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Relaxation of Vibrational Excitons in Molecular-Ionic Crystals Measured by Picosecond Time-Resolved CARS*

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The decay times of the internal vibrations in K_2SO_4, $KClO_4$, $NaNO_3$ and $CaCO_3$ single crystals have been measured at different temperatures by picosecond time-resolved CARS. The low temperature experimental data and their temperature dependence are interpreted on the basis of an energy relaxation mechanism, involving two-phonon and higher order decay processes.

1. INTRODUCTION

Interest in vibrational relaxation in molecular solids has grown considerably since ultra-short pulsed laser sources made picosecond time-resolved experiments possible. Time resolved stimulated Raman (TRSR)[1] and coherent antistokes Raman scattering (CARS)[2] experiments are in fact useful techniques for direct measurement of the relaxation time τ of coherently excited vibrational states. A limited number of internal vibron and external phonon vibrational bands in molecular crystals has been studied by time resolved techniques[3-8]. Recently, the same kind of information has been obtained in the frequency domain (linewidth 2Γ and relaxation time τ are related by $2\Gamma = 1/(2\pi c\tau)$) by means of high-resolution spontaneous Raman experiments[9-11].

Parallel to the experimental work, much effort has been devoted to the development of computational procedures for calculating phonon linewidths or relaxation times on the basis of anharmonic intermolecular potentials, using perturbative methods[12-18].

In spite of the experimental and theoretical interest of the subject, some relevant aspects of the problem are still open to discussion:

i) the relative importance of pure dephasing (T_2*) with respect to population decay processes (T_1) in determining the observed relaxation times;

ii) the role of the different multi-phonon scattering processes responsible for the linebroadening of vibrational transitions in molecular crystals.

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Important information on points (i) can be obtained from linewidth measurements at temperatures near 0 K. At a very low temperature the thermal bath is completely depopulated and all phonon dephasing processes which require the interaction with thermal phonons are switched off[19]. The vibrational energy can relax thus (in a perfect crystal) only through T_1 phonon decay processes. On the other hand, models proposed for the decay mechanisms, involving different anharmonic terms of the crystal potential, can be tested against their ability to reproduce the experimental temperature dependence of the linewidths[16] (point ii).

Molecular-ionic crystals like nitrates, carbonates, sulphates, perchlorates etc. represent an ideal class of compounds for studying vibrational relaxation. Owing to the small number of atoms and to the high symmetry of the molecular anions, the internal vibrational levels are few and well separated in energy: the interpretation of the observed linewidths in terms of the different possible decay channels is then relatively simple. In addition, good quality single crystals, required for laser spectroscopy, can be easily obtained.

In the present paper, we report therefore on vibrational relaxation times of some internal vibrations of K_2SO_4, $KClO_4$, $NaNO_3$ and $CaCO_3$ single crystals, directly measured by time-resolved picosecond CARS experiments.

2. EXPERIMENTAL

K_2SO_4 and $KClO_4$ crystallize in the orthorhombic system space groups D_{2h}^{16}; $CaCO_3$ and $NaNO_3$ are rombohedral crystals with space groups D_{3d}^{6}. Optically transparent large single crystals of the water soluble compounds were obtained by slow evaporation of saturated solutions in a temperature controlled environment. The crystals were cut as parallelepipeds with edges aligned to the principal directions of the optical indicatrix with the help of a polarizing microscope. A single crystal of $CaCO_3$ was cut from a commercial cube polarizer. The Raman and Infrared spectra of these crystals are reported in Refs. 20, 21, 22 and 23, respectively. In a typical time domain CARS experiment, two laser beams of frequency ω_1 and ω_2, chosen so that the difference $\omega_1 - \omega_2$ corresponds to the energy of a $k = 0$ vibron, are focused on the sample and the forced vibrational coherence produced is probed by a delayed ω_1' pulse. The Antistokes intensity generated in this parametric process is then collected as a function of the time delay between ω_1, ω_2 and the probe pulse. An exponential decay of the CARS signal is usually obtained. The coherence decay time is extracted from the signal by deconvolution with experimental function and fitting.

