Raman Spectrum of Rubidium Thiocyanate at 37 K and Room Temperature

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Abstract

The single crystal Raman spectrum of RbSCN from 0 to 2200 cm^{-1} was studied between 37 K and room temperature. A new peak was observed in the B_{2g} polarisation and is believed to be an external mode. The low temperature data indicate that previous interpretations of the external modes are in error. A new classification of these modes is given. Further, whereas the internal modes are in agreement with previous studies, some multiphonon modes are not. The assumed isomorphism between RbSCN and KSCN suggests a correction to the most recent interpretation of the spectrum of KSCN as well.

1. Introduction

Many studies of the alkali thiocyanates have been undertaken in the past in order to build a consistent, overall picture of their behaviour (Hua and Ninio 1986; Irving *et al.* 1985; Ra *et al.* 1978; Ti *et al.* 1976; Dao and Wilkinson 1973). KSCN in particular has been studied in much detail, but less is known about the closely related crystal RbSCN. The infrared and Raman spectra of RbSCN and KSCN were measured by Ti *et al.* (1976), and were analysed together, assuming that the two crystals are isomorphic. Because only room temperature data were available, their assignment of several of the low energy (<200 cm^{-1}) modes was tentative. In particular, some features were assumed to arise from multiphonon processes, but this was not verified. Later, the same authors (Ra *et al.* 1978) reassigned several of the KSCN modes on the basis of a theoretical analysis.

By analysing the low temperature behaviour of the Raman spectrum of RbSCN, we are able to verify whether multiphonon peaks are present, since such peaks decrease rapidly in intensity as the temperature is lowered. Further, since the Raman linewidths generally get narrower at lower temperatures, it is possible to resolve closely spaced features which may merge at room temperature. In fact, a new feature was observed at very low temperature. Thus, we are able to make a more definitive assignment of the Raman features than was possible in the past. Several tentative assignments made by Ti *et al.* (1976) have been confirmed and the theoretical results of 1978 are called into question.

KSCN belongs to the space group $P_{bcm}(D_{2h}^{11})$, with four formula units per unit cell (Klug 1933). The SCN$^-$ ions lie in the $z = \frac{1}{4}$ and $\frac{3}{4}$ planes, with the cations

sitting between the thiocyanate layers, as shown in Fig. 1. We assume that RbSCN is isomorphic to KSCN, so the unit cell will be identical except that the atomic coordinates will be scaled by the dimensions of the corresponding unit cells (Klement 1976). This scaling was used in order to confirm orientation of our crystal by the Laue method. The assumption of isomorphism also requires RbSCN and KSCN to have the same number of modes in each orientation.
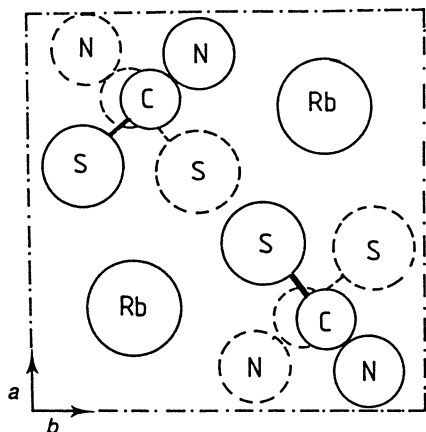
Fig. 1. Crystal structure of RbSCN, looking along the x-axis. The dashed thiocyanate ions lie in the $z = \frac{1}{4}$ plane, while the solid ones lie in the $z = \frac{3}{4}$ plane. The Rb$^+$ ions lie in the $z = \frac{1}{2}$ plane.

2. Experimental

Several crystals of RbSCN were used in this study. These were grown from an aqueous solution that had been prepared from NH_4CO_3. Almost all the larger crystals that had formed had well-developed (100) faces, but were narrow (~1–2 mm) in this dimension. The largest crystal obtained was $2 \cdot 2 \times 10 \times 17$ mm^3.

The two large, parallel (100) faces were easy to identify and made simple, but fairly accurate alignment between crossed polarisers possible. The crystals were then aligned more accurately using Laue backscattering, the X-ray result compared with a computer generated picture. The agreement of the X-ray to the computer simulation was good, indicating our scaling assumptions to be reasonable. Final alignment of the crystals was done on the Raman spectrometer by making small adjustments to minimise obvious leakthrough.

