Hyper-Raman scattering from alkali halides

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Hyper-Raman spectra of five alkali halides (NaCl, KCl, KBr, KI, and RbI) have been measured at room temperature. The results are compared in detail with infrared data. Satisfactory agreement is found. The hyper-Raman line shapes are shown to provide a sensitive test for theoretical calculations of the complex frequency-dependent self-energy function. We estimate the absolute hyper-Raman scattering efficiency by relating the electro-optic coupling coefficients to the nonlinear third-order susceptibility known from the literature. We obtain scattering efficiencies between 10^{-18} and 10^{-15} cm⁻¹ sr⁻¹ for a laser intensity of 100 MW/cm². We also measure the relative values of all hyper-Raman tensor elements and discuss them in terms of simple models.

I. INTRODUCTION

Electric-field-induced morphic effects in pure alkali halides are known to be weak and have been studied rather rarely.¹ Although attempts have been made,² it has not yet been possible to measure the first-order Raman spectra after relaxing the Raman selection rules by a static or low-frequency electric field. To our knowledge, only a broadening of a peak in the second-order Raman spectrum of NaCl at a field strength of 30 kV/cm has been reported.³

The experimental situation is improved when electrical modulation is achieved by the same laser radiation which excites the Raman process. This technique is known as hyper-Raman (HR) spectroscopy.⁴ It avoids many of the difficulties which usually accompany the application of high voltages to crystals, in particular electrodes, surfacelayer effects, space-charge buildup, and inhomogeneous joule heating by prebreakdown currents. Moreover, there is no need to take into account a field-induced relative displacement of the ions in addition to the tilting of the electronic energy bands, because the ions cannot follow the laser frequency. Thus, several reasons exist why HR scattering from pure alkali halides can be observed and interpreted more easily than first-order Raman scattering induced by a static or low-frequency electric field, although the symmetry selection rules are identical in both cases and the maximum permissible field strengths, determined by the threshold of electric breakdown,⁵ have the same order of magnitude.

In the quantum picture, the HR effect under consideration is described as a three-photon process in which two photons of the incident laser beam are simultaneously annihilated and one photon is created under emission or absorption of a phonon. The HR lines are observed in the spectral vicinity of the second harmonic of the exciting radiation and are shifted from it by the phonon frequencies. Accordingly, HR scattering can be regarded as phonon-assisted second-harmonic generation (SHG) where the phonon induces the nonlinear optical susceptibility prerequisite for SHG. In centrosymmetric crystals the HR-active phonon must have odd parity in order to provide the necessary disturbance of inversion symmetry.

Recently, the technique of HR scattering has been successfully applied to the study of ferroelectric soft modes in cubic perovskites.^{6,7} The imaginary part of the dielectric function $\epsilon(\omega)$ was deduced from the HR spectra and compared with infrared (ir) data. Considerable discrepancies were found which were attributed either to the inaccuracy of ir measurements at very low wave numbers or to the influence of surface conditions on the ir reflectivity.^{6,8}

The first aim of this paper will be to further clarify the relation between HR and ir results. Alkali halide crystals are particularly suited for this purpose because their dielectric functions are known from many ir measurements with a considerable degree of accuracy. Moreover, the ir reflectivity certainly probes bulk properties because the penetration depth of the ir radiation rarely decreases below $\sim 1 \ \mu m$ and there are no indications of surface layers extending so far into the crystal. Thus we expect HR and ir spectroscopy to yield consistent information about $\epsilon(\omega)$. Confirming this expectation, we prove that the discrepancies found for the perovskites must result from peculiarities of these materials and cannot be explained by a principal incompatibility of the experimental techniques.

We present HR spectra of NaCl, KCl, KBr, KI, and RbI at room temperature for various scattering configurations. Two HR lines are observed corresponding to the transverse-optic (TO) and longitudinal-optic (LO) phonons at the center of the Brillouin zone. On one hand, the line shape of the TO phonon almost follows the response function of a damped harmonic oscillator characterized by its frequency ω_{TO} and damping constant γ . On the other hand, the line shape of the LO phonon is anomalously broad and shows a complicated structure with subsidiary maxima and asymmetrical bulges. The line shapes of the TO and LO phonons are determined by the imaginary parts of $\epsilon(\omega)$ and $\epsilon^{-1}(\omega)$, respectively. Hence we can directly compare our HR results with ir data. From the multitude of ir works on alkali halides we