In our CARS experiment, two dye lasers were synchronously pumped with 60% and 40%, respectively, of the intensity of the 5145 A output of a mode-locked Ar^+ ion laser (1 W at 76 MHz, pulse length $\simeq$ 200 ps). The experimental set up used is shown schematically in Figure 1. The higher intensity green beam pumps the DL1 laser with rhodamine 6G dye, yielding pulses of about 140 mW average power at 580 nm and 5 ps FWHM. The other beam pumps rhodamine 610 dye in the DL2 laser with an output of about 70 mW at 610 nm and about 16 ps FWHM. The jitter between the two beams gives a cross-correlation of about 30 ps. This does not, however, affect the instrumental resolution which is limited by the autocorrelation of the narrowest emission, *i. e.*, ω_1 of DL1. Part of this emission ($\simeq$ 15%), hereafter called ω_1', is split and sent to a computer controlled optical delay line (OD) and used as probe beam. A decisive improvement in the S/N ratio was obtained using a folded (Boxcar) CARS geometry and inserting in the laser beam paths dispersive elements (P) which considerably reduce the superradiance of the DL1 and DL2 emission. The CARS beam was spatially filtered, collimated, dispersed in a high rejection Jobin-Yvon U1000 double monochromator and sent to a cooled photomultiplier. The amplified signal was either sent to a lock-in amplifier triggered by a chopper in the DL2 beam for alignment or to a photon counting system for data acquisition. The sweep of the delay line and the collection of Raman photon counts were synchronized with a computer. Decay over 5 decades of signal (with aquisition time of 1 sec

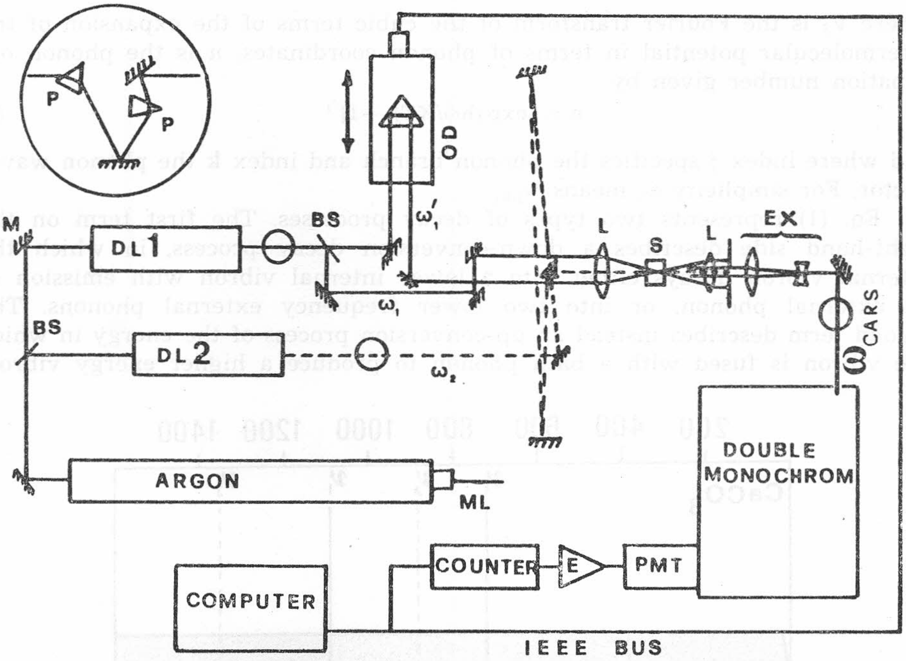

Figure 1. Scheme of the experimental set-up

per channel) was observed in most favorable cases. Measurements as a function of temperature were performed in a closed circulation He cryostat.

3. RESULTS AND DISCUSSION

As already pointed out before, time resolved CARS spectroscopy cannot provide information on the relative contribution of energy relaxation T_1 and of pure dephasing T_2^* processes to the observed linewidth. However, previous experimental[3,24] and theoretical[15,16] work indicate the T_1 mechanism as the prevalent one even at relatively high temperatures. For this reason, we shall first interpret our data in terms of energy relaxation mechanisms. Since the T_1 mechanisms are based on phonon-assisted non radiative transitions among vibrational states, a knowledge of the distribution of the internal and external vibrational levels of the crystal represents a key piece of information.

In the next two sections we will discuss separately the results obtained for the low temperature (10 K) linewidths and for their dependence on the temperature.

