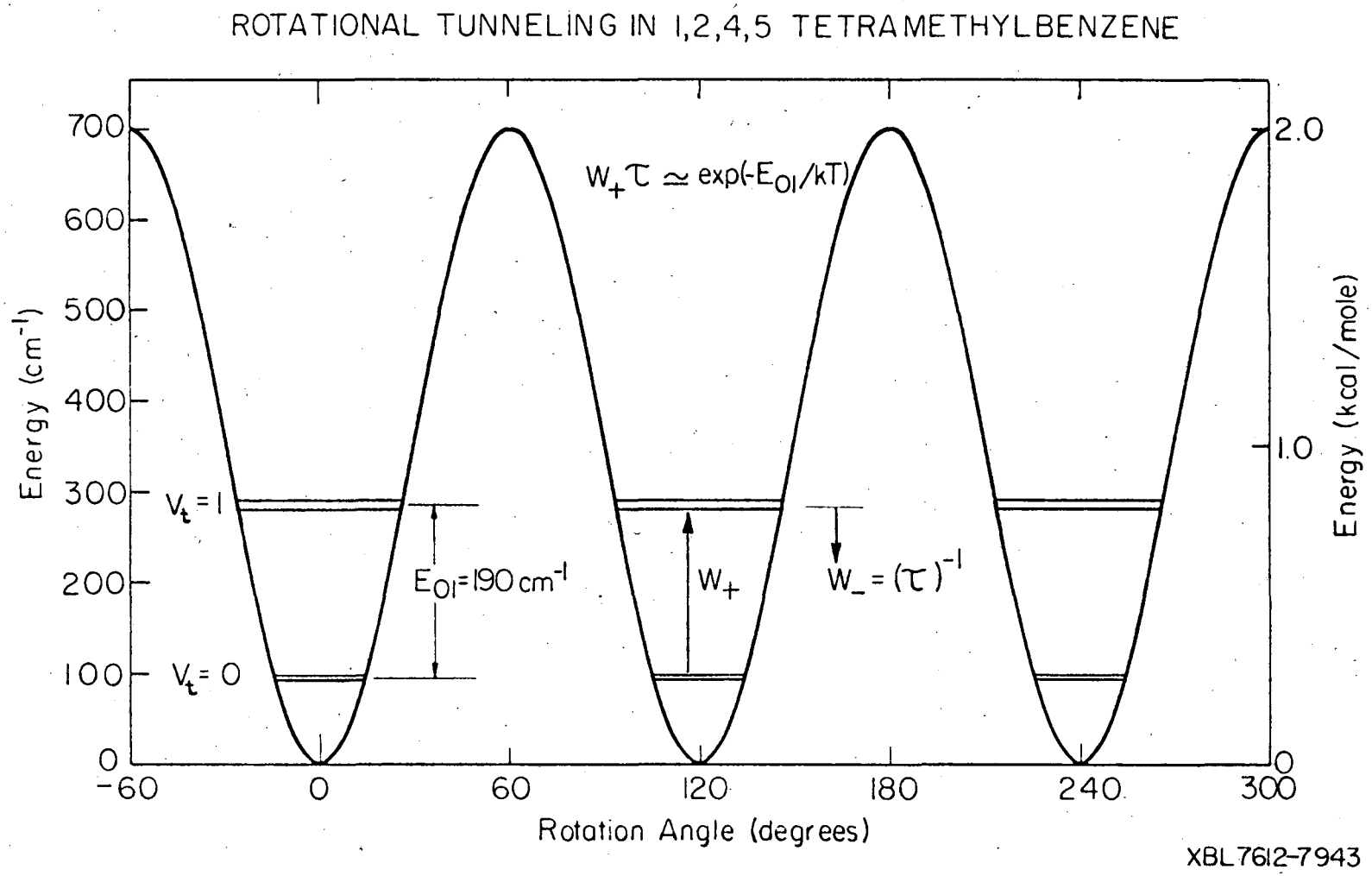