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reference only a selected few, i.e., transmission measurements on thin films^{9,10} and more recent reflectivity measurements using asymmetric Fourier spectroscopy.^{11–13} Infrared data obtained by a Kramers-Kronig analysis of the power reflectivity are not sufficient because considerable structure is lost in the LO-phonon region where this reflectivity is small:¹¹ We also demonstrate that the HR spectra, especially the LO-phonon HR lines, provide a sensitive test for model calculations of the complex frequency-dependent self-energy function.^{14–16}

The second aim of this paper will be to obtain a better understanding of the HR tensor. As in the case of normal Raman scattering by ir-active phonons, we have to distinguish between a deformation-potential and an electrooptic contribution to the HR tensor elements. The latter is related to the third-order nonlinear susceptibility $\chi^{(3)}$ which has been measured by various techniques.¹⁷ Taking the absolute value of $\chi^{(3)}$ from the literature, we are able to estimate the order of magnitude of the absolute HR efficiency. We also determine the relative values of all HR tensor elements. The results are interpreted in terms of simple models.

Some preliminary reports on the HR spectra of alkali halides have been published elsewhere.¹⁸⁻²⁰ They demonstrated the feasibility of observing the HR effect in these materials and already revealed the difference in the line shapes of the TO and LO phonons.

II. EXPERIMENTAL DETAILS

Measurements were performed on commercially available single crystals (Dr. Korth, Monokristalle-Kristalloptik, Kiel, Federal Republic of Germany) of dimensions $8 \times 10 \times 10$ mm³. Their surfaces were either (100) or (110) planes. They were ground with a suspension of corundum in glycerine and polished with diamond paste and alumina.

As source of exciting radiation we used an acousto-Q-switched Nd-YAG (yttrium-aluminumoptically garnet) laser (Quantronix, model 117) with a pulse repetition rate of 5 KHz and a pulse width of 150 ns. After an expansion by a dispersing lens, the laser beam was focused into the sample by an objective with f = 4.6 cm, corrected for spherical aberration. The peak power of about 5 kW was far below the critical power threshold for selffocusing which has the order of magnitude of 100 kW.²¹ To exclude any intensity distortion due to refractive-index nonlinearity, we checked the relation between HR signal and laser power. We used a combination of two fixed polarizers and a rotatable $\lambda/2$ plate for attenuating the laser power without affecting its spatial distribution. We always found the HR signal to be proportional to the square of the laser power. The laser intensity at the focus reached the range of 100 MW/cm^2 , but was still below the threshold of electric breakdown which has the order of magnitude of GW/cm².²¹

In order to determine the width of the TO-phonon lines, the spectral slit width of the double monochromator had to be decreased to 2.5 cm^{-1} . A counting time of 400 s per spectral element was necessary for accumulating a sufficient number of photon counts. Since the HR lines

of the LO phonons were much broader, they could be measured with a spectral slit width of 9 cm^{-1} . Other details of our HR spectrometer can be found in Ref. 19.

III. HYPER-RAMAN LINE SHAPES

A. Results

Figure 1 shows representative HR spectra of KI for three different scattering configurations. The cubic axes are denoted by x, y, and z, while x' and y' stand for the directions [110] and [110], respectively. In the x(yy)zspectrum, only the TO-phonon line appears together with side wings corresponding to sum and difference processes. Here the TO phonon is excited off resonance and decays by either creating two phonons or creating one and destroying another, energy and momentum being conserved.¹² The scattering configurations x(yx)z and x'(y'y)z permit the observation of both the TO and LO phonon. In addition, a hyper-Rayleigh line at exactly twice the laser frequency can be seen. For NaCl we have found the hyper-Rayleigh intensity to be much more sensitive to the quality of the samples than the intensity of the HR lines. Therefore we conclude that the observed hyper-Rayleigh scattering from alkali halides results from second-harmonic generation due to local disturbances of the inversion symmetry by crystal imperfections. Indeed, one can hardly imagine an odd-parity excitation of almost



FIG. 1. Hyper-Raman spectra of KI at room temperature. The horizontal bar indicates the spectral slit width Δv .