3.1. Low Temperature Results

At the lowest order of perturbation, the general expression for the linewidth of a $k = 0$ vibron ω_0 due to energy decay mecanisms is given by[25]

$$\Gamma = 18\hbar^{-2} \Sigma_{j_1 j_2} \Sigma_{k_1 k_2} \left| V_3 (0j, j_1\mathbf{k}_1, j_2\mathbf{k}_2) \right| \times \tag{1}$$

$$\{(n_1 + n_2 + 1)[\delta(\omega - \omega_1 - \omega_2) - \delta(\omega + \omega_1 + \omega_2)] + (n_2 - n_1)[\delta(\omega + \omega_1 - \omega_2) - \delta(\omega - \omega_1 + \omega_2)]\}$$

where V_3 is the Fourier transform of the cubic terms of the expansion of the intermolecular potential in terms of phonon coordinates, n is the phonon occupation number given by

$$n = [\exp(\hbar\omega/KT) - 1]^{-1} \tag{2}$$

and where index j specifies the phonon branch and index $\mathbf{k}$ the phonon wavevector. For simplicity ω_i means $\omega_{j_i k_i}$.

Eq. (1) represents two types of decay processes. The first term on the right-hand side describes a down-conversion decay process, in which the internal vibron decays either into a lower internal vibron with emission of an external phonon, or into two lower frequency external phonons. The second term describes instead an up-conversion process of the energy in which the vibron is fused with a bath phonon to produce a higher energy vibron.

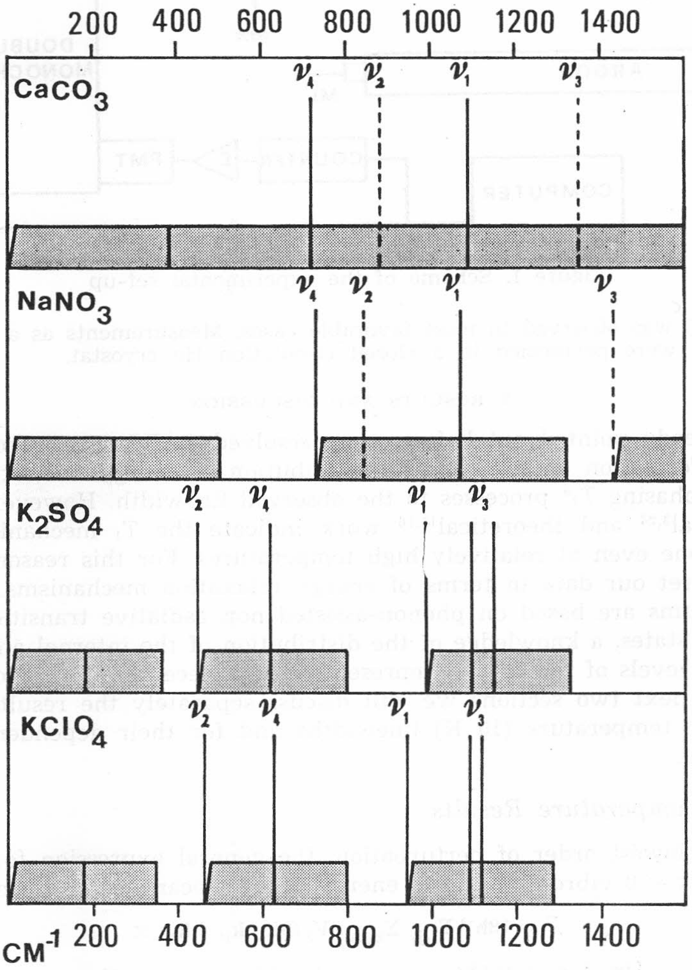

Figure 2. Scheme of the one- and two-phonon states of the four ionic crystals. The vertical lines represent the internal vibrations; the extension of the two-phonon density of states is represented by the shaded areas.

At a very low temperature, the thermal bath is depopulated and only down-conversion processes are possible. The 0 K two-phonon density of states then dominates the relaxation near the absolute zero.

Figure 2. shows the fundamental internal vibrational levels (vertical lines) of the four crystals considered, together with the corresponding 0 K two-phonon density of states (shaded areas). These are built from: i) the sum of two external vibrations and ii) the sum of one internal and one external vibration. The dispersion of the internal vibrons is negligible for all modes except for the strong infrared active antisymmetric stretching vibrations ν_3; only the position of the Raman active components of A_g species is shown in the Figure for these modes in K_2SO_4 and $KClO_4$.

According to the population decay mechanism of eq. (1), the internal vibrons whose frequency corresponds to a region of non-zero density of two-phonon states, have many decay channels available, and are then expected to show a relatively broad linewidth even at very low temperatures. On the contrary, the internal vibrons ν_4 in $NaNO_3$, ν_1 and ν_2 in K_2SO_4 and $KClO_4$ which fall in a region where no two-phonon state is available, cannot decay into two lower frequency modes and should appear as narrow lines. The experimental results reported in Table I are fully consistent with these predictions: only ν_4 in $NaNO_3$ and ν_1 and ν_2 in K_2SO_4 and $KClO_4$ show long relaxation times.