The exciting source was a Coherent CR3 argon ion laser. Two Varian-Techtron monochromators connected via external optics were used, with a photon counting system to collect the spectra. Resolution was generally 4 cm^{-1} but for some room temperature spectra it was 2 cm^{-1}. In view of the disagreement with previously published data, all possible combinations of crystal orientation and polarisation except those of the type Y(...)Z were observed. This allowed cross checking of scattering tensor components. The peaks in the ZZ spectrum (A$_g$ symmetry) of both RbSCN and KSCN are very weak, however, so this orientation is not particularly useful for studying the Raman spectrum of these crystals. (If we consider the effect of incident z-polarised light on the crystal, it will only effectively induce motions of the cation or thiocyanate ions in the z-direction, but such motions are not allowed under A$_g$ symmetry—only those motions where the thiocyanate ions stay in the $z = \frac{1}{4}$ or $\frac{3}{4}$ plane and the cations stay in the $z = 0$ or $\frac{1}{2}$ plane are

allowed. We therefore expect any peaks present in the ZZ orientation to be very weak.) Five different lasing lines were used (459·7, 476·5, 488·0, 496·5 and 514·5 nm), with powers in the range 100–200 mW.

Table 1. The $k = 0$ phonon modes of MSCN (M = Rb, K)

N is the total number of degrees of freedom; T', the acoustic modes; T, the optical translational modes; R, the rotational modes; and η, the internal thiocyanate modes

	N	T'	T	R	η	Raman/IR active
A_g	7		3	1	3	$\alpha_{xx,yy,zz}$
B_{1g}	8		4	1	3	$\alpha_{(xy)}$
B_{2g}	5		3	1	1	$\alpha_{(xz)}$
B_{3g}	4		2	1	1	$\alpha_{(yz)}$
A_u	4		2	1	1	
B_{1u}	5	1	2	1	1	T_z
B_{2u}	8	1	3	1	3	T_y
B_{3u}	7	1	2	1	3	T_x

3. Results and Discussion

Standard factor group methods were used to determine the expected number of modes (at $k = 0$) for each orientation Bhagavantum and Venkataraydu (1969), and the results are summarised in Table 1. Internal thiocyanate modes involve bending and stretching of the SCN⁻ ions, and occur at large energies (>400 cm⁻¹). The other modes are conveniently called external modes. The rotational mode of the SCN⁻ ion is Raman active in each crystal orientation and, assuming no coupling between modes, occurs at the same frequency in each of these orientations. Also, if the interatomic forces are the same in KSCN and RbSCN, this mode will be at the same frequency in both crystals. Pure modes corresponding to cation translation should occur in the energy ratio 1:0·68 (K:Rb), whereas SCN⁻ translations should be cation dependent. Coupling between modes will cause these ratios to differ from these ideal values.

External Modes

The external mode spectra of RbSCN at 37 K and room temperature are shown in Fig. 2. These spectra were also observed at various temperatures between these values. The temperature dependence of the spectra yielded much new information that was used in the classification of modes. In particular:

(i) it was found that all the observed modes occurring below 200 cm⁻¹ were single phonon modes, since none became less intense as the temperature was decreased; and

(ii) a new mode was observed in the B_{2g} polarisation at 88 cm⁻¹ (Fig. 3).

