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Nonlinear ir properties of an LO phonon in thin $KReO_4$ films

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Nonlinear ir absorption has been measured in an LO phonon in thin $KReO_4$ films at room temperature. The excited-state lifetime is at least two orders of magnitude longer than that observed for the corresponding single-ion vibrational mode in matrix-isolated ReO_4^-. We attribute the long lifetime to the restrictions imposed by phonon momentum conservation within the film.

Nonlinear infrared absorption of matrix-isolated ReO_4^- molecules in single-crystal alkali-halide hosts occurs because of vibrational mode anharmonicity.[1,2] Since crystal momentum is not conserved at a defect, the decay path from the excited state of the molecule is determined solely by energy conservation. We report here on the first observation of intensity-dependent infrared transmission of an LO phonon in thin $KReO_4$ films. The saturation intensity is at least a factor of 10 smaller than for the same vibration in matrix-isolated ReO_4^- while the T_1 excited-state lifetime is orders of magnitude larger than that observed for the single-ion mode.[3,4] We attribute the long lifetime of the LO phonon to the added constraint of phonon $\vec{k}$-vector conservation within the film.

The samples were prepared by evaporating (10^{-6} Torr) 500- to 6300-Å-thick films onto room-temperature alkali-halide, germanium, and metal mirror substrates. Figure 1(a) shows TM-polarized transmission spectra of a 700-Å $KReO_4$ film on a dielectric substrate for 0° and 45° angles of incidence. The LO absorption at 951 cm^{-1} is produced by the component of the ir electric field perpendicular to the surface, while the TO absorption, which appears as a strong doublet at 903 and 909 cm^{-1}, is produced by the E-field component in the plane of the film.[5] The TM-polarized reflectance spectrum of a 500-Å film on a metal mirror at a 45° angle of incidence is shown in Fig. 1(b). Because the tangential component of the ir electric field must be zero at the surface of a metal, the TO mode cannot be excited.[5] A 0.2% change observed in the measured LO frequency from evaporation to evaporation is thought to arise from film-density variations. The angular dependence of the LO mode absorption for TM-polarized radiation is described by $\sin^2\theta/\cos\theta$, the expected angular variation for the thin-film limit.[6]

Saturation measurements were made with a transversely-excited-atmosphere (TEA) CO_2 laser which produces smoothed, spatially Gaussian, gain-switched pulses of radius 0.05 mm and length 130 nsec. Intensity-dependent transmission and reflection measurements were made with TM-polarized radiation incident at 30°, 45°, and 60° to the film normal at the $P(10)$, $P(12)$, and $P(14)$ transitions of the 10.6-μm CO_2 branch.

Since both the incident and the reflected waves from the substrate interfere, the laser intensity incident on the thin film, I_{in}, is not the same as the intensity I incident on a bulk sample. Superimposing the normal components of the incident and reflected waves, one obtains

$$I_{in} = I|1+\hat{r}(\theta)|^2\sin^2\theta \ , \qquad (1)$$

where θ is the angle of incidence and $\hat{r}(\theta)$ is the TM-polarized amplitude reflectance from the bare substrate determined by the Fresnel equations.[7] All intensities quoted in the remainder of this paper refer to I_{in}. The saturation intensity I_s is the particular value of I_{in} where nonlinear transmission or reflection begins. (The exact determination of I_s will be described later.)

Because the LO mode has a full-width–at–half-maximum absorption of 3.8 cm^{-1}, coincidences at both $P(12)$ and $P(10)$ occur. Within the experimental errors, the measured values of I_s at these two frequencies are identical and in-