FIG. 2. Hyper-Raman lines of the zone-center TO phonons of alkali halides at room temperature. All lines refer to the same laser power.

zero frequency which can participate in the HR process.¹⁹

The TO-phonon line shapes are compiled in Fig. 2. As indicated by the full curves, they are well described by a harmonic oscillator response function multiplied by the Bose-Einstein population factor and properly convoluted with the triangular instrumental profile of the spectrometer. The oscillator frequencies ω_{TO} and the damping constants γ are listed in Table I. All TO-phonon lines in Fig. 2 refer to almost the same laser intensity. Hence they indicate the increase of the HR efficiency with decreasing energy gap as one passes from the chlorides via the bromides to the iodides.

The LO-phonon line shapes are presented in Fig. 3. The zone-center LO frequency is always in a range where the two-phonon density of states is rather high and displays distinct maxima. In particular, it almost coincides with the peak in the two-phonon density of states



FIG. 3. Hyper-Raman lines of the zone-center LO phonons of alkali halides at room temperature. All lines refer to the same laser power.

corresponding to the sum tone of the TA (transverse acoustic) and TO mode at the L point.¹⁴ Thus twophonon decay channels with a high density of states become operative, leading to a broad and structured line shape.

B. Comparison between hyper-Raman and infrared spectra

The fluctuation-dissipation theorem relates the efficiencies S_{TO} and S_{LO} for HR scattering by TO and LO phonons to the far-infrared dielectric function $\epsilon(\omega)$. Omitting factors which are nearly independent of the HR shift ω , we may write²³

$$S_{\rm TO}(2\omega_L - \omega) \sim [n(\omega) + 1] \operatorname{Im}[\epsilon(\omega)], \qquad (1)$$

$$S_{\rm LO}(2\omega_L - \omega) \sim [n(\omega) + 1] \, {\rm Im} \left[-\frac{1}{\epsilon(\omega)} \right],$$
 (2)

where ω_L is the laser frequency and $n(\omega)$ the Bose-Einstein population factor.

The dielectric function $\epsilon(\omega)$ is obtained by expanding the dipole moment in a power series of the phonon coordi-

 $\omega_{\rm TO}~({\rm cm}^{-1})$ γ (cm⁻¹) Hr HR ir ir Material This work Ref. 9 This work Ref. 10 Ref. 22 Theory 9.0 3.8^a NaCl 164.7 164 5.0 5.1 6.4 9.1 2.9^b 142 KCl 142.5 3.9 KBr 114.8 114 3.8 6.6 2.3° 2.4^b KI 100.8 102 4.5 7.0 4.9 RbI 75.9 75.5 2.74.4 4.4

TABLE I. Frequency and damping constant of the zone-center TO phonon of alkali halides as obtained from hyper-Raman (HR) and infrared (IR) spectroscopy as well as theory.

^aReference 14. ^bReference 16.

^cReference 15. The quoted value was calculated under neglection of intra-ionic nonlinearities($\mu = 0$) and three-phonon damping. When the latter was taken into account, a value of 6.7 cm⁻¹ was obtained.

nates. In the case of the alkali halides, $\epsilon(\omega)$ is dominated by the term of first order with respect to the normal coordinate of the zone-center TO mode.²⁴ At a given temperature, $\epsilon(\omega)$ has the form^{11-16,24}

$$\epsilon(\omega) = \epsilon(\omega) + \frac{[\epsilon(0) - \epsilon(\omega)][\omega_{\rm TO}^2 + 2\omega_{\rm TO}\Delta(0)]}{\omega_{\rm TO}^2 - \omega^2 + 2\omega_{\rm TO}[\Delta(\omega) - i\Gamma(\omega)]} .$$
(3)

Here $\epsilon(\infty)$ and $\epsilon(0)$ are the high-frequency and static dielectric constants, respectively, while ω_{TO} denotes the quasiharmonic frequency of the reststrahlen or zonecenter TO phonon. The complex frequency-dependent self-energy is split into the shift function $\Delta(\omega)$ and the width or damping function $\Gamma(\omega)$. For many alkali halides both functions have been calculated by taking into account the cubic and quartic anharmonicities of the lattice potential in lowest-order perturbation theory. Since the anharmonic force constants can be derived from the short-range repulsive interaction. Usually, a Born-Mayer potential has been assumed the parameters of which have been obtained by fitting a harmonic shell model to measured phonon dispersion curves.¹⁴

