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The vibration spectra of crystals—Part VI. Sylvine

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1. Introduction

The optical behaviour of sylvine shows clearly that the characteristic frequencies of atomic vibration lie more remotely in the infra-red than in the case of rock-salt. The question whether this is due solely to the atomic weight of potassium being greater than that of sodium or whether it is also partly due to a diminution in the strength of the interatomic forces is a point of considerable interest. The infra-red behaviour of sylvine has been studied by several investigators very thoroughly and their results furnish the data needed to decide this question. We shall accordingly proceed to evaluate the eigenfrequencies and to consider them in relation to the experimental facts. It may be remarked that some as yet unpublished work by Dr R S Krishnan on the second-order spectrum of light-scattering in sylvine has assisted in determining the appropriate values of the force-constants.

2. The nine eigenfrequencies of sylvine

As the atomic weight of chlorine is less than that of potassium, the two modes in which the chlorine atoms alone oscillate would have a higher frequency than the corresponding two modes in which the potassiums alone vibrate. The difference in atomic weights (35·5 and 39) is however not large, and it follows that the frequencies of these four modes would not differ very much from each other and that the sequence in which they appear would depend on the precise values of the force constants. Table 1 shows the calculation of the frequencies. The values of P and T are both a little smaller than for rock-salt. For convenience, the symbols ν_4 and ν_5 have been used to designate the oscillations of the chlorine atoms while ν_6 and ν_7 designate those of the potassium atoms. It will be noticed, however, that ν_6 is greater than ν_5.

Table 1. Eigenfrequencies of KCl
($P = 2{\cdot}30 \times 10^4$ dynes per cm; $T = -0{\cdot}05 \times 10^4$ dynes per cm)

Designation	$4\pi^2c^2m_R{}^2\nu^2$	Frequency	Wavelength
		cm^{-1}	μ
ν_1	0·0538P + 0·00T	145	69
ν_2	0·0538P + 0·214T	138	72
ν_3	0·0538P + 0·430T	132	76
ν_4	0·0282P − 0·226T	114	89
ν_5	0·0282P + 0·113T	100	100
ν_6	0·0256P − 0·205T	108	93
ν_7	0·0256P + 0·102T	95	105
ν_8	−0·429T	60	167
ν_9	−0·214T	43	233

3. The infra-red behaviour of sylvine

The so-called "fundamental" oscillation in which the potassium and chlorine atoms move in opposite phases is ν_3 in our table, corresponding to an infra-red wavelength of 76 μ. It is to be remarked that this does not coincide either with the "rest-strahlen" wavelength of 63·4 μ with the wavelength of 70·7 μ at which the maximum absorption is exhibited by the thinnest films (Barnes 1932). It will be noticed that the latter is nearer ν_1 which has a wavelength of 69 μ. These remarks reinforce the point that owing to the anharmonicity and the mutual coupling of the various eigenvibrations, all of them must be considered to be active in greater or less degree, and that we must take account also of the activity of the various overtones and summations of the nine fundamental frequencies. On this basis, it is possible to understand the facts established by experimental study regarding the infra-red behaviour of sylvine.

Czerny (1930) investigated the reflecting power over the entire range of infra-red wavelengths for which sylvine is opaque in moderate thicknesses. He found a small but quite definite swell in reflecting power in the wavelength range between 42 μ and 48 μ with a maximum of 20% at 46 μ. Referring to table 1, we recognize that this is the region in which the octaves of the fourth, fifth and sixth eigenfrequencies are grouped together, and the increase of reflection is therefore to be ascribed to their presence and conjoint effect. At 48 μ, the reflecting power reaches a minimum of 18% and then rises again steadily, reaching a maximum of about 90% in the range of wavelengths 60–65 μ. It then falls down to 78% at 70 μ, 65% at 75 μ, 45% at 80 μ, 32% at 85 μ and 26% at 90 μ. The large increase in reflecting power in the range between 50 μ and 70 μ is a particularly noteworthy feature, and is readily understood when we recall that in this region lie numerous frequencies in the second-order spectrum, viz., $2\nu_7$, $(\nu_6+\nu_9)$, $(\nu_5+\nu_9)$, $(\nu_4+\nu_9)$, $(\nu_3+\nu_9)$, $(\nu_2+\nu_9)$, $(\nu_1+\nu_9)$, $(\nu_7+\nu_8)$, $(\nu_6+\nu_8)$, $(\nu_5+\nu_8)$, $(\nu_4+\nu_8)$, $(\nu_3+\nu_8)$ and $(\nu_2+\nu_8)$. The fairly rapid drop of reflecting power at about 80 μ is an indication that the infra-red activity is considerable only for the three highest fundamentals ν_1, ν_2, ν_3 and is relatively small for the fundamentals of lower frequency. The behaviour of sylvine in this respect is closely parallel to that of rock-salt.

Mentzel (1934) has very elaborately investigated the absorption coefficient of sylvine plates of various thicknesses over a wide range of wavelengths. His work confirms the existence of the variations which we should expect in the range between 40 μ and 45 μ owing to the presence of the octaves of ν_3, ν_4 and ν_6 in that vicinity. The large drop in the absorption coefficient which occurs between 34 μ and 23 μ, and again between 23 μ and 17 μ is also readily understood, since 34 μ, 23 μ and 17 μ are respectively the shortest wavelengths in the second-order, third-order and fourth-order spectra.

4. Summary

The nine eigenfrequencies of sylvine are evaluated, and it is shown that the wavelength at which the maximum absorption is exhibited by very thin films is much nearer the first than the third of them which is the so-called active oscillation of the potassium against the chlorine atoms. The absorption and reflection data over the whole range of wavelengths are in general accord with the indications of the theory. The force-constants for sylvine are a little smaller than for rock-salt.

References

1. Barnes *Z. Phys.* **75** 729 (1932).
2. Czerny *Ibid.* **65** 600 (1930).
3. Mentzel *Ibid.* **88** 178 (1934).