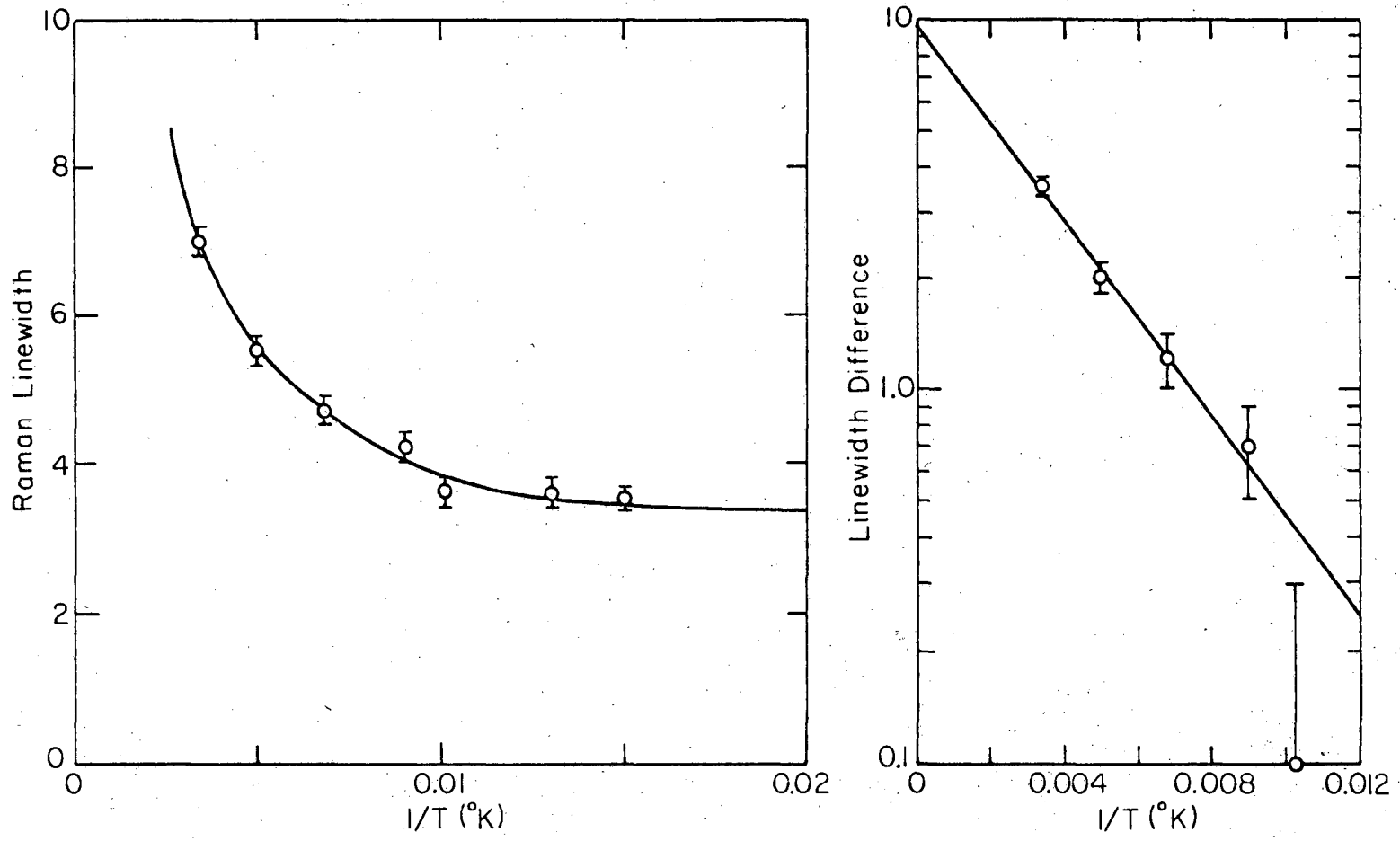

