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Picosecond vibrational relaxation modulated by critical slowing down in ferroelectric $K_4Fe(CN)_6 \cdot 3H_2O$

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Accurate time-resolved stimulated Raman measurement of anomalous line broadening of a vibrational excitation weakly coupled to a lattice mode which shows critical slowing down is presented. Dephasing of the Raman-active internal A_{1g} CN stretching mode in ferroelectric $K_4Fe(CN)_6 \cdot 3H_2O$ is found to result from a superposition of energy-exchange dephasing from coupling to the internal T_{1g} Fe—C≡N bending mode and pure dephasing from coupling to the (tunneling motion of the) crystal water. Anomalous broadening of the A_{1g} line at the Curie temperature (248.5 K) results from critical slowing down of the water reorientational tunneling motion.

I. INTRODUCTION

Ferroelectric phase transitions can generally be classified into two categories:[1] (1) a displacive transition, in which the spontaneous electrical polarization results from a change in crystal structure, and (2) an order-disorder transition of a system of permanent electrical dipoles. The structural complexity of many ferroelectrics may complicate the identification of the exact mechanism of the phase transition, e.g., when soft modes cannot be observed.

Each of the aforementioned mechanisms will have a different effect on the dynamics of vibrational excitations in the ferroelectric, as reflected in their spectral line shape. Accurate measurement of vibrational line shapes, combined with an analysis in terms of possible vibrational relaxation channels, may therefore allow one to identify the driving mechanism of the phase transition. Also, these studies yield valuable information on the interactions between vibrational excitations in a solid. In this paper we present the results of a Raman study on vibrational relaxation in the order-disorder ferroelectric potassium ferrocyanide trihydrate (KFCT).

KFCT has the chemical formula $K_4Fe(CN)_6 \cdot 3H_2O$. The water molecules are located in layers perpendicular to the [010] axes. Between each layer of water there are two layers of $Fe(CN)_6{}^{4-}$ groups and interspersed K^+ ions, with the iron nuclei located at the center of regular octahedra formed by six cyanide ions.[2] The symmetry of the unit cell is either tetragonal, which is metastable at room temperature, or monoclinic, which is stable at room temperature. The monoclinic modification contains four molecules per unit cell. Under practical conditions of crystal growth, polytypic structures often appear, in which alternating monoclinic and tetragonal layers are found.[3] At 218 K the tetragonal modification of KFCT is changed irreversibly into the monoclinic. Below 248.5 K the monoclinic modification of KFCT shows a spontaneous electrical polarization in the $[10\bar{1}]$ direction.[4] The second-order ferroelectric phase transition at 248.5 K is accompanied by a change in crystal symmetry,[5,6] from space group C_{2h}^6 (C_2/c) (paraelectric phase) to $C_s(C_c)$. KFCT loses its crystal water at 343 K.

There has been a lot of confusion about the nature of the phase transition. It is most likely an order-disorder–type transition, in which the spontaneous polarization in the $[10\bar{1}]$ direction arises from collective ordering of the water molecules.[5–16] Our results confirm the order-disorder nature of the phase transition.

In this study both picosecond coherent Raman scattering and spontaneous Raman scattering were used. Although time-resolved coherent stimulated Raman techniques yield the same dynamic information as conventional Raman spectroscopy,[17] there are advantages in the sense that considerably greater accuracy can be reached. This enables us to observe very subtle changes in the dynamics of vibrational excitations.

The temperature dependence of the line shift and linewidth of the Raman-active internal A_{1g} CN stretching mode of the ferrocyanide octahedron, oscillating at ≈ 2095 cm^{-1}, is analyzed using the vibrational-energy-exchange (VEE) model.[18–21] In this model, dephasing arises from random modulation of the vibrational frequency, caused by anharmonic coupling to low-frequency modes which undergo energy exchange with the bath. From the experimental data the exchange modes and coupling strengths may be identified, yielding quantitative information on the dynamic interactions between vibrational excitations.