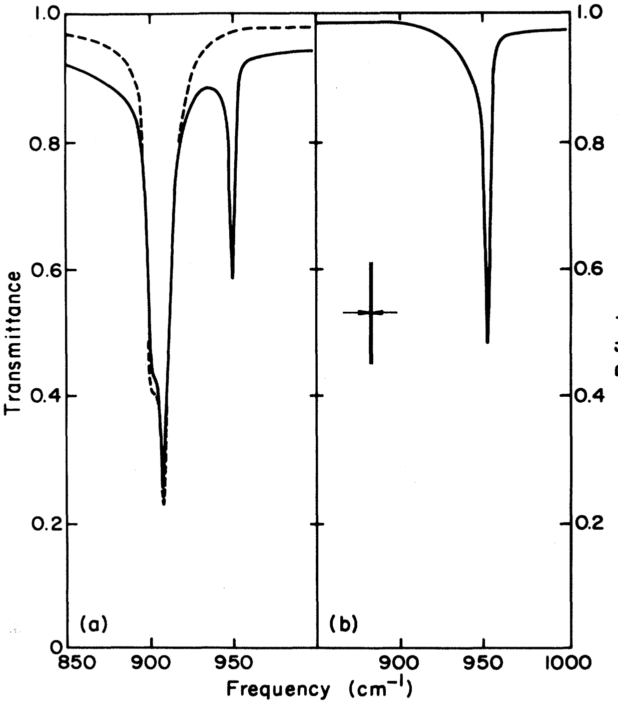

FIG. 1. Room-temperature spectra of thin $KReO_4$ films: (a) 700-Å film on KCl and (b) 500-Å film on Al. The dashed line is for normal incidence and full lines are for TM-polarized light incident at 45°. Resolution is 0.5 cm^{-1} as indicated by the arrows.

dependent of the angle of incidence. No coincidence with the LO mode occurs at $P(14)$ and no change in transmission or reflection with intensity is observed at this frequency.

The intensity-dependent reflectance of a 500-Å-thick $KReO_4$ film on an Al mirror is shown in Fig. 2(a). The value of $I_s = 140$ kW/cm^2 is identified by the arrow. Figure 2(b) shows a similar measurement of the intensity-dependent transmittance through a 6300-Å-thick $KReO_4$ film on an NaCl window; the value of $I_s = 300$ kW/cm^2. We have also made measurements on a number of other thin-film-substrate combinations. All of our measurements on films with thickness ≤ 1500 Å show intensity-dependent curves similar to that shown in Fig. 2(a). Inspection of Table I indicates that the measured I_s does not depend on the film substrate. The more rapid change in the transmission with intensity for the NaCl substrate shown in Fig. 2(b) and the apparent large value of I_s are probably due to interference effects within the film. The thin-film approximation used to obtain Eq. (1) is not valid for this film thickness.

We have also measured the transmittance of the corresponding ν_3 mode of matrix-isolated ReO_4^- molecules in KCl (Ref. 4) and KBr. The results for KCl are shown in Fig. 2(c). The I_s values for this homogeneously broadened mode are recorded in Table II.

The high-intensity limit in the thin-film data is determined by the onset of surface damage at approximately 3 mJ. Damage is clearly indicated by a decrease in low-signal absorption as $KReO_4$ is expelled from the surface. A white spot appears on the evaporate surface and grows somewhat in area with each subsequent pulse. Phase contrast microscopy reveals the damage as a laser-induced periodic structure[8,9] in either parallel or circular patterns with periodicity roughly equal to $\lambda/(1-\sin\theta)$, where λ is the wavelength of the light and θ is the angle of incidence. Patterns of twice this periodicity are also observed. Keilman[8] has shown such structure to be a result of the superposition of surface polaritons resulting from a phase matching of the incident light to the surface plasmon through microscopic disturbances in the surface such as a scratch or pit, thereby producing a parallel or circular pattern, respectively. The increase in the damage area results from the induced grating acting as an antenna for the surface polaritons.