In the vicinity of ω_{TO} , the values of $\Delta(\omega)$ and $\Gamma(\omega)$ turn out to be rather small, because ω_{TO} is too low to interact significantly with the sum band and too high to do it with the difference band. Then Eq. (3) can be approximated by a classical dispersion formula, i.e.,

$$\epsilon(\omega) = \epsilon(\infty) + \frac{[\epsilon(0) - \epsilon(\infty)]\omega_{\rm TO}^2}{\omega_{\rm TO}^2 - \omega^2 - i\omega\gamma} , \qquad (4)$$

with $\gamma = 2\Gamma(\omega_{\rm TO})$. As mentioned in section A, the TOphonon line shapes shown in Fig. 2 are well described by Eqs. (1) and (4). In Table I the fitting parameters ω_{TO} and γ are compared with infrared data and theoretical values of $2\Gamma(\omega_{\rm TO})$. While there is excellent agreement between HR and infrared spectroscopy concerning ω_{TO} , the HR values of γ are generally smaller than the infrared ones. In view of the experimental uncertainties, however, the discrepancies do not seem to be very significant, especially when compared with the order-of-magnitude discrepancies found for perovskites.⁶ The theoretical values of γ quoted in Table I are smaller than the experimental ones because they only take into account two-phonon processes. As demonstrated by Eldridge and Staal,^{13,25} threephonon damping has to be also considered in order to achieve agreement between experiment and theory.

Figures 4 to 7 present a detailed comparison of the LO phonon-line shapes as obtained by HR scattering, infrared Fourier spectroscopy,¹¹⁻¹³ and theory.¹⁴⁻¹⁶ The imaginary part of the inverse dielectric function is plotted as a function of frequency. The HR data are derived from Fig. 3 by means of Eq. (2), the proper overall scaling factor being provided by the Kramers-Kronig relation:

$$\frac{1}{\epsilon(\infty)} - \frac{1}{\epsilon(0)} = \frac{2}{\pi} \int_0^\infty \frac{\mathrm{Im}[-\epsilon^{-1}(\omega)]}{\omega} d\omega .$$
 (5)

The limits of integration can be approximately restricted to the frequency range of the LO phonon. The infrared



FIG. 4. Line shape of the zone-center LO phonon of NaCl as obtained from hyper-Raman spectroscopy (circles, this work), asymmetric infrared Fourier spectroscopy (dashed line, Ref. 13), and theory (solid line, Ref. 14).

data are calculated from the reflectivity amplitude and phase angle, whereas the theoretical data follow from Eq. (3) by inserting calculated shift and width functions.

Assuming $\Delta(0) \ll \omega_{\rm TO}$, we may write



FIG. 5. Line shape of the zone-center LO phonon of KCl as obtained from hyper-Raman spectroscopy (circles, this work), asymmetric infrared Fourier spectroscopy (dashed line, Ref. 11), and theory (solid line, Ref. 16).



FIG. 6. Line shape of the zone-center LO phonon of KBr as obtained from hyper-Raman spectroscopy (circles, this work), asymmetric infrared Fourier spectroscopy (dashed line, Ref. 11), and theory (solid line, Ref. 15).



FIG. 7. Line shape of the zone-center LO phonon of Ki as obtained from hyper-Raman spectroscopy (circles, this work), asymmetric infrared Fourier spectroscopy (dashed line, Ref. 12), and theory (solid line, Ref. 16).

$$\operatorname{Im}\left[-\frac{\epsilon(\infty)}{\epsilon(\omega)}\right] = \frac{2\omega_{\mathrm{TO}}\Gamma(\omega)[\omega_{\mathrm{LO}}^{2}-\omega_{\mathrm{TO}}^{2}]}{[\omega_{\mathrm{LO}}^{2}-\omega^{2}+2\omega_{\mathrm{TO}}\Delta(\omega)]^{2}+[2\omega_{\mathrm{TO}}\Gamma(\omega)]^{2}}, \quad (6)$$

where ω_{LO} is the LO phonon frequency given by the Lyddane-Sachs-Teller relation, i.e., $\omega_{LO} = \omega_{TO} [\epsilon(0)/\epsilon(\infty)]^{1/2}$. The above expression is proportional to the spectral function of the LO phonon usually derived from the imaginary part of the Green's function.^{14,24,26}

The structure of the LO-phonon line shapes can be approximately explained as follows.

(a) Maxima appear where either the first or the second term in the denominator of Eq. (6) passes through a minimum. In particular, the highest maximum is found where $\omega_{\rm LO}^2 - \omega^2 + 2\omega_{\rm TO}\Delta(\omega) = 0$, i.e., at the renormalized LO-phonon frequency.

(b) The minimum in the middle of the profile results from a maximum in $\Gamma(\omega)$.

