PHONON STRUCTURE OF THE NO_2^- ABSORPTION AT 400 nm IN THE ALKALI HALIDES*

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The NO_2^- ion has a transition in the near ultraviolet with resolved vibrational structure. This structure is little affected by the surrounding of the ion and has been studied in alkali nitrite single crystals[1,2] and as a substitutional impurity in the alkali halides.[3] In this Letter we would like to report new results on the detailed structure of the NO_2^- ion spectra in alkali halides at low temperature. At high temperature, the vibrational lines are broadened by interaction with lattice vibrations, but below 20°K we have resolved sharp no-phonon lines accompanied by phonon bands. Recent neutron-diffraction data for[4] KBr allow detailed comparison of the NO_2^- spectra with the phonon spectra of the pure lattice.

The crystals used were grown from reagent-grade material by the Kyropoulos method in air. They were doped with the addition of 0.6% of the appropriate alkali nitrite to the melt. A Cary-14 spectrophotometer with a high-pressure mercury lamp was used for the absorption spectra at 4.2°K. The emission was excited with a similar lamp through suitable filters and analyzed with a Zeiss G-II monochromator with 10-cm^{-1} band pass. The absorption spectra are taken with 4-cm^{-1} band pass.

The overall vibrational structure of the absorption for $KBr{:}KNO_2$ is shown in Fig. 1. The position of all the sharp lines, indicated by arrows, can be fitted by a formula $\nu_n = \nu_\infty + n_1\nu_1' + n_2\nu_2'$, where ν_∞ is the frequency of the purely electronic transition; ν_1' and ν_2' are vibrational frequencies of the NO_2^- ion; $n_1 = 0, 1, 2$; and $n_2 = 0, 1, 2, \cdots, 7$. We will call all these lines "no-phonon lines" since here no lattice modes are excited. We have also observed an emission due to the NO_2^-. It is mirror-symmetric to the absorption but with slightly different frequencies: ν_1 and ν_2. Table I summarizes the vibrational frequencies. As one would expect, ν_1 and ν_2 are equal to the frequencies of absorption lines in the infrared, although the lines we found are weak compared to the 1395-cm^{-1} and 1280-cm^{-1} lines that are prominent in NO_2^--doped crystals. The vibrational structure is very similar to that of $NaNO_2$ analyzed in detail by Sidman.[2] It is assumed that the ν_1 and ν_2 correspond to the symmetric stretching and bending vibrations, respectively, of the NO_2^- ion.

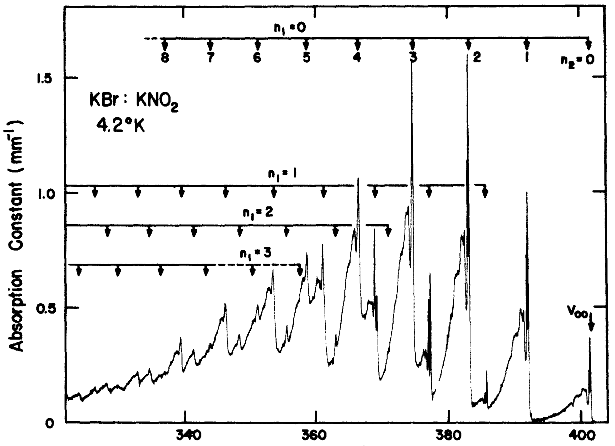

FIG. 1. Optical absorption of $KBr{:}KNO_2$ at 4.2°K. The sharp lines denoted by arrows are no-phonon transitions to different vibrational levels of the NO_2^- ion.

Table I. Vibrational frequencies of the NO_2^- ion coupled to the electronic transition. It is assumed that ν_1 is the symmetric stretching mode and ν_2 the bending mode. ν_∞ is the frequency of the purely electronic transition. The primes refer to the absorption.[a]

	$KBr{:}KNO_2$ (cm^{-1})	$KCl{:}KNO_2$ (cm^{-1})
ν_∞	24 948 ± 10	25 046 ± 10
ν_1'	1005	1025
ν_2'	594	598
ν_1	1302	1317
ν_2	805	800
ν_1 (IR)	1315	1321
ν_2 (IR)	808	801

[a] Errors are ±5 cm^{-1} except on ν_∞, which is ±10 cm^{-1}.