In KFCT the dominant exchange mode is found to be another internal mode of the ferrocyanide octahedron, the T_{1g} Fe—C≡N bending mode at 350 cm^{-1}. The reorientational tunneling motion of the water molecules is also found to perturb the A_{1g} mode, introducing pure dephasing[22] as a second dephasing channel which results in anomalous broadening of the A_{1g} line at the Curie temperature.

In Sec. II of this paper the theory on vibrational-energy-exchange relaxation is shortly reviewed, while in Sec. III the experiment is described. In Sec. IV the observed temperature-dependent behavior of the Raman line shift and vibrational dephasing rate of the A_{1g} CN stretching mode in KFCT is presented. In Sec. V the results are discussed.

II. VIBRATIONAL-ENERGY-EXCHANGE DEPHASING

For polyatomic molecules in a condensed phase, the degrees of freedom of the molecule and its surroundings can be separated into three groups:[19] (1) the (high-frequency) vibrational mode under study; mode A, (2) the (low-frequency) exchange modes B; and (3) the bath. The exchange modes B interact strongly with mode A, through anharmonic terms in the vibrational potential. This interaction leads to a shift in the vibrational frequency of mode A from ω to $\omega+\delta\omega$, upon occupation of modes B through energy exchange with the thermalized bath. The same coupling mechanism will lead to a partial loss of phase memory of mode A. The thermal occupation of modes B manifests itself as a temperature-dependent broadening *and* shift of the spectral line of mode A, reflecting detailed balance.

The Hamiltonian of the system takes the form

$$\begin{aligned} H &= H_A + H_{AB} + H_B + H_{\text{bath}} + H_{B\,\text{bath}} \\ &= H_A + H_{AB} + H_P \ , \end{aligned} \tag{1}$$

where H_A and H_B are the Hamiltonians for the unperturbed vibrational mode A and exchange modes B, H_{AB} describes the coupling between modes A and B, H_{bath} describes the thermalized bath, and $H_{B\,\text{bath}}$ is the Hamiltonian which couples modes B to the bath. Assuming a Markovian behavior of the bath dynamics, Harris *et al.*[19] obtained an approximate Lorentzian expression for the line shape of mode A.

For the case where the VEE process is the dominant process which introduces temperature dependence into the line shape of high-frequency mode A, the Raman line shift is given by

$$\omega(T)=\omega_0+\omega_{\text{VEE}}(T) \ , \tag{2}$$

whereas the linewidth, or vibrational relaxation rate, is given by

$$T_2^{-1}(T)=(T_2^{-1})_0+T_{\text{VEE}}^{-1}(T) \ . \tag{3}$$

Here, ω_0 is the Raman line shift of mode A at $T=0$ K, $\omega_{\text{VEE}}(T)$ is the temperature-dependent part of the Raman line shift which results from the VEE process, $(T_2^{-1})_0$ is the vibrational relaxation rate of mode A at $T=0$ K, and $T_{\text{VEE}}^{-1}(T)$ is the VEE contribution to the vibrational relaxation rate. The T_1 contribution to the line shape of mode A is assumed to be invariant with temperature. For the A_{1g} mode of KFCT, this contribution can probably be neglected since population relaxation of high-frequency internal modes $[\omega(A_{1g})\approx 2095 \text{ cm}^{-1}]$ is often strongly inhibited.[23]

In the low-temperature limit, when the thermal occupation of modes B is low, the temperature-dependent Raman line shift and linewidth which result from the VEE process are given by

$$\omega_{\text{VEE}}(T)=\frac{\delta\omega}{1+(\delta\omega)^2\tau^2}\exp(-E_B/kT) \ , \tag{4}$$

and

$$T_{\text{VEE}}^{-1}(T)=\frac{(\delta\omega)^2\tau}{1+(\delta\omega)^2\tau^2}\exp(-E_B/kT) \ , \tag{5}$$

respectively.[19] Here, $\delta\omega$ represents the coupling strength between modes A and B, τ is the correlation time of modes B, determined by the population relaxation time of and resonant energy transfer between exchange modes B (formally, τ is determined by Hamiltonian H_P), and E_B is the excitation energy of modes B (low-temperature limit: $E_B \gg kT$). It should be noted that $\delta\omega$ can have either a positive or negative value. Both $\delta\omega$ and τ are assumed to be invariant over the temperature range studied.