TABLE I

Vibrational Decay Times of Some Vibrons of Typical Molecular-Ionic Groups in Ionic Crystals at 10 K

crystal	mode	ν (cm^{-1})	τ (ps)*
$CaCO_3$	ν_1 (symm. stretch.)	1083	17
	ν_4 (symm. bending)	715	<5
$NaNO_3$	ν_1 (symm.stretch.)	1065	7.5
	ν_4 (symm. bending)	725	64
K_2SO_4	ν_1 (symm. stretch.	983	294
	ν_2 (symm. bending)	447	21
	ν_3 (antisym. stret.)	1094 1145	<9
	ν_4 (antisym. bend.)	617	<9
$KClO_4$	ν_1 (symm. stretch.)	940	180
	ν_2 (symm. bending)	460	81
	ν_3 (antisym. stret.)	1088 1118	<5
	ν_4 (antisymm. bend.)	626	<5

* Typical error: ±0.5 ps

The three phonon decay processes of eq. (1) provide therefore a qualitatively satisfactory explanation of the experimental data at a low temperature. We discuss now the differences observed between the lifetimes of modes ν_1 and ν_2 in K_2SO_4 and $KClO_4$ for which, two-phonon decay is not possible. At a very low temperature, linebroadening for these vibrons can only occur through: a) higher order anharmonic processes, like fission of $k = 0$ phonon in three lower frequency phonons; b) impurity- and defect-induced dephasing.

Hochstrasser and coworkers[26] have shown that scattering and trapping by ^{13}C isotopic impurities in natural abundance represent a very large contribution to the total linewidth for some internal modes of benzene crystal. The different linewidths measured for ν_1 and ν_2 in K_2SO_4 and $KClO_4$ could in principle be explained on the basis of such isotopic effects, as discussed in ref. 27. In fact, sulfur and chlorine atoms are at rest in the symmetric stretching vibrations ν_1, and the corresponding phonon lifetime cannot be affected by the presence of isotopic impurities, whereas the same is not true for the bending mode ν_2 for which the central S or Cl atom is displaced during the vibration. Since data on the isotopically pure compounds are not available at the moment, we cannot draw any definite conclusion on the role played by the impurities.

We discuss now the vibrations ν_1 and ν_4 of $CaCO_3$. In this case, due to the very high frequency of the lattice vibrations, all internal modes find a large number of two phonon decay channels at a low temperature. The different lifetimes observed for ν_1 and for ν_4 can then be explained as due to an intrinsically higher anharmonicity (with respect to the intermolecular potential) of the bending mode if compared to the stretching mode. If such a conclusion could be extended to the other crystals, one would expect that high order (for instance fourth order) anharmonic processes are likely to have a much more relevant role in the relaxation of the bending than of the stretching modes.

3. 2. *Temperature Dependence*

Figures 3. to 5. show the reciprocal lifetimes observed at different temperatures up to 200 K. The behavior of the bands considered differs remarkably from case to case:

a) ν_1 in K_2SO_4 and in $KClO_4$ (Figure 3.) has a definite linear dependence on the temperature for $T > 50$ K, as predicted by eq. (1) in the high temperature limit ($K_BT > \hbar\omega$) where eq. (2) can be approximated by $n \simeq K_BT$. In both crystals, the symmetric stretching mode ν_1 relaxes trough three-phonon scattering processes, involving the anharmonic cubic terms of the intermolecular potential. Of course, only up-conversion thermally activated processes are possible for these modes: if a single process of the type $\nu_1 + \omega_L = \nu_3$ is assumed as representative of all the three-phonon up-conversion processes, eq. (1) can be written as

$$\Gamma = D\, n\, (\omega_L) \tag{3}$$

where ω_L is the frequency of a lattice phonon.