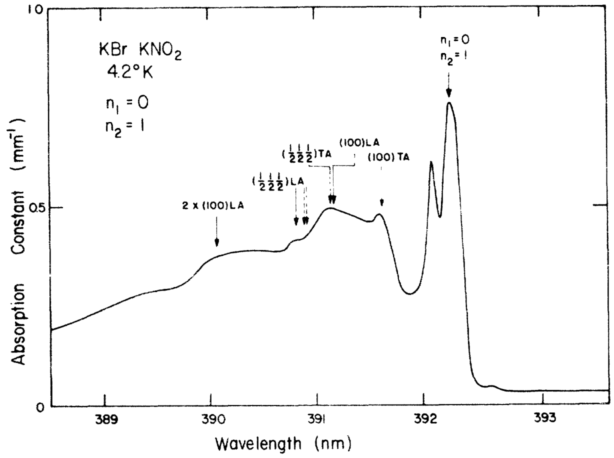

FIG. 2. Detailed phonon structure at the $n_1 = 0$, $n_2 = 1$ vibrational level for KBr:KNO$_2$. The arrows denote acoustic phonon energies at singularities in the Brillouin zone as determined by Woods et al.[4] by neutron diffraction. The dotted arrows refer to singular points. $(\frac{1}{2}, \frac{1}{2}, 0)$LA and $(0.6, 0, 0)$LA not associated with distinct maxima.

The width of the purely electronic line ν_{∞} in KI:KNO$_2$ is 7.0 cm^{-1}, and the no-phonon bands of the higher vibrational levels broaden progressively. The highest levels have a width of the order of 70 cm^{-1} ($n_1 = 1$, $n_2 = 3$ in KI). In contrast the emission lines are sharp. Their width is small, of the order of the purely electronic lines. The shape of the higher no-phonon lines is best described by a Lorenzian curve and it is likely that their width arises from radiationless transitions to the ground state or to the conduction band.

Figure 2 shows the phonon structure for KBr:KNO$_2$ at the $n_1 = 0$, $n_2 = 1$ vibrational level. The arrows denote the critical points in the phonon spectrum of pure KBr as determined by neutron diffraction.[5] Critical points of the acoustical branches along the main symmetry directions are shown. At these points the phonon density of states will have singularities. It will be seen that the absorption structure reflects these sin-

