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Raman Spectra of Sulfate-Doped Alkali Halides

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Sulfate ions in alkali halide crystals give rise to four internal-oscillation Raman-active frequencies. These are slightly different from the free sulfate-ion frequencies observed in solution. The values of these four frequencies in NaCl, KCl, KBr, and KI at room temperature are reported. As may be expected, the principal frequency representing the total symmetric oscillation is the only line which is found to be well polarized, while the others are depolarized.

INTRODUCTION

Raman spectra of molecular impurities in alkali halides have assumed considerable importance in view of the currently available laser sources. Some work has been reported[1] wherein simple ionized molecules like O_2^-, S_2^-, S_3^- have been used as the molecular impurities. Recently, nitrite ions in alkali halides have also been studied[2] by this method. In this paper we report results concerning the Raman scattering in alkali halides containing SO_4^{--} (sulfate) ions. The alkali halide crystals containing sulfate ions have been grown from a melt starting from analytical grade material. The impurity was added in the form of K_2SO_4 powder. The sulfate ions occupy chlorine sites in the lattice. Raman spectra were recorded by using a CODERG Raman spectrometer with a photoelectric recording system. A Spectra-Physics He-Ne laser was the source of light operating at 6328 Å and 50-mW power output. By using a quarter-wave plate in the path of the incident laser beam, scattered spectra representing the vertical and horizontal components, respectively, were recorded.

TABLE I. Raman frequencies of sulfate ion (in cm^{-1}) observed in solution and in various crystal matrices.

	ν_1	ν_2	ν_3	ν_4
SO_4 in solution	981	451	1104	613
in NaCl	958	410	1110	610
in KCl	970	430	1120	610
in KBr	965	430	1115	605
in KI	960	425	1110	615

RESULTS AND DISCUSSION

Raman spectra in sulfate-doped NaCl, KCl, KBr, and KI are reported in this paper. The presence of a molecular impurity like SO_4 in the chlorine lattice position in the NaCl structure destroys the

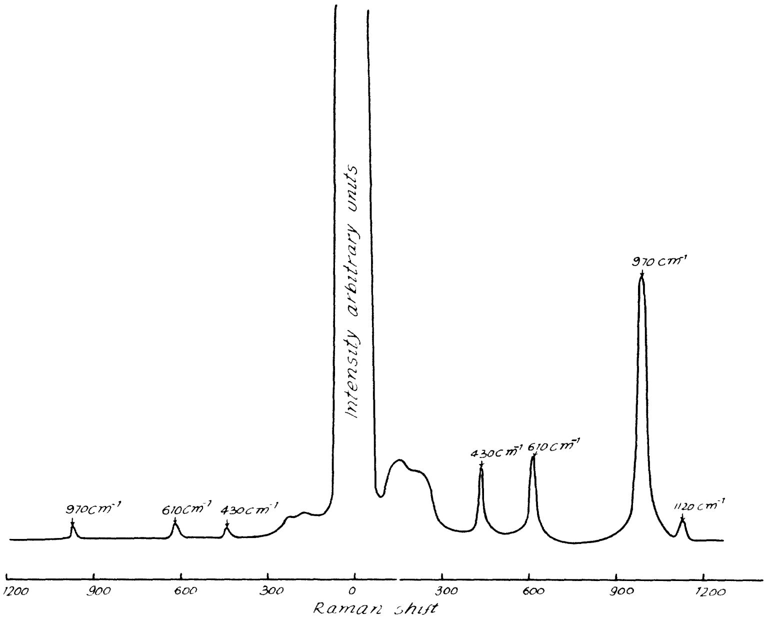

FIG. 1. Raman spectrum of a KCl crystal containing sulfate ions.