We begin our interpretation of the external spectra with the B_{3g} orientation, since this is the most straightforward. Three modes are expected (Table 1), and clearly three (only) are observed. Ti *et al.* have assigned the 123 cm⁻¹ mode (124 cm⁻¹ in their spectra) as the SCN⁻ rotation on the basis of the energy ratio when compared with KSCN, and our data agree with this interpretation.
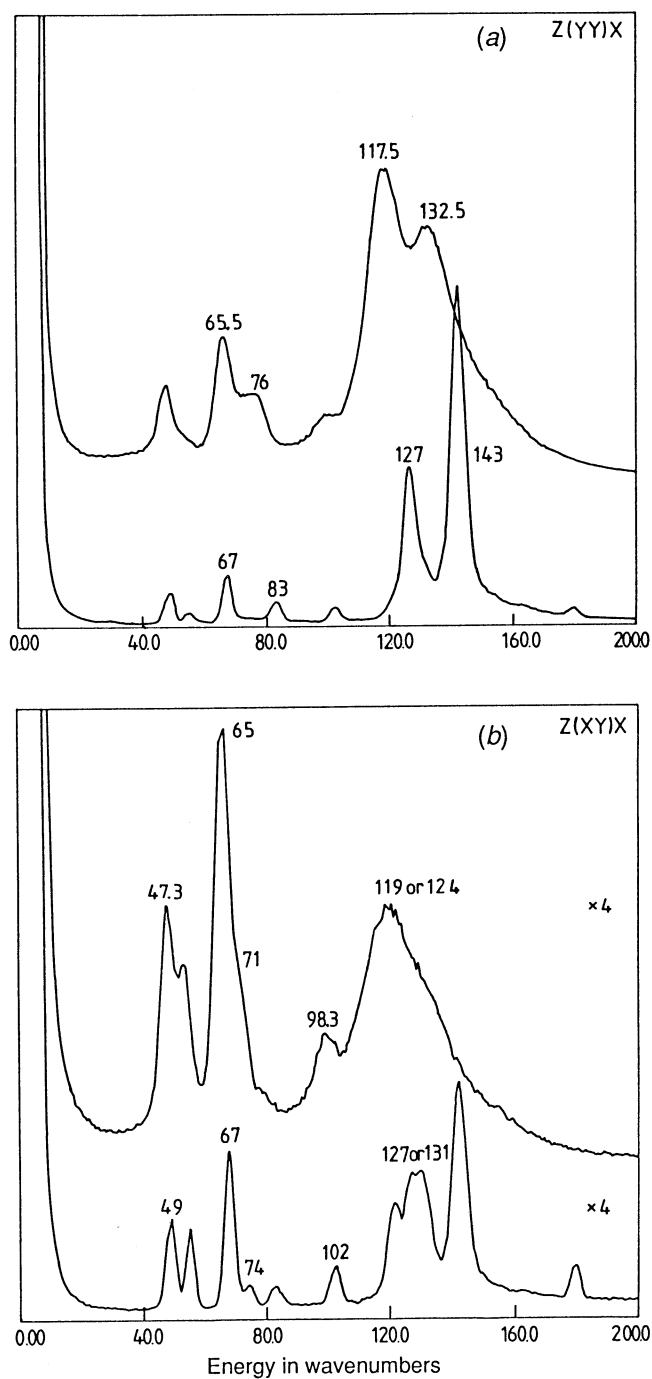
Fig. 2. Polarised Raman spectrum of the external modes of RbSCN. The upper (lower) trace was taken at room temperature (37 K), with a resolution 2 cm^{-1} (4 cm^{-1}). The peak at 180 cm^{-1} in the low temperature spectra is a laser emission line. Peaks not labelled are believed to be due to leakthrough: (*a*) A$_g$, (*b*) B$_{1g}$, (*c*) B$_{2g}$ (*d*) B$_{3g}$.
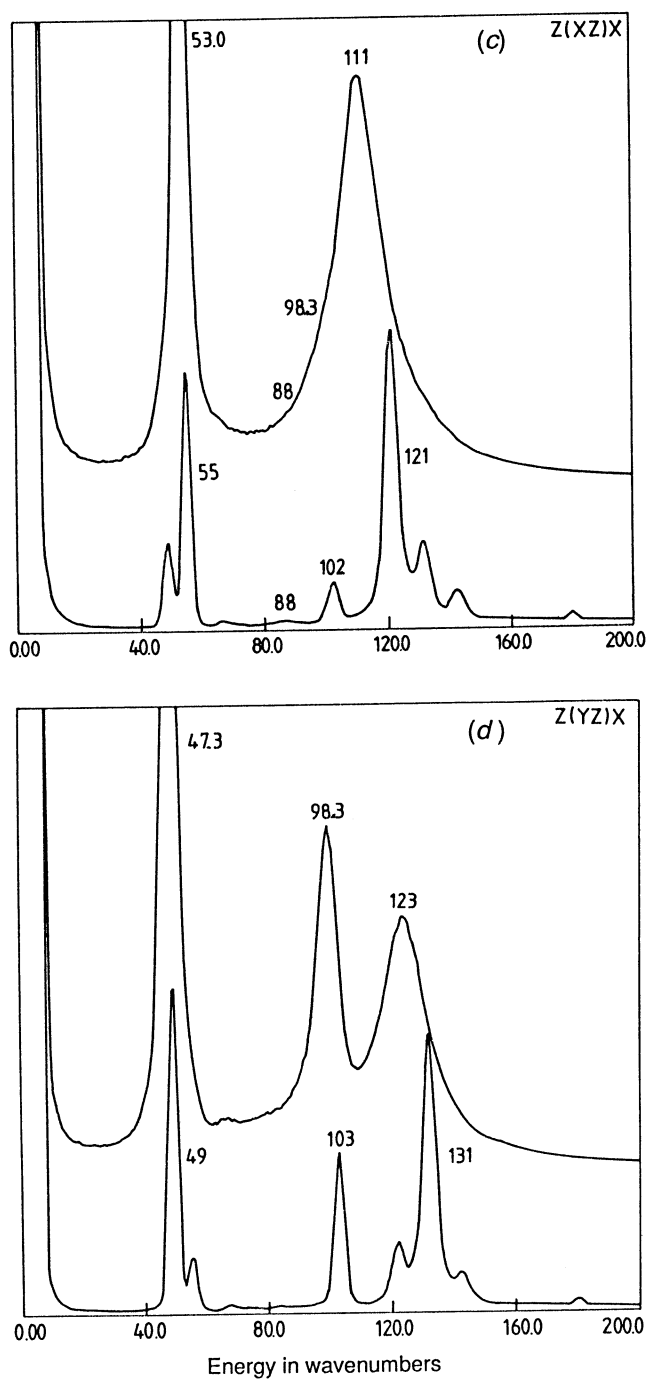
Fig. 2. *(Continued)*