For all materials under study, the agreement between HR and infrared spectroscopy on the LO-phonon line shape is quite satisfactory. The theoretical calculations fail drastically only in the case of KI where a third peak is predicted which is not confirmed by experiment. This artifact, however, disappears when the width function of Haque¹⁶ is replaced by that of Berg and Bell¹² which does not decrease so rapidly with increasing frequency.

IV. HYPER-RAMAN TENSOR

A. Estimation of the hyper-Raman efficiency

Formulas for the spectral HR scattering efficiency including all factors omitted in Eqs. (1) and (2) have been derived in Ref. 23. To simplify the discussion, let us consider the special scattering configurations x(yx)z. We obtain (cgs units)

$$S_{\rm TO}(\Omega) = \frac{\hbar}{4\pi} \frac{I_L}{\eta c N^2} \left[\frac{\Omega}{c} \right]^4 [n(\omega) + 1] \frac{|b|^2}{Z^2} \operatorname{Im}[\epsilon(\omega)],$$
(7)

$$S_{\rm LO}(\Omega) = \frac{\hbar}{4\pi} \frac{I_L}{\eta c N^2} \left[\frac{\Omega}{c} \right]^4 [n(\omega) + 1] \\ \times \left| \frac{b\epsilon(\infty)}{Z} + 4\pi b_{e0} N \right|^2 \operatorname{Im} \left[-\frac{1}{\epsilon(\omega)} \right]. \quad (8)$$

Here $\Omega = 2\omega_L - \omega$ is the frequency of the scattered light, N the number of primitive cells per unit volume, I_L the laser intensity, Z the transverse effective charge, and η the refractive index, the dispersion of which is neglected because the photon energy of both the exciting and scattered light is far below the energy gap of the alkali halides. The HR tensor elements b and b_{e0} are defined by

$$b = \frac{\partial \chi_{xyy}^{(2)}}{\partial W_x^*} \text{ and } b_{e0} = \frac{\partial \chi_{xyy}^{(2)}}{\partial E_x^*} , \qquad (9)$$

where the third-rank tensor $\chi^{(2)}$ represents the nonlinear

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susceptibility responsible for SHG. The relative displacement of the ions is denoted by W and the electric field associated with the LO phonon by E, respectively. The asterisk is used to indicate Stokes scattering. The electrooptic coefficient b_{e0} may be interpreted as third-order susceptibility $\chi^{(3)}_{xxyy}$ and can be independently obtained from third-harmonic generation, four-wave mixing, and measurements of the nonlinear refractive index.¹

The quantity of interest in this section is the total HR efficiency derived from Eqs. (7) and (8) by integration over the full line shape. Using the Kramers-Kronig relations we find

$$S_{\rm TO} = \frac{\pi}{\eta c} \left[\frac{\Omega}{c} \right]^4 \frac{\hbar}{2NM\omega_{\rm TO}} [n(\omega_{\rm TO}) + 1] |b|^2 I_L , \qquad (10)$$

where M is the reduced mass of the vibrating ions. The expression for $S_{\rm LO}$ follows from Eq. (10) if $\omega_{\rm TO}$ is replaced by $\omega_{\rm LO}$ and b by

$$b_{\rm LO} = b + 4\pi b_{e0} \frac{NZ}{\epsilon(\infty)} . \tag{11}$$

 $S_{\rm TO}$ or $S_{\rm LO}$ can be estimated from the ratio $S_{\rm LO}/S_{\rm TO}$, measured in our experiment, and from the absolute value of b_{e0} , available from the literature.^{17,27,28} Being far off resonance, we may assume the coefficients b, b_{e0} , and $b_{\rm LO}$ to be real. From $S_{\rm LO}$ / $S_{\rm TO}$ we calculate the ratios $|b_{LO}/b|$ and $|b_{e0}/b|$ by means of Eqs. (10) and (11). Neglecting dispersion, we equate

$$b_{e0} = \chi_{xxxx}^{(3)} \left(\frac{\chi_{xxyy}^{(3)}}{\chi_{xxxx}^{(3)}} \right), \qquad (12)$$

and take values of both factors from Ref. 27. Finally, we use Eq. (10) again to determine S_{TO}/I_L from $|b| = |b_{e0}| |b/b_{e0}|$. The results are shown in Table II. Two values are quoted for $|b_{e0}/b|$, |b|, and $S_{\rm TO}$ / I_L because $b_{\rm LO}$ and b may have equal or opposite signs and we are not yet able to decide between them.