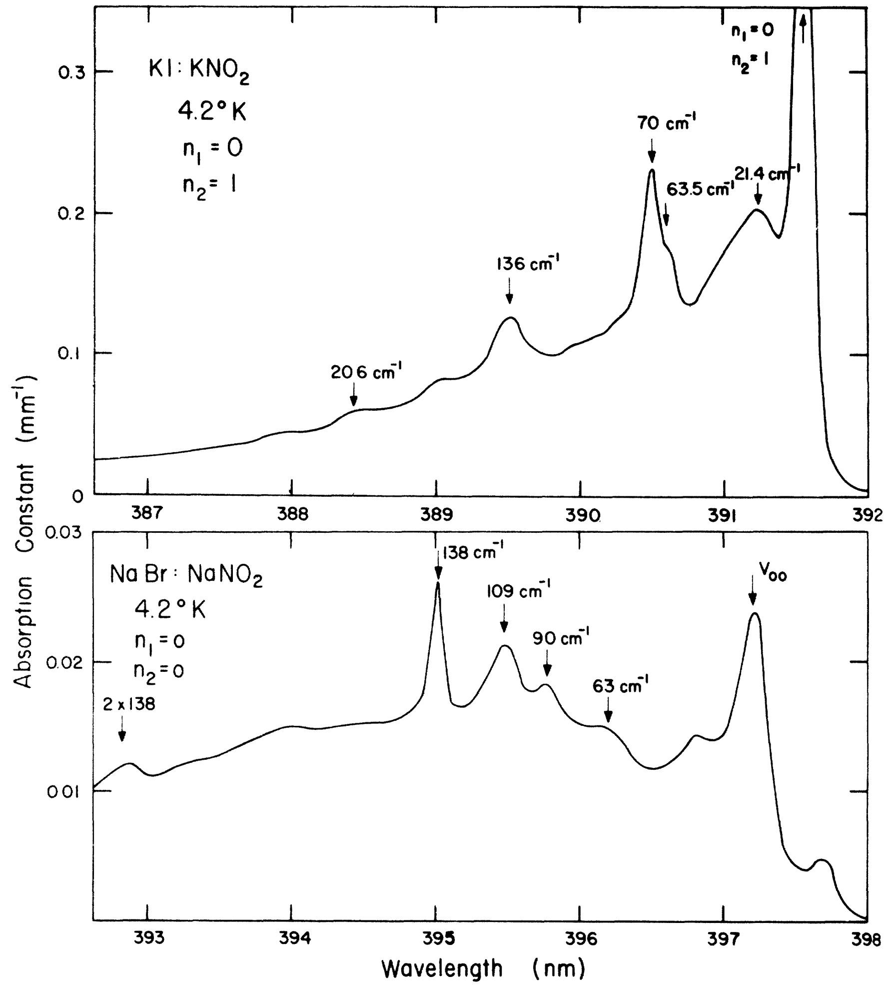

FIG. 3. Phonon structure of KI:KNO$_2$ and NaBr:NaNO$_2$. It is suggested that the structure at 70 cm^{-1} in KI and possibly the line at 138 cm^{-1} NaBr is due to a local mode of the NO$_2^-$ in the gap between the optical and acoustical branches.

gularities very closely. Apparently the coupling to the acoustical branches is stronger than that to the optical ones, for there is no structure resolved in the optical region. Also, there is very little structure in the two and more phonon parts of the spectrum. This is to be expected since widths of bands arising from dispersion of frequencies would be increased proportionally to the number of phonons involved. For other crystals no neutron-diffraction data are available, but a comparison with calculated phonon spectra[5] shows that the maxima correspond to the acoustical region.

Figure 3 shows the phonon spectra for $KI:KNO_2$ and $NaBr:NO_2$. The sharp line at 70 cm^{-1} in $KI:KNO_2^-$ differs from the other phonon structure in sharpness; even the corresponding three-phonon line is resolved at 206 cm^{-1}. We estimate that any width arising from dispersion for this line is less than 2 cm^{-1}. Its position is in the energy gap between the acoustical and optical branches of KI, as suggested by the calculations of Karo and Hardy.[5] It is possible that this line is due to a local mode in the gap. Such modes have been discussed in the literature[6] and, for our case of a light mass substituted for the normally heavier mass, the local mode would be possible in the gap, provided the force constants are not too small. There is a similar sharp line at 138 cm^{-1} in $NaBr:NaNO_2$.

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ANALYSIS AND INTERPRETATION OF H^3 AND He^3 FORM FACTORS*

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Recently the electric and magnetic-moment form factors of H^3 and He^3 have been measured by Collard and Hofstadter[1] and Collard et al.[2] The form factors have then been analyzed by Schiff et al.[3] and Levinger[4,5] under various assumptions to obtain independent determinations of the charge form factor of neutron and other quantities such as the exchange magnetic-moment form factors and F_0 and F_L. The charge form factor given by Schiff et al.[3] is consistently smaller than that obtained from the electron-scattering experiments with deuteron,[6,7] while that given by Levinger is larger (Fig. 1). Further, Schiff et al.[3] introduced the S' state of mixed spatial symmetry in the nuclear wave function, giving large difference in F_0 and F_L, which is in contradiction with other observations.[8,9] In both above analyses the contributions from meson-exchange currents to the charge form factors of H^3 and He^3 have been neglected.

The aim of this Letter is to report an analysis of the form factors of H^3 and He^3, assuming that the contributions of the meson-exchange currents to the charge form factors of H^3 and He^3 is not negligible. It follows from Siegert's theorem[10] that the static electric multipole moments of nuclei are independent of any exchange currents. We shall therefore normalize the exchange charge form factors of H^3 and He^3 to zero momentum transfer.

Following Schiff[11] we write down the following general expressions for the three-dimensional Fourier transforms of the charge and moment distributions of H^3 and He^3:

$$2F_{\mathrm{ch}}^{\mathrm{H}}(q^2) = 2F_{\mathrm{L}}(q^2)F_{\mathrm{ch}}^{p}(q^2) + F_0(q^2)F_{\mathrm{ch}}^{n}(q^2) + F_{0,\mathrm{ch}}^{S}(q^2) - F_{\mathrm{ch}}^{V}(q^2); \quad (1)$$