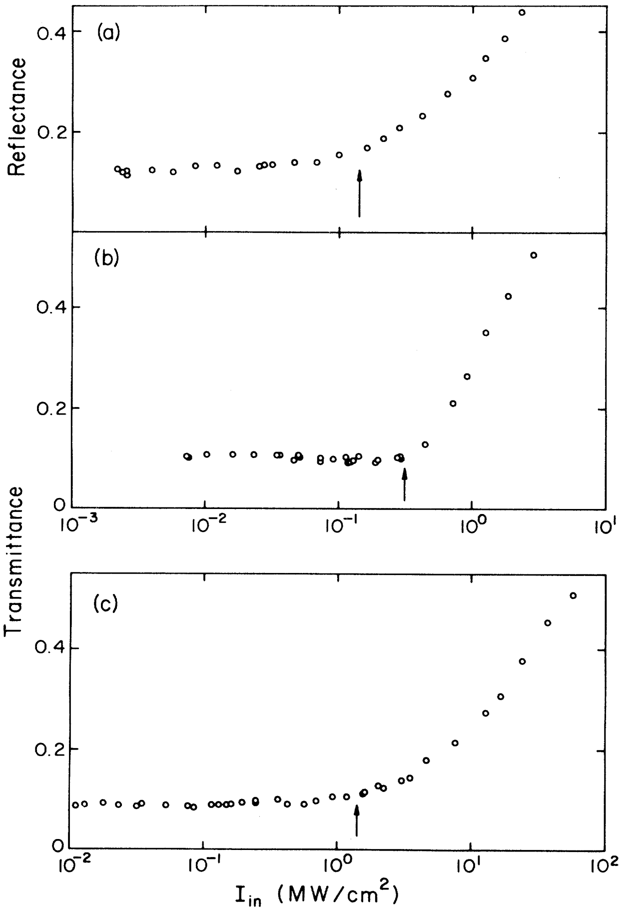

FIG. 2. Saturation of a vibrational mode at room temperature. (a) Reflectance from a 500-Å $KReO_4$ film on an Al mirror. (b) Transmittance through a 6300-Å $KReO_4$ film on an NaCl window. TM-polarized CO_2 $P(12)$ radiation incident at 45°. (c) Transmittance through a KCl single crystal doped with ReO_4^- CO_2 $P(28)$ radiation.

Passive mode locking has been observed with the alkali-halide-based films. The saturable absorber was placed at a low-power point of a grating-controlled unsmoothed TEA CO_2 laser, 140 cm from the grating at an angle of 50° to the axis. The mode-locked pulse trains consisted of 2-nsec detection-limited pulses separated by 18 nsec, corresponding to the round-trip cavity time. The output integrated energy

TABLE I. Saturation intensities of thin $KReO_4$ films. TM-polarized $P(12)$ radiation is incident at 45° to the normal.

Substrate	Thickness (Å)	I_s (kW/cm^2)	Reflection (R) or transmission (T)
Al on glass	500	140	R
Ag on Ge	1500	170	R
Ag on KCl	1200	170	R
Ge	500	140	R
Ge	500	120	T
KCl	700	100	T
NaCl	6300	300	T

TABLE II. Saturation intensities and lifetimes of thin $KReO_4$ films and matrix-isolated ReO_4^- at 300 K. The cross section for the LO mode is 1.5×10^{-17} cm^2, for the single-ion mode (Ref. 4) it is 6.8×10^{-17} cm^2.

	I_s (MW/cm^2)	T_1 (sec)	T_2 (sec)
Thin $KReO_4$ films[a]	0.14 ± 0.03	9×10^{-9}	9×10^{-12}
$KCl:ReO_4^-$ [b]	1.45	1×10^{-10}	1.6×10^{-11}
$KBr:ReO_4^-$ [a]	7 ± 3	4×10^{-11}	1.2×10^{-11}
$KI:ReO_4^-$ [c]	6.7	3×10^{-11}	9.7×10^{-12}

[a] This work.
[b] Reference 4.
[c] Reference 2.

was about 10% of the unlocked pulse due to the incomplete saturation of the absorber. A higher level of output power could not be obtained without film damage.

The LO-mode linewidth which is a factor of 3 larger than the single-ion width at room temperature and increases approximately linearly with temperature from 300 to 500 K appears to be homogeneously broadened. In order to calculate I_s we introduce a homogeneously broadened two-level model. The experimental values of I_s are determined from a three-parameter fit to the saturation data.[10] One uncertainty in the saturation parameter calculation occurs because the film damage threshold is crossed before the high-intensity portion of the saturation curve can be reached so that the nonsaturable loss cannot be measured. Although the temporally smooth pulses were neither purely Gaussian nor a (flat-top) impulse in character, this is probably not a significant source of error as the laser system was calibrated from the KCl single-ion data.[4] For thin $KReO_4$ films we find the saturation intensity at room temperature to be $I_s=140\pm30$ kW/cm^2, independent of substrate.