The values for D and ω_L can be obtained by fitting the experimental curves: we obtain for K_2SO_4 $D = 1.06$ cm^{-1}, $\omega_L = 135$ cm^{-1} and $D = 0.82$ cm^{-1} and $\omega_L = 90$ cm^{-1} for $KClO_4$. It is interesting to notice that the frequency of the lattice phonon ω_L is in both cases in very good agreement with the frequency separation between ν_1 and ν_3; the lower value of ω_L in $KClO_4$ causes the linewidth of ν_1 to reach the linear regime at a temperature lower than in K_2SO_4.

b) ν_2 in $KClO_4$, and less evidently in K_2SO_4 (as a consequence of the smaller temperature range considered for this crystal), shows (Figure 4) a well defined T^2 dependence, indicating that anharmonic processes of higher order

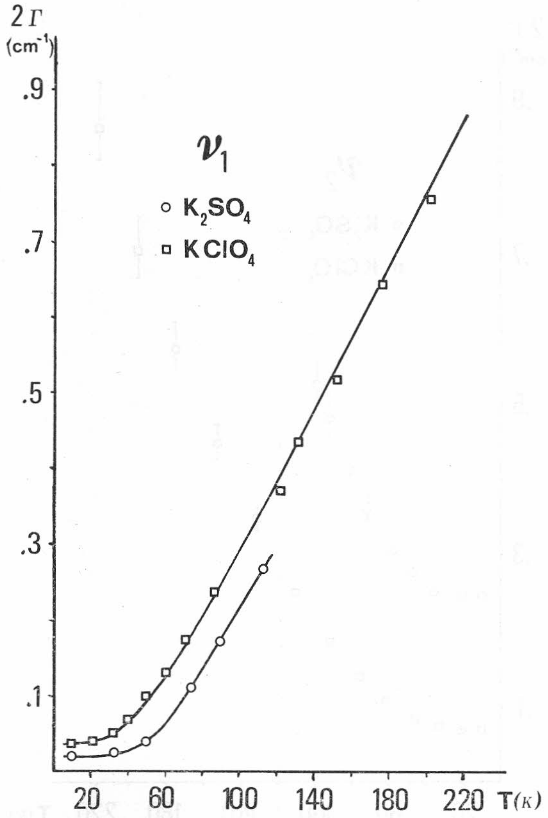

Figure 3. Linewidths of ν_1 stretching mode in K_2SO_4 and $KClO_4$ measured as a function of the temperature. The solid lines are calculated from eq. (1) (see text).

than those of expression (1) take place. A number of different processes are possible: decay into three low-frequency phonons (involving quartic terms of the anharmonic potential), or multiple scattering of phonons due to the cubic anharmonicity. In all those cases, the linewidth depends quadratically on the occupation numbers[28], and a T^2 dependence is expected in the classical limit.

The 10 K linewidth of ν_2 and its temperature dependence in both crystals indicates that the bending mode is remarkably more sensitive to the intermolecular anharmonicity than the stretching mode.

c) The behavior of the ν_4 bending mode of $NaNO_3$ (Figure 5) can be reasonably well fitted by eq. (1) up to about 120 K; at higher temperatures the slope of the experimental curve changes drastically, showing that higher order processes are switched on.

d) As already noticed in section 3.1, $CaCO_3$ differs from the other crystals considered in that all internal vibrations have two-phonon decay channels available also at very low temperatures: only ν_1, however, has a lifetime long enough to be measured with our instrumental set-up. As shown in Figure 5,

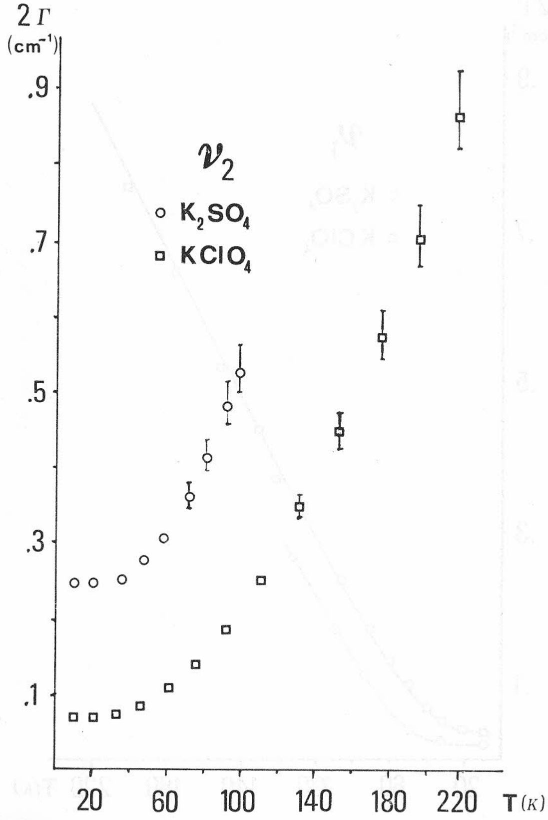

Figure 4. Linewidths of ν_2 bending mode in K_2SO_4 and $KClO_4$ measured as a function of the temperature.

