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Multiphonon Optical Spectrum of NaF

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The high-frequency exponential wing of the reststrahlen band of NaF is decomposed into a number of N-phonon absorption spectra ($N=2,3,4,5$) by means of a temperature analysis. Overall agreement of the individual spectra with recent theoretical predictions is good, except for a fairly pronounced structure which indicates particularly strong contributions from certain frequencies of the TO and LO phonon branches.

The infrared (i.r.) multiphonon spectrum of many ionic crystals is characterized by a uniform, almost exponential, decay of absorption with frequency.[1] The lack of distinct peaks at the main combination frequencies (like in homopolar crystals) prevents conclusions on the number of participating phonons from the shape of the spectrum alone. The mechanisms responsible for the unstructured wing absorption have recently attracted considerable theoretical attention.[2,3] Various classical and quantum-mechanical approaches with different assumptions for the interionic potential and the phonon dispersion were used to explain this phenomenon.

A key to the experimental identification of the various multiphonon processes is the temperature dependence of the absorption.[4-6] The larger the number N of phonons participating, the steeper the increase of absorption α_N with temperature. For this reason we made a systematic analysis of the i.r. properties of NaF between 600 and 1500 cm^{-1} and from 100 to 850°K. The obtained data yield empirical probabilities for N-phonon processes, $N=2$, 3, 4, 5, and 6, which, for the first time, allow an experimental decomposition of the multiphonon wing into a series of N-phonon spectra. In this way a much more direct control of theoretical predictions becomes possible.

Two NaF samples [(A) 54.98 mm,[7] and (B) 3.82 mm,[8] thickness] of extreme purity were employed. There were no indications of any extrinsic absorption which is important in view of the very small absorption at large frequencies. The crystals were mounted either in a cryostat (90 to 400 400°K) or in a small oven (300 to 850°K). The absorption was measured by means of a Beckman Acculab-6 i.r. spectrophotometer. Values of the transmission between 1 and 98–99% could be well detected. The corresponding absorption ranges from about 10 cm^{-1} down to less than 0.002 cm^{-1}. At temperatures different from ambient, corrections to the measured nominal transmission were required. The instrument was not compensated for the thermal radiation from the sample with respect to the variable attenuator in the reference beam. Knowledge of the source characteristic,[9] i.e., its temperature (1240°K) and emissivity ($\simeq 0.85$, NiCr wire), however, allowed the required corrections with fair accuracy. Up to 500°K, the correction was quite unimportant except for the smallest wave numbers investigated.

In Fig. 1, the experimental absorption $\alpha(T)$ is plotted for several wave numbers. In order to facilitate the later comparison with theory, the temperature is normalized to $\hbar\omega/k_B$ (the symbols have the usual meaning). The obvious increase of temperature dependence at larger wave numbers is characteristic for the growing number of phonons participating in the absorption process.

Theoretically, multiphonon absorption is governed by three major factors[2,3]: the oscillator strengths of all transitions involving one photon ($\vec{k} \simeq 0, \omega$) and an appropriate set of N phonons ($\vec{k}_i$, ω_i), the densities of state of these phonons, and the respective phonon occupancies $n(\omega_i, T)$. The absorption at a given frequency ω is obtained by convolution over all branches of the phonon spectrum with the constraints of energy and momentum conservation.

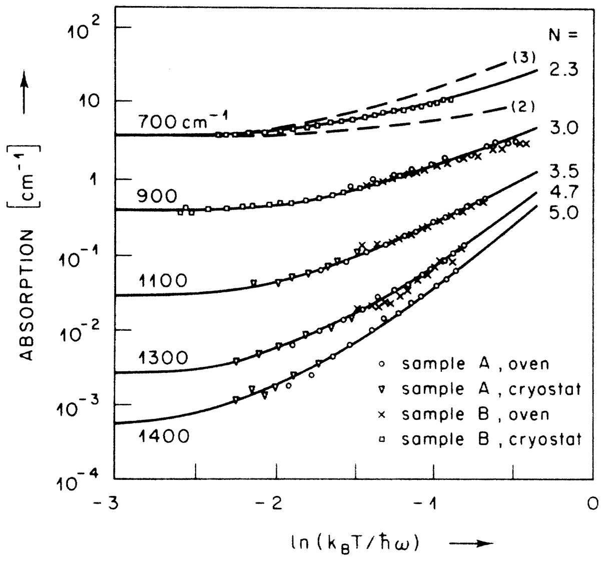

FIG. 1. Experimental and calculated absorption versus temperature.