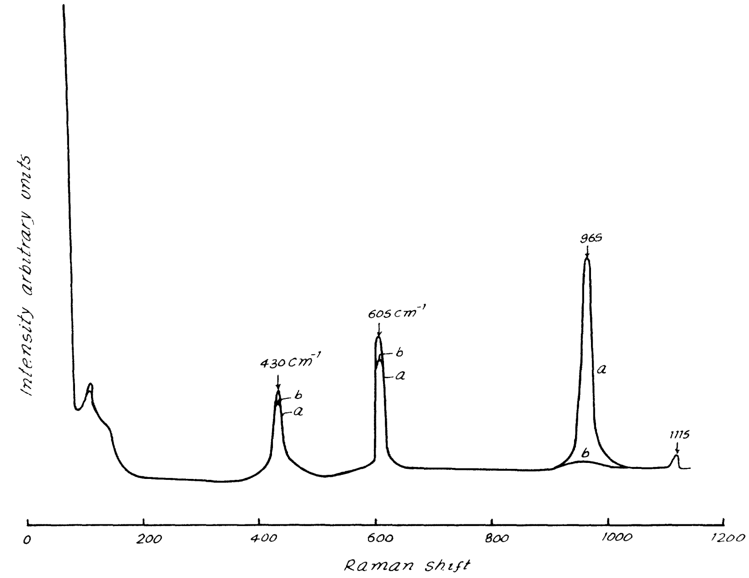

FIG. 2. Raman spectrum of a KBr crystal containing sulfate ions. Curve a is obtained when the incident beam is vertically polarized and curve b when the incident beam is horizontally polarized.

inversion symmetry for the neighboring ions and gives rise to the forbidden first-order Raman spectrum. Such results, obtained by breaking the inversion symmetry, have been reported earlier.[3,4] These impurity-induced first-order lines are also observed in our crystals. Figure 1 shows the Raman spectrum of a KCl crystal containing SO_4^{--} ions. Both the Stokes (decrease in energy) and the anti-Stokes (increase in energy) components are shown in the figure. The spectrum below 300 cm^{-1} corresponds to the impurity-induced first-order spectrum. This region clearly contains more than one frequency (where frequency here is in wave-number units) and all these are depolarized indicating that they arise from degenerate vibrations. In addition to these, we observe very strong and sharp lines beyond 400 cm^{-1}. Four well-resolved lines at 430, 610, 970, and 1120 cm^{-1} can be seen in this figure. The line at 970 cm^{-1} is well polarized while the others are depolarized. These frequencies arise because of the internal oscillations of the sulfate ion in the KCl crystal. A comparison of these frequencies (shown in Table I) with the natural sulfate-ion frequencies in the free state confirms this interpretation. In all the four alkali halides, a similar result is obtained in crystals containing more than 1.0% of K_2SO_4 added in the melt. In crystals containing concentrations lower than this, neither the induced first-order spectrum nor the internal oscillation spectrum was found. Figure 2 shows the Raman spectrum of SO_4^{--} ions in a KBr crystal. Curve a is for the incident laser beam polarized vertically and curve b is for the incident laser beam polarized horizontally. This shows the results of polarization studies.

TABLE II. Raman frequencies of molecules (in cm^{-1}) observed in a crystalline matrix. (Values for diatomic molecules taken from Ref. 1; values for NO_2^- taken from Ref. 2).

	O_2^-	N_2^-	S_2^-	Se_2^-	NO_2^-	SO_4^{--}
Free ion	1090	• • •	• • •	• • •	1316, 831	981, 451, 1104, 613
NaCl	1144	• • •	• • •	• • •	1360 (Ref. 6)	958, 410, 1110, 610
KCl	1145	1836	• • •	• • •	1327, 811 1286[a]	970, 430, 1120, 610
KBr	1135	1821	612	• • •	1317, 806 1274[a]	965, 435, 1115, 605
KI	1123	1870	594	325	1309, 803	960, 425, 1110, 615
NaBr	1131	• • •	610	• • •	• • •	• • •

[a] These frequencies observed at liquid-nitrogen temperatures.

The sulfate ion is a tetrahedral five-atomic molecule (XY_4 type) in which the sulfur occupies the center and the four oxygens occupy the corners of a tetrahedron. Such an ion will exhibit[5] four frequencies all of which are Raman active. There is one nondegenerate vibration (ν_1) of species A_1 (total symmetric), one doubly degenerate vibration (ν_2) of the E type, and two triply degenerate vibrations (ν_3) and (ν_4) of the F_2 type. Table I gives these[6] frequencies when the sulfate ion is in solution and when it is placed in a crystalline matrix.

The total symmetric (A_1) vibration characterized by the ν_1 frequency is well polarized in all these cases while the others are depolarized. The fact that no additional lines are observed when the sulphate ion is introduced into the lattice of O_h type means that there is no splitting caused by the internal crystal field. The frequencies are somewhat shifted in each case. The width in most .of these cases is about 20 cm^{-1}. Table II shows this shift in frequencies from the frequencies observed in solution for some typical molecules.

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