In the case where the high-frequency mode A (dominantly) couples to one exchange mode B only, one finds from Eqs. (4) and (5) that the ratio of $T_{\text{VEE}}^{-1}(T)$ and $\omega_{\text{VEE}}(T)$ yields the temperature-invariant quantity $(\delta\omega)\tau$. The value of this quantity determines the broadening limit for mode A, imposed by the VEE process: homogeneous broadening when $(\delta\omega)\tau \ll 1$, intermediate broadening when $(\delta\omega)\tau\approx 1$, and inhomogeneous broadening when $(\delta\omega)\tau \gg 1$.

III. EXPERIMENT

Time-resolved stimulated Raman gain (TSRG) scattering, first proposed by Heritage,[24] makes use of two synchronously pumped tunable mode-locked dye lasers operating at different frequencies (ω_l,ω_s). The frequency difference matches a Raman-active mode of the system under investigation. Two synchronized combinations of an ω_l and an ω_s pulse are formed (cf. Fig. 1). The first pulse pair, the pump pair, creates a coherent vibrational excitation. After a variable time delay τ_D, the probe pair scatters off the remaining coherent excitation, yielding a variation of the intensities of both components of the probe beam which is of opposite sign. Vibrational relaxation is determined through the measurement of the variation of the intensity of the ω_s component of the probe beam as a function of τ_D.

As the delay is scanned rapid oscillations (gain-versus-loss) in the measured signal are observed. The oscillations exactly correspond to the Raman frequency while being confined within an envelope which describes the relaxation of the coherent excitation.[25] Detection of this signal is performed with a double lock-in technique using an 8-MHz electro-optic (EO) modulator and an amplitude-modulation (AM) radio,[26] yielding a detectable gain limit of 10^{-7}. Use of a 500-Hz ramped phase modu-

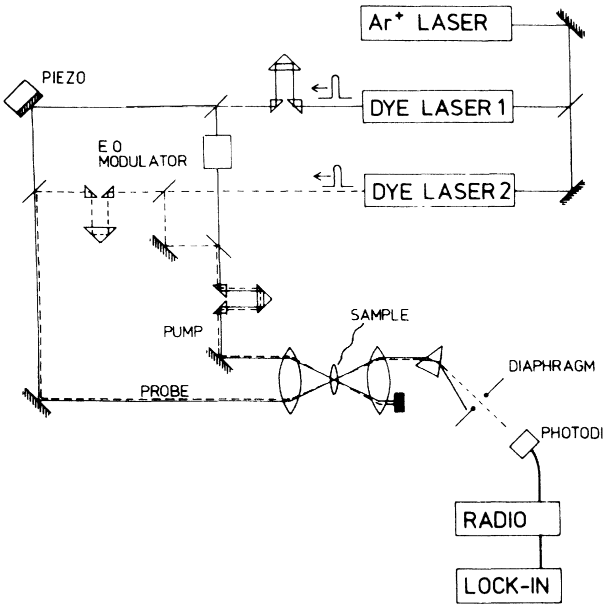

FIG. 1. Setup used in time-resolved stimulated Raman gain (TSRG) measurements. An explanation is given in the text.

lation (employing a mirror mounted on a piezo electronic transducer) instead of a 500-Hz sinusoidal phase modulation enables one to directly obtain the envelope of the gain-versus-loss profile without measuring the actual fringes.[27] The vibrational relaxation rate T_2^{-1} is determined to within an accuracy of ±2%. The time resolution of the measurement is typically 1 ps. Delay of the probe pair with respect to the pump pair is obtained using an optical delay line.

Spontaneous Raman spectra have been obtained using a cw argon-ion laser operating at 45 mW and 514.5 nm. The spontaneous Raman-scattering signal was collected in a backscattering geometry, dispersed by a double-grating spectrometer and then processed by a photon-counting system. This setup enabled us to determine the Raman line shift and linewidth to within an accuracy of $\pm 0.05\ \mathrm{cm}^{-1}$.