A surprisingly good description of multiphonon absorption is obtained by assuming that (i) the oscillator strengths depend on N only, and (ii) the average occupancy is the same as if all participating phonons had the energy $\hbar\omega/N$. Under these conditions, the convolution can be confined to the one over the one-phonon density of states $\rho_1(\omega_i)$ providing a "multiphonon density of states" $\rho_N(\omega)$. The latter will obviously be peaked at the combinations of the dominant single-phonon frequencies, but the original structure will become more and more washed out with an increasing number of convolutions. For the derivation of the absorption, we closely follow Ref. 3. However, the average oscillator strength $\langle f_N \rangle$ is defined here to be temperature independent; it represents the coupling to the electromagnetic field at $T \to 0$. The absorption due to N-phonon processes can then be written as

$$\alpha_N(\omega, T) = (\pi/2nc)\langle f_N\rangle \omega^2 \rho_N(\omega) \times [(\langle n_N\rangle + 1)^N - \langle n_N\rangle^N]; \tag{1}$$

Eq. (1) is equivalent to Eq. (31) of Ref. 3. $\langle f_N\rangle$ depends on the anharmonic part of the interionic potential φ represented by its derivatives $\varphi^{(N)}$ and on the mean square displacement $\langle \Delta r^2\rangle$ at $T = 0$:

$$\langle f_N\rangle \propto \langle \Delta r^2\rangle^{N-1}[\varphi^{(N+1)}/\varphi^{(2)}]^2 = (\langle \Delta r^2\rangle/\rho^2)^{N-1}. \tag{2}$$

The second part of Eq. (2) is obtained under the assumption of a Born-Mayer potential ($\varphi \propto e^{-r/\rho}$ + Coulomb term; $\rho = 0.29$ Å for NaF).[10] Δr^2 is determined from the harmonic part of the potential; its weighted average is

$$\langle \Delta r^2\rangle = (\hbar/2m)\int \rho_1(\omega)\,d\omega/\omega, \tag{3}$$

where m is the reduced mass and $\int \rho_1(\omega)\,d\omega \equiv 1$.

It is not yet known to what extent acoustic phonons participate in higher-order absorption processes. For this reason we computed $\langle \Delta r^2\rangle$ from the known[11] $\rho_1(\omega)$ for the two limiting cases that all modes contribute equally (a) and that only optical modes are active (o). The result is $\langle f_N\rangle_a \propto 0.049^{N-1}$ and $\langle f_N\rangle_o \propto 0.036^{N-1}$, somewhat smaller than the value of the Debye approximation, $\langle f_N\rangle_\text{D} \propto 0.054^{N-1}$. The strong decrease of all $\langle f_N\rangle$'s with N guarantees that the total absorption at any given frequency is dominated either by the process of lowest order allowed or, in fairly narrow transition zones, by only two processes of consecutive orders. This situation considerably facilitates the interpretation of the experimental results.

The frequency dependence of $\alpha_N(\omega)$ at $T = 0$ is expressed by $\omega^2\rho_N(\omega)$. We calculated these functions under the conditions (a) and (o) on the basis of energy conservation. Momentum conservation was neglected[3] since it would have tremendously complicated the computation and since, at larger N, its main effect is a reduction in the number

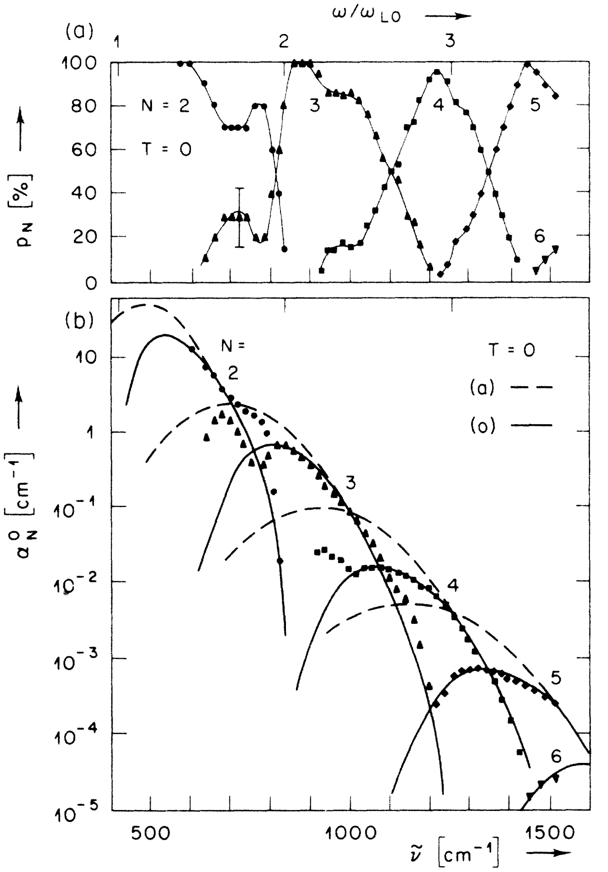

FIG. 2. (a) Experimental probability for two- through five-phonon processes. (b) Experimental and theoretical decomposition of the multiphonon spectrum.

of combinations of modes fairly independent of frequency. The results are the dashed and solid curves in Fig. 2(b) which will be discussed later together with the experimental data.