The relative HR efficiency S_{TO} / I_L of alkali halides in the scattering configuration x(yx)z has the order of magnitude of 5×10^{-20} cm sr⁻¹/MW, so that even at a laser intensity of 100 MW/cm² the HR efficiency S_{TO} is about nine orders of magnitude smaller than the normal Raman efficiency of calcium fluorite.²⁹ In normal Raman spectroscopy it would be hopeless to look for a scattering process with an efficiency of 5×10^{-18} cm⁻¹ sr⁻¹. The reason, however, is not a lack of laser power or sensitivity of the photon counting system, but the limited stray light

suppression of the spectrometer. This problem is ideally solved in HR spectroscopy by shifting the frequency of the scattered light far away from the laser frequency.

In order to test the reliability of our estimate of $S_{\rm TO}/I_L$, we compared normal Raman scattering from CaF₂ with HR scattering from NaCl. Only the laser was changed, all other components of the experimental arrangement remaining the same. Using the 530.9-nm line of a Kr ion laser, we obtained an integral Raman signal of about 1.5×10^5 counts per second for an incident cw power of 50 mW. Using the Q-switched Nd-YAG laser, we obtained an integral HR signal of about 0.07 counts per second for an incident average power of 5 W. Thus the efficiency ratio $S(CaF_2)/S_{TO}(NaCl)$ was about 2×10^8 . Since we did not know the exact focus conditions of both the Kr ion and the Nd-YAG laser, this number can only be regarded as a crude approximation, but nevertheless has the expected order of magnitude.

B. Relative values of the hyper-Raman tensor elements

HR scattering by the zone-center phonons of alkali halides is described by the HR tensors quoted in Ref. 23 for the F_{1u} modes of SrTiO₃. We have to distinguish between four HR tensor elements denoted by a, b, a_{e0} , and b_{e0} . The definitions of b and b_{e0} have already been given in Eqs. (9). Similarly, a and a_{e0} are defined by

$$a = \frac{\partial \chi_{xxx}^{(2)}}{\partial W_x^*}, \text{ and } a_{e0} = \frac{\partial \chi_{xxx}^{(2)}}{\partial E_x^*}.$$
 (13)

Owing to the cubic symmetry, the indices x and y in Eqs. (9) and (13) may be interchanged and also substituted by z.

The ratio |a/b| can be easily determined by switching between the scattering configurations x(yy)z and x(yx)z. For this purpose we only had to rotate a $\lambda/2$ plate in front of the entrance polarizer of the spectrometer. As mentioned in the foregoing section, the scattering configuration x(yx)z allows to measure $|b_{LO}/b|$.

To obtain more information about the relative values of the HR tensor elements, we compared the intensities of the LO-phonon lines in the scattering configurations $x(yy^*)z^*$ and $x(yx)z^*$ with $y^* \equiv [01\overline{1}]$ and $z^* \equiv [011]$. The ratio of the corresponding HR efficiencies is given by

$$\frac{S_{\rm LO}[x(yy^*)z^*]}{S_{\rm LO}[x(yx)z^*]} = \frac{1}{4} \left[\frac{a_{\rm LO}}{b_{\rm LO}} - 1 \right]^2, \tag{14}$$

TABLE II. Estimation of HR scattering efficiencies of alkali halides for the scattering configuration x(yx)z.

Material	$S_{\rm LO}$ / $S_{\rm TO}$	b _{LO} /b	Z/e	$ b_{e0}/b $ (10 ⁻¹³ esu)	$ b_{e0} $ $(10^{-14} \text{ esu})^{a}$	$\frac{ b }{(10^{-2} \text{ esu})}$	$\frac{S_{\rm TO} / I_L}{(10^{-20} {\rm ~cm~sr^{-1}/MW})}$
NaCl	25	7.2	1.11	0.97;1.3	0.73	7.5;5.6	4.5;2.5
KCl	9.6	4.3	1.13	0.65;1.1	0.70	11;6.4	13;4.4
KBr	10	4.3	1.14	0.81;1.3	0.91	11;7.0	16;6.5

^aObtained from $b_{e0} = \chi_{xxxx}^{(3)} (\chi_{xxyy}^{(3)} / \chi_{xxxx}^{(3)})$, the factors being taken from Ref. 27.