the temperature behavior of this band is quite peculiar: its linewidth in fact increases with T much less than the other bands in Figures 3, 4 and 5. The energy level scheme in Figure 5a shows that ν_1 in $CaCO_3$ can only decay into ν_2 plus an external phonon of about 210 cm^{-1}: the temperature dependence of 2Γ predicted by eq. (1) is then very small, at least in the temperature range considered here. The only possible up-conversion process $\nu_1 + \omega_L \rightarrow \nu_3$ requires an even higher external phonon (about 270 cm^{-1}), and its contribution is negligible. By using an average D anharmonic coefficient obtained by fitting of the 10 K linewidth, and taking the frequency of the external phonon equal to the difference between ν_1 and ν_2, eq. (3) predicts a temperature dependence of the linewidth which is about one half of the observed one. A non-negligible contribution from higher order processes should be invoked to explain the observed curve.

4. CONCLUSION

The decay times measured for the internal vibrations in K_2SO_4, $KClO_4$, $NaNO_3$ and $CaCO_3$ are in good agreement with population relaxation mecha-

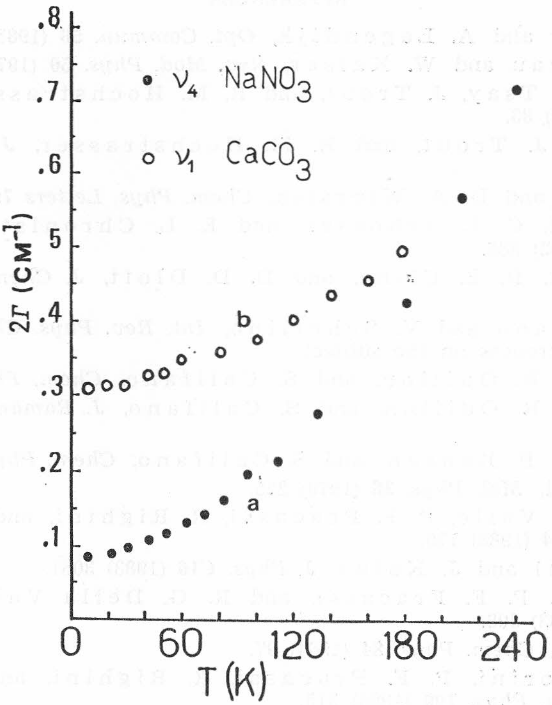

Figure 5. Temperature dependence of the linewidth of: a) ν_4 bending mode in $NaNO_3$ b) ν_1 stretching mode in $CaCO_3$.

nisms for the vibrational dephasing. The symmetric stretching modes in K_2SO_4 and in $KClO_4$ are only sligthly affected by the intermolecular anharmonicity: the linear temperature dependence shown by the linewidths of such modes implies that only two-phonon decay processes are involved. A similar behavior has been observed in molecular crystals like naphthalene[16] and anthracene[11,29]. It is interesting to note that the slope of curve 2Γ versus T measured for the 766 cm^{-1} ν_8 band in naphthalene is similar to those of K_2SO_4 and $KClO_4$. The anharmonic effects in the two different types of crystals are then of the same order of magnitude; this observation confirms previous theoretical results on the negligible contribution of the coulomb interactions to the intermolecular anharmonicity[18].

The results obtained for the bending modes indicate that such vibrations are affected to a larger extent by the intermolecular anharmonicity. The non-linear temperature dependence of the bending linewidths observed in K_2SO_4, $KClO_4$ and $NaNO_3$ indicates that high order anharmonic effects, involving multi-phonon scattering, are effective also at relatively low temperatures.

A better understanding of the decay processes in this class of crystals, and in particular of the different behavior of the bending and stretching modes, would be provided by anharmonic lattice dynamics calculations; work in this direction is in progress in our laboratory.

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SAŽETAK

Relaksacija vibracijskih ekscitona u molekulsko-ionskim kristalima mjerena pikosekundnom vremenski razlučenom CARS

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Mjerena su raspadna vremena unutarnjih vibracija monokristala K_2SO_4, $KClO_4$, $NaNO_3$ i $CaCO_3$ pri različitim temperaturama pikosekundnom vremenski razlučenom CARS. Nisko temperaturni eksperimentalni podaci i njihova temperaturna ovisnost interpretirani su na temelju energijskog relaksacijskog mehanizma, koji uključuje dva fonona i raspadne procese višeg reda.