

their origin provides a unique opportunity to probe a primary molecular relaxation process and any associated microstructural or conformational changes in an important class of amorphous semiconductors.

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Effects of Energy Exchange on Vibrational Dephasing Times in Raman Scattering

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

Department of Chemistry and Materials and Molecular Research, Division of Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

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It is shown that the Raman line-shape 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.

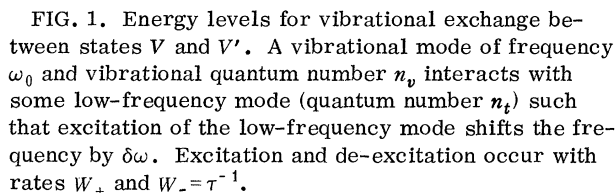
The effects of molecular interactions and molecular motion are fundamental to an understanding of vibrational relaxation and redistribution in liquids and solids. Until recently, most of the information on vibrational dephasing and relaxation has come from an analysis of the spontaneous Raman linewidth and line shape which Gordon¹ first represented as the Fourier transform of a polarizability autocorrelation function. In general terms it is thought that contributions to the vibrational part of the correlation function decay via events which cause relaxation or redistribution of the excited vibrational population among other degrees of freedom (T_1 processes) and events which randomly modulate the vibrational phase (T_2 processes).

Recent experiments by von der Linde, Laubereau, and Kaiser² have separated the two contributions in the case of symmetric C-H stretching modes in a variety of liquids. The decay time of the vibrational correlation function was obtained from a convolution of their laser pulse shape with

an assumed vibrational correlation function whose Fourier transform was related to a Lorentz spontaneous Raman line-shape function. Both the interpretation of the Raman line shape and the deconvolution of the vibrational dephasing time from stimulated Raman scattering assumed 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 intermolecular 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 im-

The application of exchange to vibrational dephasing and relaxation is shown in Fig. 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 intermolecular or intramolecular coupling, and that the vibrational state V associated with the frequency $\omega_0 + \delta\omega$ is at an energy E_i above 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 Kubo³ and Anderson⁴ 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 define the problem realistically. In terms of the polarizability correlation function,^{1,6} the intensity of scattered light with a Raman frequency ω is given by

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

and the correlation function is given by

If the W_+ and W_- are constant in time, $\omega_v(t')$ is a Markovian random function and $\varphi(t)$ is given by⁴

The matrix $\bar{\omega}_v$ is diagonal and contains the possible values of $\omega_v(t)$, and the transition matrix $\bar{\Pi}$ incorporates the rates of transitions between these values. \bar{W} is a row vector consisting of the steady-state probability distribution of $\omega_v(t)$, while $\bar{1}$ is a column vector whose elements are all unity. Aside from other contributions to the total correlation function, the spectral line shape is given by

$$I(\omega) \sim \int_{-\infty}^{\infty} \exp(-i\omega t) \vec{W} \cdot \exp[t(i\vec{\omega}_v + \vec{\Pi})] \cdot \vec{I} dt \\ = \text{Re}[\vec{W} \cdot \vec{A}^{-1} \cdot \vec{I}], \quad (5)$$

where $\tilde{A} = i(\tilde{\omega}_v - \omega\tilde{I}) + \tilde{\Pi}$.

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

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

The rates for vibrational energy exchange are incorporated into the effective frequency,

$$\omega_e = \omega_0 + (\delta\omega W_+ \tau) / [1 + (\delta\omega)^2 \tau^2], \quad (7)$$

and the effective relaxation time,

$$(T_{\text{eff}})^{-1} = T_1^{-1} + T_2^{-1} + W_+ (\delta\omega)^2 \tau^2 / [1 + (\delta\omega)^2 \tau^2], \quad (8)$$