The temperature dependence of $\alpha_N(\omega, T)$ is dominated by the occupancy function

$$\langle n_N\rangle = [\exp(\hbar\omega/k_BTN) - 1]^{-1}. \qquad (4)$$

$\langle f_N\rangle$ and $\rho_N(\omega)$, in principle, depend also on T because of thermal expansion and shifts of the dispersion curves.[5] But these variations are relatively small and tend to be masked by the multiple convolutions.[6] Experimentally, there was no evidence for such additional temperature dependence. The existence of minor contributions, however, cannot be ruled out because of the limited experimental accuracy at higher temperatures. The theoretical temperature dependence can be well fitted to the experimental curves by choosing N and $\alpha(\omega, T=0)$ properly as depicted in Fig. 1 (noninteger N's are to be interpreted as mixtures of two processes with probabilities p_N and $p_{N+1} = 1 - p_N$). The absolute accuracy of this assignment is restricted to about 15% by the relatively small variation of shape versus N.

The above "temperature analysis" was performed for every twenty wave numbers. The resulting $p_N(\tilde{\nu})$ are plotted in Fig. 2(a). The solid curves are guidelines to the eye only. Note that Fig. 2 refers to $T=0$; at finite temperatures the curves would be shifted towards smaller frequencies. At the smallest wave numbers, the absorption is clearly dominated by the two-phonon interaction. At the largest wave numbers, even six-phonon processes contribute. It is interesting to compare the experimental regimes of multiphonon absorption with the integer multiples of $\omega_{LO}(k=0)$ that provide upper limits for the respective N-phonon processes (upper scale of Fig. 2) and with the corresponding multiples of the fundamental mode ω_{TO}. The experimental probabilities p_N, in fact, vanish at $\omega > N\omega_{LO}$. They peak at frequencies larger than $N\omega_{TO}$ indicating significant contributions from LO modes. Considerable structure shows up in the probability curves which is beyond the relative experimental error. Such a structure would not have been expected from the smooth behavior of $\alpha(\omega, T=\text{const})$. For example, a distinct secondary peak is seen in the two-phonon probability which must be caused by LO phonons near $\omega_{LO}(k=0)$. Similarly, a shoulder on the high-frequency side of the three-phonon probability indicates strong contributions from these phonons. Rudimentary TO combinational peaks show up on the low-frequency sides of both the $N=3$ and 4 curves.

A more quantitative comparison with theory is obtained by calculating from the experimental data the zero-temperature N-phonon absorption coefficient $\alpha_N^0(\tilde{\nu}) = p_N(\tilde{\nu})\alpha(\tilde{\nu}, T=0)$. The resulting curves, depicted in Fig. 2(b), represent the decomposed exponential wing of the i.r. absorption at $T=0$, i.e., at zero occupancy. The calculated dashed ("a") and solid ("o") curves $\omega^2\rho_N(\omega)$ have been adjusted vertically to fit the experimental data. The poor agreement at $N=2$ for both (a) and (o) is obviously a penalty for neglecting momentum conservation; but an increasingly better fit of "o" to the experimental curves is found for larger N. In the five-phonons regime the agreement between theory (o) and experiment becomes perfect. Thus absorption processes involving a large number of phonons depend very little on the exact phonon spectrum,

TABLE I. Experimental and theoretical decay of oscillator strength $\langle f_{N+1}\rangle/\langle f_N\rangle$.

N	Expt	Calculated (a)	Calculated (o)	"Debye"
2	0.020 ± 0.07	0.049	0.036	0.054
3	0.023			
4	0.037			
5	(0.04?)			

individual interaction strengths, selection rules, etc. Such a blur of structure is to be expected from the exponentially rising number of phonon combinations and has been predicted in several papers.[2-5]

The last step of this analysis is devoted to the relative magnitude of the different $\alpha_N{}^o$. The fit of the "o" curves in Fig. 2(b) provides empirical ratios of $(\langle f_{N+1}\rangle/\langle f_N\rangle)_{\rm exp}$, which are presented in Table I together with the values calculated above. Agreement within a factor of 2 is found in all cases—a surprisingly good result in view of the various assumptions entering Eqs. (2) and (3). Similarly as for the shape of $\alpha_N{}^o(\omega)$, the tendency of the ratio to approach the "optic-phonon" value 0.036 is obvious. In a logarithmic plot, however, even the too large Debye value 0.054 would represent a quite satisfactory fit to reality.

The above analysis suggests that more extended experimental investigations of the i.r. absorption in alkali halides could considerably substantiate insight into the mechanisms of multiphonon-photon interaction and eventually might allow conclusions on the actual higher-order anharmonic forces in these crystals. For $N > 5$, thermal emission spectroscopy or calorimetry will be more appropriate techniques than the absorption spectroscopy used in this investigation.

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