In the A_g spectrum, Ti *et al.* assigned the 76 cm^{-1} peak (75 cm^{-1} in their spectrum) to a two phonon process, but the low temperature spectrum (Fig. 2*a*) clearly shows this is not correct. We therefore include this peak as a translational mode, as shown in Table 2.
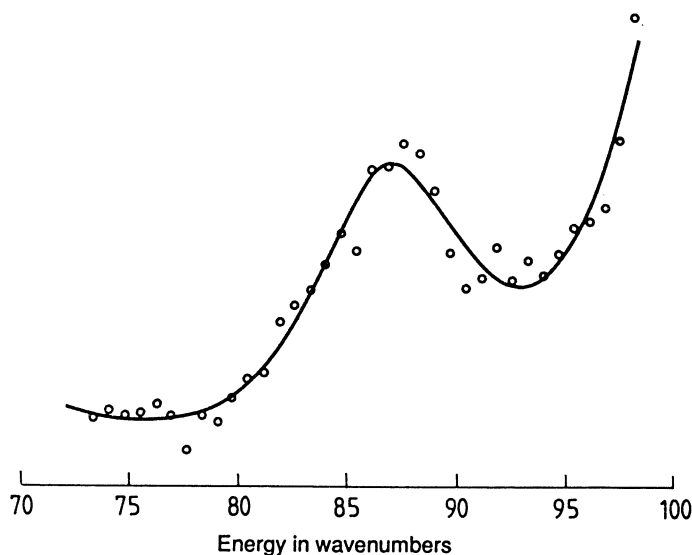

Fig. 3. A very weak peak in the B_{2g} spectrum at 37 K. This is believed to be an external mode.

Table 2. Classification of room temperature external modes of RbSCN and KSCN

Corresponding energies at 37 K can be noted in Fig. 2. Frequencies with a decimal place are accurate to ±1 cm^{-1}, the others to ±2 cm^{-1}. Rotational modes are given in italics

Symmetry		External mode				
A_g	RbSCN	65·5	76	*117·5*	132·5	
	KSCN	78	96	*122*	144	
B_{1g}	RbSCN	47·3	65	71	98·3	*119 or 124*
	KSCN	68	98	?	112	*124*
B_{2g}	RbSCN	53	88	98·3	*111*	
	KSCN	68	87	96	*122*	
B_{3g}	RbSCN	47·3	98·3	*123*		
	KSCN	68	112	*126*		