ROTATIONAL TUNNELING IN 1,2,4,5 TETRAMETHYLBENZENE
Energy (cm⁻¹)
700
600
500
400
300
200
100
0
Energy (kcal/mole)
2.0
1.0
0
$W_+\tau \simeq \exp(-E_{01}/kT)$
$V_t = 1$
$V_t = 0$
$E_{01} = 190\ cm^{-1}$
W_+
$W_- = (\tau)^{-1}$
-60
0
60
120
180
240
300
Rotation Angle (degrees)
XBL7612-7943

Figure 6.

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



XBL 793-5980

Figure 7a.

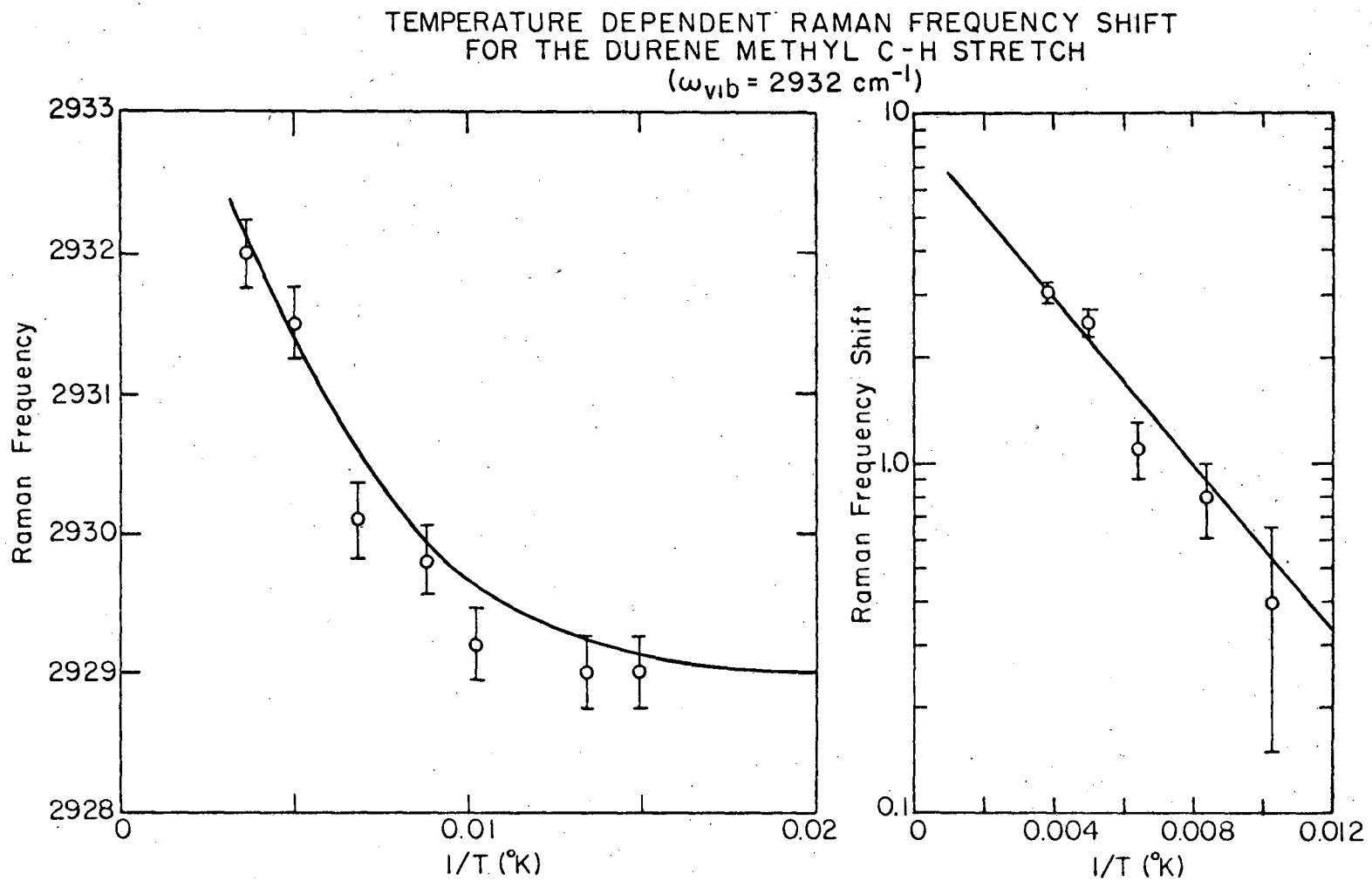

TEMPERATURE DEPENDENT RAMAN FREQUENCY SHIFT
FOR THE DURENE METHYL C-H STRETCH
(ω_{vib} = 2932 cm^{-1})
Raman Frequency
2933
2932
2931
2930
2929
2928
0
0.01
0.02
1/T (°K)
Raman Frequency Shift
10
1.0
0.1
0
0.004
0.008
0.012
1/T (°K)
XBL 793-5979