Samples were grown from a saturated aqueous solution of KFCT by slowly evaporating the water at room temperature using a dry nitrogen-gas purge. The single crystals grow in flat, rectangular plates measuring approximately $0.1 \times 1 \times 1\ \mathrm{cm}^3$, with the (010) plane forming the face of the plate and the crystallographic a and c axes oriented at 45° to the edges. The samples were placed in an optical cryostat in which the sample temperature was kept stable to within ±1K. Sample capacitance was measured at 2000 Hz in the direction of the [010] axis using a GenRad type-1615-A capacitance bridge. The crystals were loosely held in between two parallel plates, each containing a small hole to allow light beams to pass through the sample. Prior to the optical experiments, the samples were cycled between room temperature and 180 K three times in order to eliminate any tetragonal KFCT that might be present in the sample. This process was indeed observed to take place from the increased smooth-

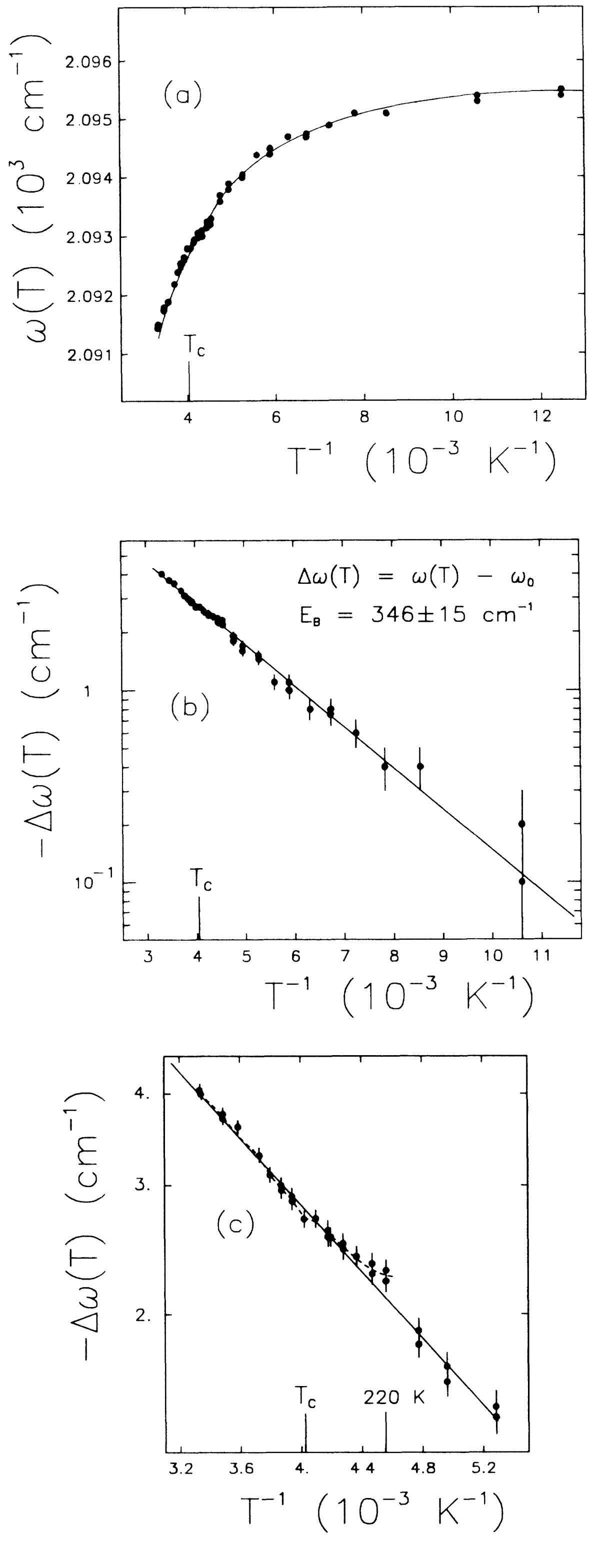

FIG. 2. (a) Variation of the Raman line shift of the A_{1g} CN stretching mode in KFCT with inverse temperature. The solid line is a guide to the eye. (b) The temperature-dependent part $\Delta\omega(T) = \omega(T) - \omega_0$ of the Raman line shift of the A_{1g} mode. The solid line is a fit to the VEE model which yields $E_B = 346 \pm 15\ \mathrm{cm}^{-1}$. (c) An enlarged view of $\Delta\omega(T)$ around T_C. The dashed line shows the influence of the water reorientational motion, superimposed on the exponential VEE behavior [depicted by the solid line, obtained in (b)].

ness of the sample capacitance-versus-temperature curves with the number of cooldowns. At the third cooldown, perfectly smooth curves were obtained, showing no anomalies at temperatures other than the Curie temperature (indicating the crystals to be practically free of lattice imperfections[4,6,7]) while being invariant under further repeated cooling.