In the B_{2g} spectrum, there is no peak near 123 cm^{-1} (the rotational mode frequency) and so it is believed that this mode is strongly coupled to the lowest energy mode in this orientation. The rotational mode has therefore shifted to 111 cm^{-1} and the low energy mode, which is at 47·3 cm^{-1} in B_{1g} and B_{3g}, has correspondingly shifted up to 53·0 cm^{-1}. This coupling was also observed by Ti *et al.*; however, they found the 47·3 cm^{-1} peak (48 cm^{-1} in their spectrum) to be present in the (room temperature) B_{2g} spectrum, and so included it as an active mode under this symmetry. Our room temperature spectra do not show this (47·3 cm^{-1}) peak, so we believe it is due only to leakthrough in their spectrum. We 'replace' this peak with a new one we observed at 37 K

(Fig. 3). This peak, which occurs at 88 cm^{-1}, cannot be due to leakthrough since it is only found in this orientation, and must be single phonon since it is roughly constant in intensity with temperature. It also remains constant in energy as the temperature rises, although it cannot be observed at room temperature since it disappears into the tail of the 98·3 cm^{-1} peak.

This new peak corresponds closely in energy to a peak observed in KSCN (at 87 cm^{-1}) by Ti *et al.* Ra *et al.* (1978) suggested that either the 68 or 87 cm^{-1} peak observed in KSCN might be two-phonon and, on the basis of intensity, rejected the higher energy peak in favour of a very low energy (<13 cm^{-1}) mode which they predicted would be present under this symmetry. The observation of this 88 cm^{-1} peak in RbSCN seems to imply that the 87 cm^{-1} peak in KSCN is in fact single phonon, and suggests that the earlier interpretation of the B$_{2g}$ spectrum of KSCN, as listed in Table 2, is better. A remeasurement of the KSCN B$_{2g}$ Raman spectrum, especially at low temperature, would be appropriate to clarify this.

The B$_{1g}$ spectrum is weaker than the other three. It was not possible to obtain a spectrum free of leakthrough (Fig. 2*b*) and so this spectrum is difficult to interpret. We have assigned the peaks of this spectrum as shown in Table 2, which is very similar to the interpretation of Ti *et al.* Several differences from their results were seen, however. Firstly, although Ti *et al.* observed the rotational mode at 124 cm^{-1} in this orientation, we see no peak at that energy. Instead, we see a peak at 119 cm^{-1}. Possibly this peak is due to leakthrough from the nearby A$_g$ mode (117·5 cm^{-1}), but careful crystal alignment and the slight shift in position seem to imply that this is not the case. It is not possible to say with certainty therefore exactly where the rotational mode occurs in this orientation, so in Table 2 it is labelled 119 or 124 cm^{-1}.

The second discrepancy between our spectra and the measurements of Ti *et al.* is that we see no evidence for a peak near 153 cm^{-1}. Such a peak was observed by Ti *et al.* and initially denoted two-phonon, since it was weak. A corresponding peak in KSCN (145 cm^{-1}) was also then assigned in this way. Later, Ra *et al.* concluded that this peak was a fundamental mode, but the fact that we do not observe it at all calls this into question.

Ti *et al.* (1976) suggested (as we have in Table 2) that a mode in KSCN corresponding to the 71 cm^{-1} peak observed in RbSCN might occur. This 'unknown' mode was later rejected (Ra *et al.* 1978) in favour of the 145 cm^{-1} mode. We note that the 71 cm^{-1} peak observed in RbSCN must be a fundamental mode since it remains present at 37 K, and it is not due to leakthrough since a peak of this energy only occurs in this orientation. The corresponding peak in KSCN should occur somewhere between 70 and 90 cm^{-1} and thus, if it were weak, it could be lost in the tail of the next lower or higher peaks (68 and 98 cm^{-1}). Obviously, a careful (low temperature) search for a peak in the Raman spectrum of KSCN in the region 70 to 90 cm^{-1} should be carried out. Until this is done, a definitive assignment of the B$_{1g}$ spectrum of KSCN is not possible. We suggest that further experimental work must be performed before the '?' mode (Table 2) can be assigned.