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a_{e0}/b_{e0}												
Material	a/b	$a_{\rm LO} / b_{\rm LO}$	$\frac{a_{\rm LO}}{a} > 0$	$\frac{a_{\rm LO}}{a} < 0$	Ref. 27	Ref. 28	$ a_{\rm LO}/b $	$ a_{\rm LO}/a $	$\mid b_{ m LO} / b \mid$			
NaCl	4.5	2.3	2.0	2.6	2.3	2.4	17	3.7	7.2			
KCl	2.2	2.8	3.0	2.7	3.3	3.6	12	5.5	4.3			
KBr	2.7	2.8	2.9	3.3	2.7	2.7	12	4.4	4.2			
KI	2.7	2.8	2.8	2.8	1.6		14	5.1	4.9			
RbI	2.6	2.8	2.8	2.8			16	6.3	5.9			

TABLE III. Relative values of the HR tensor elements of alkali halides.

where $a_{\rm LO}$ is defined in analogy to $b_{\rm LO}$, i.e.,

$$a_{\rm LO} = a + 4\pi a_{e0} \frac{NZ}{\epsilon(\infty)} . \tag{15}$$

Relation (14) must be consistent with the values of |a/b|and $|b_{\rm LO}/b|$ determined before. Moreover, b_{e0}/a_{e0} must be almost identical with the second factor in Eq. (12) as obtained from four-wave mixing experiments²⁷ and third-harmonic generation.²⁸ These requirements can be only fulfilled if the ratios a/b and $a_{\rm LO}/b_{\rm LO}$ are positive. The signs of the ratios $a_{\rm LO}/a$ and $b_{\rm LO}/b$, however, remain unknown. We have listed our results in Table III.

We notice that the values of a/b, $a_{\rm LO}/b_{\rm LO}$, and a_{e0}/b_{e0} are always near 3. They would be exactly equal to 3, if the materials were isotropic.³⁰ Therefore deviations from 3 characterize what may be called cubic anisotropy²⁸ of the HR tensors.

The ratio $|a_{\rm LO}/b|$ is around 15. Thus the efficiency of HR scattering by the LO phonons reaches the order of magnitude of 10^{-15} cm⁻¹ sr⁻¹ at a laser intensity of 100 MW/cm².

The order of magnitude of the ratios $a_{\rm LO}/a$ and $b_{\rm LO}/b$ can be explained approximately in terms of a simple-shell model. Let us assume that only the anions are polarizable whereas the cations are rigid. Then HR scattering results from the second-order or hyperpolarizability β induced in the electron clouds of the anions by the lattice vibrations. Tentatively, we may consider β to be proportional to the displacement V of the anion shell relative to the anion core, because both β and V characterize an excentric deformation of electron states.

If $\beta \sim V$, we have $a = \partial \beta / \partial W \sim V / W$, where W, as in Eqs. (9) and (13), is the relative displacement of the anion

and cation cores. From the equations of motion we obtain the ratio V/W for both the TO and LO phonon. We find³¹

$$\frac{(V/W)_{\rm LO}}{(V/W)_{\rm TO}} = \frac{1 - Z/e\epsilon(\infty)}{1 - Z/e} , \qquad (16)$$

where Z and e are the transverse effective and electron charge, respectively. According to our assumptions, we may identify expression (16) with the ratio $a_{\rm LO}/a$ or likewise $b_{\rm LO}/b$. Inserting the values Z/e=1.11 (Table II) and $\epsilon(\infty)=2.33$ for NaCl, we obtain the estimate $a_{\rm LO}/a=-4.8$. The negative sign indicates that the same displacement of the anion and cation cores is accompanied by oppositely directed shifts of the anion shells. In particular, we have $(V/W)_{\rm TO} < 0$ and $(V/W)_{\rm LO} > 0$, the difference being due to the electric field E associated with the LO phonon.

Since our estimate of $a_{\rm LO}/a$ or $b_{\rm LO}/b$ yields the correct order of magnitude, we may safely assume the sign of these ratios to be negative. Thus we have obtained an estimate of all HR tensor elements and an at least qualitative understanding of their ratios.

Note added in proof. Quite recently, electric-fieldinduced first-order Raman scattering in pure KCl and KBr has been reported [M. Krantz and F. Luty, Phys. Rev. B 31, 2599 (1985)]. A theoretical estimate of the corresponding cross section has also been given [B. G. Dick, Phys. Status Solidi B 127, 131 (1985)].

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