During the cooling runs and during the optical experiments the single crystals remained perfectly transparent. To avoid the effect of thermal hysteresis, all optical and capacitance measurements series were performed with decreasing sample temperature. In the TSRG measurements the beams propagated along the [010] axis.

IV. RESULTS

The variation of the Raman line shift of the A_{1g} CN stretching mode with temperature as obtained from the spontaneous Raman-scattering results is displayed in Figs. 2(a)–2(c). We observe asymptotic behavior to 2095.50 cm^{-1} at low temperatures. After subtraction of this value for all temperatures, the resulting line shift is found to behave exponentially as a function of inverse temperature. The temperature dependence of the linewidth of the A_{1g} mode as obtained from spontaneous Raman scattering, corrected for its low-temperature value $[(T_2^{-1})_0=0.067\ \mathrm{ps}^{-1}]$, is shown in Fig. 3. Here, too, we observe exponential behavior. The values of the slopes of the curves of Figs. 2 and 3, together with the associated errors, were determined from a least-squares fit to exponential conduct. At $T \geq 220$ K the curves of Figs. 2 and 3 are seen to display additional structure, superimposed on the exponential behavior (cf. Sec. V). The spon-

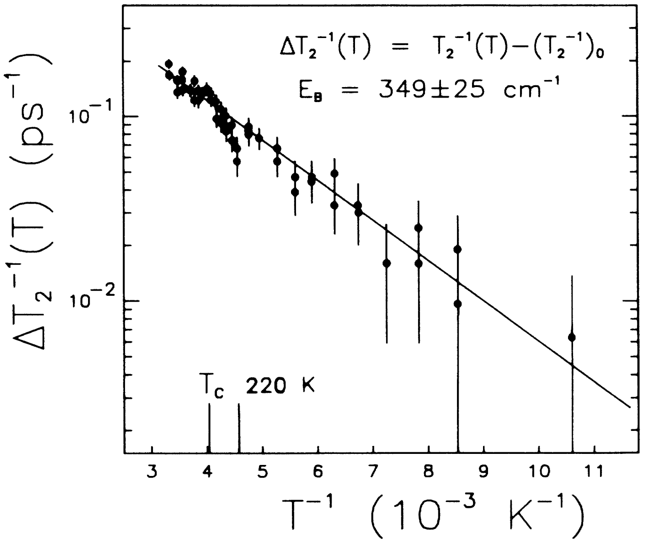

FIG. 3. Logarithmic plot of the temperature-dependent contribution $\Delta T_2^{-1}(T)=T_2^{-1}(T)-(T_2^{-1})_0$ to the Raman linewidth of the A_{1g} CN stretching mode in KFCT, yielding the same slope as the Raman line shift. The solid line is a fit to exponential behavior which yields $E_B=349\pm25\ \mathrm{cm}^{-1}$. One observes the influence of the water tunneling motion at $T \geq 220$ K.