Figure 7b

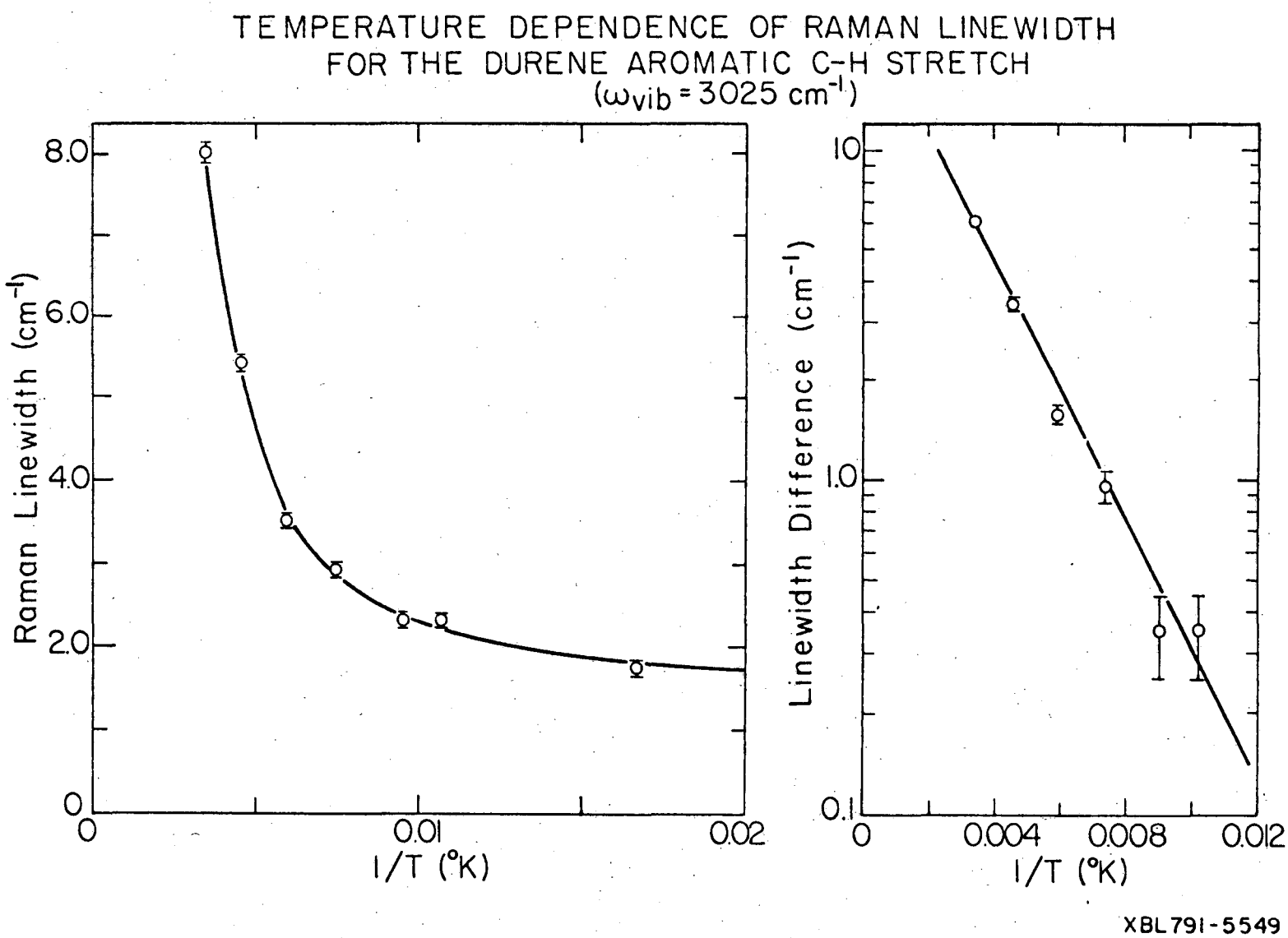

TEMPERATURE DEPENDENCE OF RAMAN LINEWIDTH
FOR THE DURENE AROMATIC C-H STRETCH
(ω_{vib} = 3025 cm^{-1})
Raman Linewidth (cm^{-1})
8.0
6.0
4.0
2.0
0
0
0.01
0.02
1/T (°K)
Linewidth Difference (cm^{-1})
10
1.0
0.1
0
0.004
0.008
0.012
1/T (°K)
XBL791-5549