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 Eq. (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 *partial* relaxation of phase memory as given by Eq. (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 ($\delta\omega\tau \sim 1$) and no fre-

quency 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 (1930 cm^{-1}) in solid 1, 2, 4, 5-tetramethylbenzene in Figs. 2 and 3, respectively. As is illustrated in the figures, the spontaneous linewidth is observed to broaden slightly in the range 30 to 100°K rapidly from 100°K to room temperature. The temperature-dependent broadening in the higher-temperature region shows [cf. Fig. 2(b)] an exponential dependence having $E_i = 227 \pm 12 \text{ cm}^{-1}$. An analysis of the Raman frequency shift as illustrated in Fig. 3(b) also shows a similar temperature dependence with $E_i = 218 \pm 45 \text{ cm}^{-1}$. The presence of both the broadening and shift each having the same E_i establishes 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

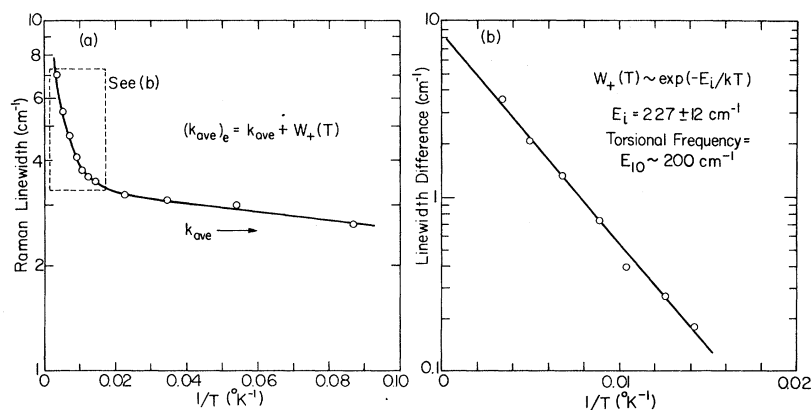


FIG. 2. (a) The linewidth temperature dependence contains an approximately constant contribution and a contribution above $\sim 30^\circ\text{K}$ due to exchange. (b) The exchange contribution displays an activation energy near the methyl-group torsional frequency.

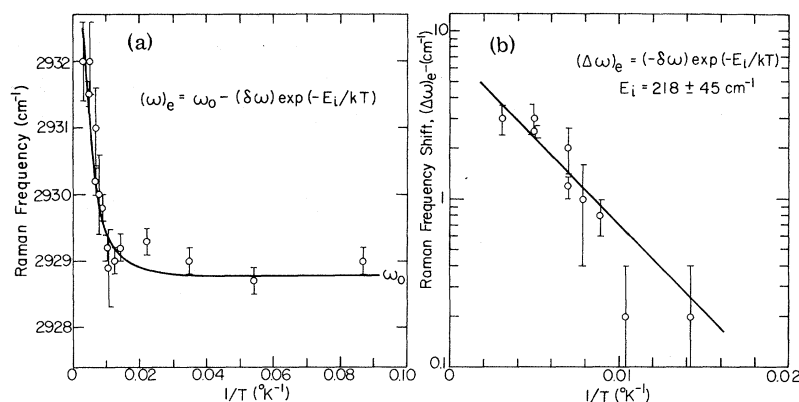


FIG. 3. (a) The Raman frequency is shown as the function of temperature. (b) The frequency shift displays the same activation energy as the line broadening.

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, one quantum 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 $E_i = \omega_{\text{torsion}}$. This leads to the observed temperature dependence of the linewidth and frequency shift:

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

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

This interpretation is also consistent with the observation that the only intramolecular lattice frequencies near 200 cm^{-1} are the methyl torsions, and similar line broadening and frequency shifts are observed for other C-H modes in this region (not shown). Four bands between 2920 and 3000 cm^{-1} appear as the result of the non- C_{3v} environment of the methyl groups which lifts a twofold degeneracy. 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.