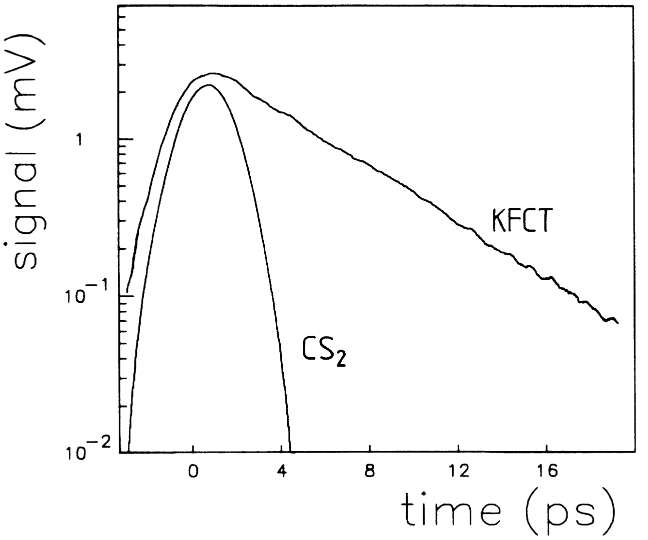

FIG. 4. Typical logarithmic plot showing the exponential decay of the stimulated Raman gain signal of the A_{1g} mode in KFCT in time (measured at $T=251$ K), corresponding to a Lorentzian line shape in the frequency domain. Also shown is a plot of the characteristic TSRG system response, obtained from instantaneous electronic and Kerr contributions to the TSRG signal of CS_2 (Ref. 25).

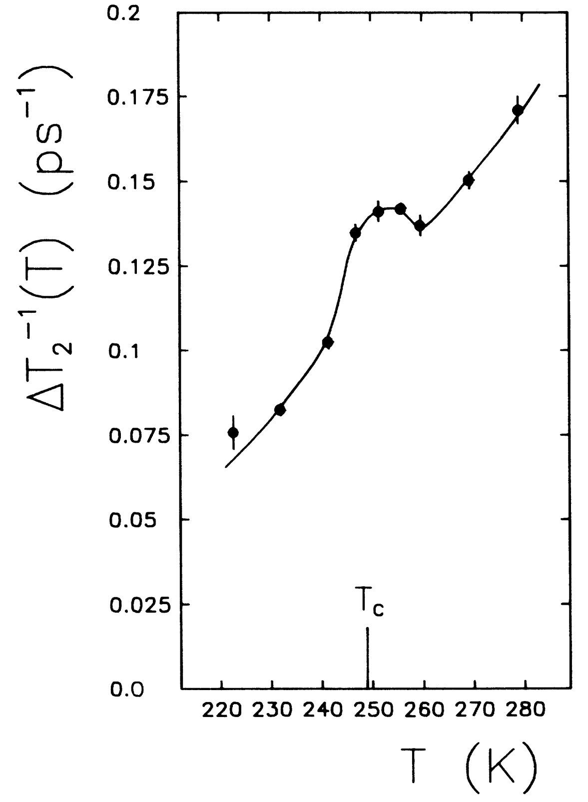

FIG. 5. Vibrational relaxation rate of the A_{1g} CN stretching mode in KFCT as obtained from TSRG measurements, corrected for $(T_2^{-1})_0$. One observes the effect of critical slowing down of the water reorientational motion at the ferroelectric phase transition. The solid line is a guide to the eye.

taneous Raman spectra yielded Lorentzian line shapes within experimental accuracy, for all temperatures studied.

A typical example of the decay of the stimulated Raman gain signal as a function of the delay is shown in Fig. 4. Digital noise filtering of the experimental data has been performed. The value of the vibrational relaxation rate, together with the associated error, was determined from a least-squares fit to an exponential decay. We observe the coherent A_{1g} vibrational excitation in KFCT (at $T=251$ K) to decay exponentially within the detection range, corresponding to a Lorentzian line shape in the frequency domain.

The behavior of the vibrational relaxation rate, obtained from TSRG measurements around the Curie temperature, corrected for $(T_2^{-1})_0$, is displayed in Fig. 5. Clearly, one observes an additional feature at the ferroelectric phase transition.