Figure 8a

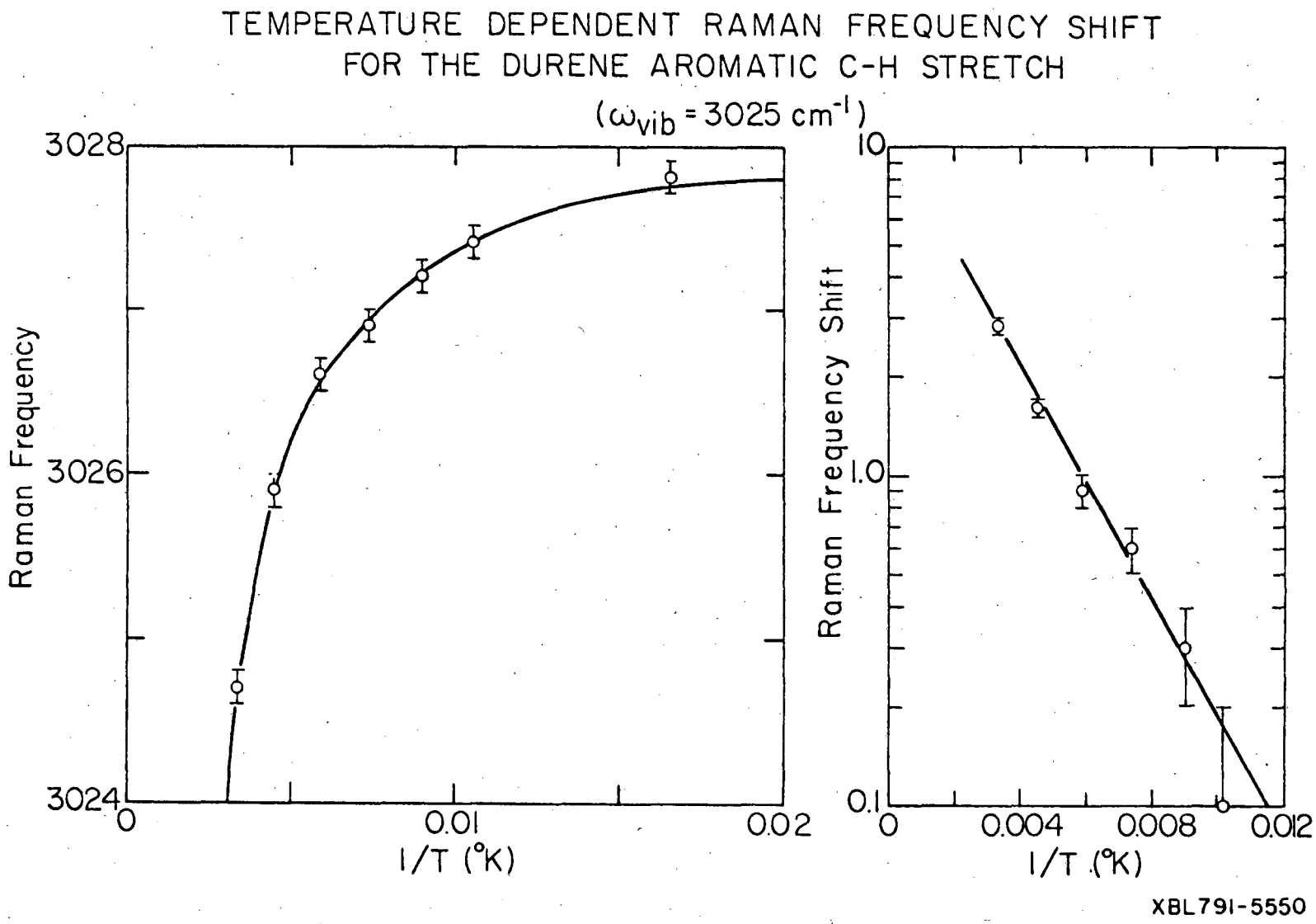

TEMPERATURE DEPENDENT RAMAN FREQUENCY SHIFT
FOR THE DURENE AROMATIC C-H STRETCH
(ω_{vib} = 3025 cm^{-1})
Raman Frequency
3028
3026
3024
0
0.01
0.02
1/T (°K)
Raman Frequency Shift
10
1.0
0.1
0
0.004
0.008
0.012
1/T (°K)
XBL791-5550

Figure 8b.

(1)

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