The T_1T_2 lifetimes product is calculated from[11]

$$T_1T_2=\hbar\omega N/4cSI_s \ , \tag{2}$$

where $N=9.8\times10^{21}$ cm^{-3} is the single-crystal $KReO_4$ concentration, c is the speed of light, $S=1.5\times10^5$ cm^{-2} is the integrated absorption coefficient for the homogeneously broadened LO absorption band, I_s is the saturation intensity, and $\hbar\omega$ is the frequency of the incident radiation. The excited-state dephasing time, proportional to the inverse of the linewidth in a homogeneously broadened system, is calculated to be $T_2=9\times10^{-9}$ sec. We then extract from Eq. (2) the excited-state lifetime $T_1=9\times10^{-9}$ sec.

The values of I_s, T_1, and T_2 for thin $KReO_4$ films are compared with the single-ion data in Table II. The interesting results are that the LO mode actually saturates a factor of 10 more easily and exhibits a T_1 lifetime approximately two orders of magnitude longer than the single-ion mode in the KCl host; the difference is even larger for the KBr and KI hosts.

Before considering the increased T_1 of the LO mode it is worth reviewing why this mode can be saturated at all. Because the LO mode originates from the ν_3 mode of the ReO_4^- molecule which is anharmonic, the LO (0-1) transition is not coincident with the (1-2) transition. Only (0-1) transitions can be excited with a single-frequency CO_2 laser. Saturation occurs when the LO (0-1) phonon occupation number is roughly equal to the number of molecules in the laser beam. We now propose that it is the crystal periodicity in the thin film which accounts for both the low saturation intensity and the long T_1.

The excited-state lifetime of a vibrational mode depends on the number of phonons required to complete the decay process. For matrix-isolated ReO_4^- it has been shown that the strong anharmonic coupling between the internal modes of the molecule provides an additional decay route.[8] An excitation in the ν_3 mode first decays into two internal mode excitations, $\nu_2+\nu_4$ or $2\nu_4$, and then into a number of band phonons. Only energy conservation is required to determine the multistep anharmonic decay path.

For the $\vec{k}=0$ LO phonon in $KReO_4$ films, both phonon energy and crystal momentum must be strictly conserved so that

$$\hbar\omega_{LO}=\sum\hbar\omega\ (\text{phonons}) \ , \tag{3}$$

$$0=\sum\vec{k}\ (\text{phonons}) \ . \tag{4}$$

In analogy with the single-ion results, a possible decay mechanism conserving both energy and momentum involves the ν_3 internal mode at $k=0$ decaying into two other internal modes (ν_2 or ν_4, both around 340 cm^{-1}) at $+\vec{k}$ and $-\vec{k}$. Since the Debye frequency of the remaining $K^+-ReO_4^-$ diatomic spectrum is small (<100 cm^{-1}), at least three or four more energy- and momentum-conserving lattice phonons would then be required to complete the decay. Even if the same number of energy steps are required in the thin-film configuration as for the single ion, we expect the former lifetime to be significantly increased over the latter because of the reduced phase space available for this decay due to the added restriction imposed by crystal momentum conservation.

An alternate description of the LO phonon saturation may be possible. A parametric phonon instability, in which a single $\vec{k}=0$ optic phonon decays into two $\pm\vec{k}$ acoustic phonons, each of half the optic phonon energy, has been predicted to exhibit intensity-dependent absorption identical to the gain saturation of an inhomogeneously broadened system.[12] If the number of phonons required for the decay process is increased, the instability should become more abrupt, thereby causing the intensity-dependent transmission to increase more rapidly and exhibit behavior more like that of a homogeneously broadened system. Although the phonon decay path for the ν_3 LO phonon may likely involve parametric processes, we find that a simple description in terms of two-level gain saturation can account qualitatively for our experimental results.

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