V. DISCUSSION

From Figs. 2 and 3 we find that both the line shift and linewidth of the internal A_{1g} CN stretching mode in KFCT behave exponentially as a function of inverse temperature. This indicates that the A_{1g} mode is perturbed by a VEE process, dominated by one exchange mode only. From the slopes we determine this exchange mode to have an excitation energy of 347±25 cm^{-1}. Consequently, the exchange mode is most probably the internal T_{1g} Fe—C$\equiv$N bending mode (libration), found by Nakagawa and Shimanuchi[28] to be situated at 350 cm^{-1} and by Salinkova and Uzunova[29,30] to be situated at 359 cm^{-1}.

The conception that the VEE process is dominated by only one exchange mode is also obtained from the behavior of $\Delta T_2^{-1}(T)/\Delta\omega(T)$, where $\Delta T_2^{-1}(T)=T_2^{-1}(T)-(T_2^{-1})_0$ and $\Delta\omega(T)=\omega(T)-\omega_0$, as a function of inverse temperature, displayed in Fig. 6. For $T<220$ K the value of $\Delta T_2^{-1}(T)/\Delta\omega(T)$ is found to be constant within error, which confirms that the VEE process is dominated by only one exchange mode.

At $T\geq 220$ K the value of $\Delta T_2^{-1}(T)/\Delta\omega(T)$ is found to vary with temperature, the origin of which can be located in the graphs of $\Delta T_2^{-1}(T)$ versus T^{-1} (cf. Fig. 3) and, to a lesser extent, $\Delta\omega(T)$ versus T^{-1} [cf. Fig. 2(c)]. The value of $\Delta T_2^{-1}(T)/\Delta\omega(T)$ is found to decrease appreciably at 220 K, after which it rises again upon approaching the Curie temperature. The exact behavior of the vibrational relaxation rate around the Curie temperature is clarified in the TSRG measurements, displayed in Fig. 5. Around T_C, one clearly observes an anomaly in the behavior of the vibrational dephasing rate which is characteristic for an excitation weakly coupled to a critical slowing-down mode.

Our experimental results allow us to identify the nature of the phase transition in KFCT. In several cases, the linewidth of a soft mode is independent of temperature, as predicted by mean-field theory.[31,32] In that case, when a high-frequency mode A couples to a soft mode, e.g., through VEE, the line shape of mode A will be determined by the occupation number of the soft mode, assuming the coupling strength to vary slowly with the frequency of the soft mode. As the occupation number strongly increases at temperatures close to T_C, the spectral line of mode A would display anomalous line broadening and an anomalously *increased* shift of the vibrational frequency, both of which will reflect the occupation number of the soft mode.

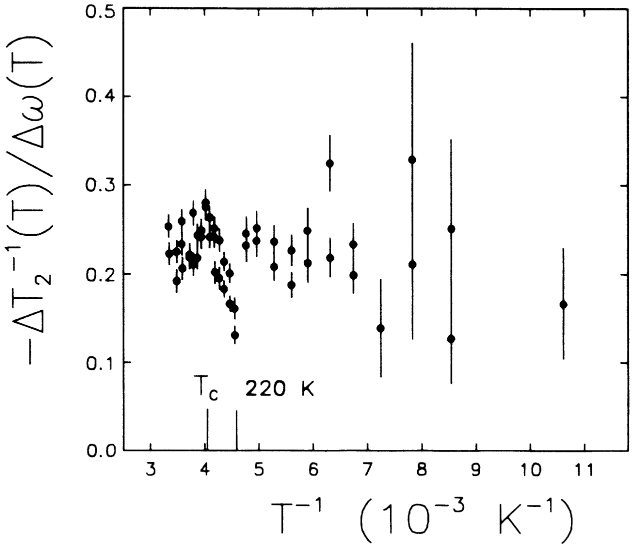

FIG. 6. Behavior of $\Delta T_2^{-1}(T)/\Delta\omega(T)$ with inverse temperature, as obtained from spontaneous Raman-scattering results. The values at $T<220$ K reveal intermediate broadening of the A_{1g} mode as a result of the vibrational-energy-exchange process. The behavior at $T\geq 220$ K is a result of changes in the water reorientational frequency.