Application of Eqs. (9) and (10) to the data in Figs. 2 and 3 allows us to determine the parameters $\delta\omega$ and τ . One finds $\delta\omega = 14 \pm 2 \text{ cm}^{-1}$ and $\tau = 0.18 \text{ psec}$. 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 dominant 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 a dephasing time, $T_2 = 0.75 \text{ psec}$.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 demonstrate 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.

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Differential Relaxation Effects and Multielectron Excitation for Molecularly Chemisorbed CO on Platinum*

J. N. Miller, D. T. Ling,† I. Lindau, P. M. Stefan, and W. E. Spicer
Stanford Electronics Laboratories, Stanford, California 94305

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Synchrotron radiation ($h\nu=80\text{--}170$ eV) was used for photoemission studies of CO chemisorption on a Pt crystal. We report the first unambiguous observation of the 3σ molecular level for CO adsorbed on a metal surface and note a relaxation shift 2.4 eV larger for the 3σ than for the 4σ as compared to the $3\sigma\text{--}4\sigma$ splitting in the gas phase. Furthermore, we observe energy-loss structure between the 3σ and 4σ levels, reminiscent of the shakeup satellites in transition-metal carbonyls.

The application of photoemission spectroscopy to the study of the electronic structure of chemisorbed species has been well established during the last few years. In the large body of experimental data gathered for the chemisorption of many different gases (but CO in particular) on transition metal surfaces, it is generally found for nondissociative chemisorption that the nonbonding molecular orbitals are uniformly shifted to lower binding energy due to extra-atomic relaxation. A fair amount of discussion has been devoted to the important question of whether orbital symmetry and differences in spatial configuration might cause differential relaxations.¹

In the work described in this Letter, we have extended photoemission work for CO chemisorption by including the deeper-lying 3σ molecular orbital level as well as the 4σ , 1π , and 5σ levels. We will further address the question of whether any of the shakeup structure, which is so prominent in the molecular gas-phase spectra, persists in the spectra of the chemisorbed species. Our data show the first unambiguous identification of the 3σ orbital of chemisorbed CO and that there is a 2.4-eV differential relaxation between the 3σ and 4σ levels as compared to the CO gas-phase spectra. Structure is observed between the 3σ and 4σ levels where the shakeup satellites are found in the gas-phase spectra.

The studies of these new and important but relatively weak features were made possible by using synchrotron radiation as the excitation source at a photon energy where optimal sensitivity for the CO-induced levels is obtained. Most important in

this regard is to choose excitation energies where the emission from the substrate valence band is suppressed relative to that from the CO-derived levels. The work by Lindau, Pianella, and Spicer² clearly demonstrates that there is a drastic energy dependence of the partial photoionization cross section and that a strong decrease in emission 120–140 eV above threshold can be associated with levels having a Cooper minimum³ (e.g., $5d$ levels, which are the main components of the Pt valence band). By tuning the excitation energy to this region, optimal surface sensitivity will be obtained for the CO-induced levels, and the background of scattered electrons from the Pt valence band will be minimized.

The photoemission measurements were performed at the Stanford Synchrotron Radiation Project⁴ in the photon energy range 80–170 eV.⁵ The sample was a stepped single crystal with a $6(111) \times (100)$ orientation and was cleaned *in situ* (10^{-11} -Torr base pressure) by heating to $\geq 1800^\circ\text{K}$ in 10^{-7} Torr of oxygen following procedure discussed in detail elsewhere.⁶ Residual contaminants were removed by argon-ion sputtering and annealing. The sample cleanliness was checked periodically with Auger electron spectroscopy (AES). Gas exposures to research-purity CO were performed with the sample at 300 and 120°K. A double-pass cylindrical mirror analyzer was used for the electron-energy analysis as described elsewhere.⁷

In Fig. 1 are shown the photoemission spectra for clean Pt and Pt exposed to 5 L (langmuir, $1\text{ L}=10^{-6}$ Torr sec) CO, taken at a photon energy of 150 eV. The valence-band structure and the to-