In other cases the linewidth of a soft mode is found to vary as $T\rightarrow T_C$.[32,33] This may significantly influence the broadening of mode A around T_C, but it would leave the anomalous shift of the vibrational frequency of mode A essentially unaltered.

In case of an order-disorder–type phase transition, coupling of a high-frequency mode A to the relaxation mode, e.g., by means of pure dephasing,[22] will cause mode A to display anomalous line broadening at T_C. At T_C the shift of the vibrational frequency of mode A will show a *decreased* value. Both processes are due to an increase in the bath correlation time[34] τ_C (determined by H_{bath}), arising from critical slowing down of the relaxation mode. The A_{1g} mode in KFCT is indeed observed to show anomalous line broadening at T_C (cf. Fig. 5). The A_{1g} line shift is *not* seen to display an increased value at T_C, with respect to the observed exponential behavior [cf. Fig. 2(c)], but rather a shallow decrease, demonstrating the phase transition to be of order-disorder nature.

We attribute the additional structure, superimposed on the exponential VEE behavior of $\Delta T_2^{-1}(T)$ and $\Delta\omega(T)$, to the reorientational tunneling motion of the water molecules. The cyanide groups are weakly coupled to the water molecules through O—H· · ·N hydrogen bonds;[5,6,14] the reorientational motion thus provides a second dephasing channel for the A_{1g} mode: pure dephasing (PD),[22] superimposed on the VEE process. For the Hamiltonian of Eq. (1) this means the addition of an extra term, $H_{A\,\mathrm{bath}}$, describing the coupling of mode A to the randomly fluctuating bath. As a result of energy separation between the coupling terms described by $H_{A\,\mathrm{bath}}$ and $H_{B\,\mathrm{bath}}$, interference effects between PD and VEE are not likely to be observed.

Weak reorientational motion was observed for $T > 140$ K.[5,6] Proton NMR studies revealed a sudden increase in the reorientational frequency around 220 K.[5,6,11] This will lead to motional narrowing of the A_{1g} line, as well as to an increased shift of the vibrational frequency with respect to the exponential behavior due to the VEE process, both of which are observed at $T = 220$ K [cf. Figs. 2(c) and 3].

As the temperature rises towards T_C, the reorientational motion of the water molecules will slow down, causing the PD contribution to the Raman line shape to increase again. Critical slowing down of the water reorientational motion will finally result in anomalous broadening of the A_{1g} line at T_C, as is clearly observed in the TSRG measurements.

The constant value of the proton NMR linewidth[5,6] at $T < 220$ K implies that the PD contribution to the A_{1g} line shape is essentially constant up to 220 K. Thus, for $T < 220$ K the temperature dependence of the A_{1g} line shape is solely determined by the VEE process. This yields the constant value of $\Delta T_2^{-1}(T)/\Delta\omega(T)$, at these temperatures equal to $(\delta\omega)\tau$. The values of $(\delta\omega)\tau$ reveal intermediate broadening of the A_{1g} mode as a result of the VEE process, $(\delta\omega)\tau = -(0.22 \pm 0.05)$. The coupling strength $\delta\omega$ between the A_{1g} and T_{1g} modes is found to be $-(23 \pm 5)$ cm^{-1}; the correlation time τ of modes B equals 0.06 ± 0.01 ps.

The increased shift of the vibrational frequency of the A_{1g} mode at $T = 220$ K, with respect to the exponential behavior due to the VEE process, is observed to be very moderate, indicating the cyanide group to be weakly coupled to the water molecules. This is confirmed by the observation of exponential decay of the TSRG signal (within the detection range), even at temperatures close to T_C.

In conclusion, it is seen that the combination of highly accurate picosecond stimulated Raman-scattering techniques and conventional Raman spectroscopy can be successfully applied to studying dynamical critical effects in solids. Relatively simple dephasing models are shown to be most useful in elucidating the complicated interactions between vibrational excitations in a solid.

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[34] See the reference quoted in Ref. 22, or see Ref. 32, pp. 39 and 40.