Internal Modes

The room temperature internal mode spectra of RbSCN are shown in Fig. 4 and listed in Table 3. These modes are related to the modes of vibration of
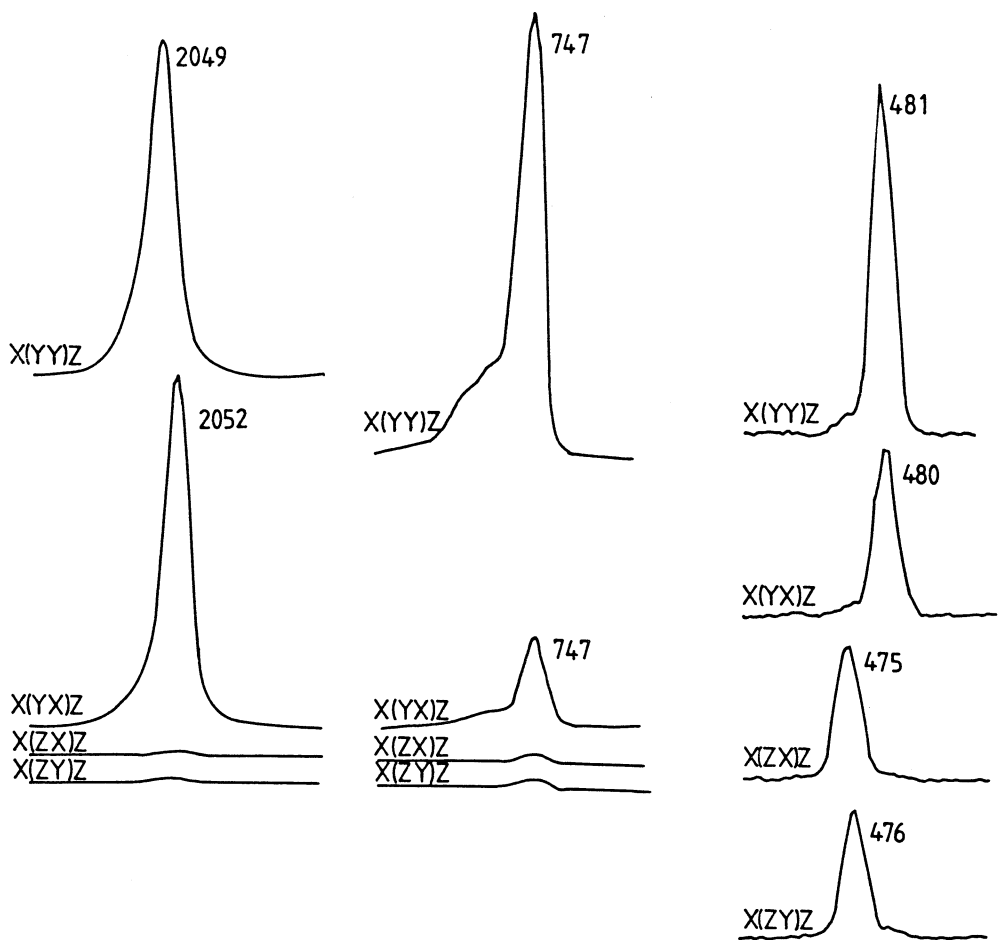
Fig. 4. Polarised Raman spectrum of the internal modes of RbSCN at room temperature. Resolution is 4 cm^{-1}.

Table 3. Internal modes of RbSCN

The motions are ν_1, C–N stretching; ν_2, SCN bending; and ν_3, C–S stretching. These frequencies are accurate to $\pm\, 2$ cm^{-1}

Symmetry	ν_1	ν_2	ν_3
A_g	2049	481	747
B_{1g}	2052	480	747
B_{2g}		475	
B_{3g}		476	

the free thiocyanate ions (Jones 1956) and, as expected, were found to vary negligibly with temperature. The internal modes were observed to occur in those polarisations predicted by the factor group analysis except that the ν_1 mode, which occurs with A_g symmetry, had a very low intensity (perhaps zero) in the ZZ orientation. It occurred as expected in XX and YY orientations.

The ν_3 stretching mode occurs at almost the same frequency in the A_g and the B_{1g} orientations. The ν_1 stretching mode, however, was observed to

be about $2 \cdot 5$ cm^{-1} higher in frequency in the B_{1g} orientation than in the A_g. This amount of splitting is larger than that reported by Ti *et al.* (1976). The degeneracy of the bending mode (v_2) is also lifted by the crystal field and in the plane bending (A_g, B_{1g}) is slightly higher in frequency than the out of plane motion (B_{2g}, B_{3g}). Since the KSCN has a smaller unit cell than the RbSCN, we expect the degree of 'field splitting' in the former to be larger, as is the case (Ti *et al.* 1976).
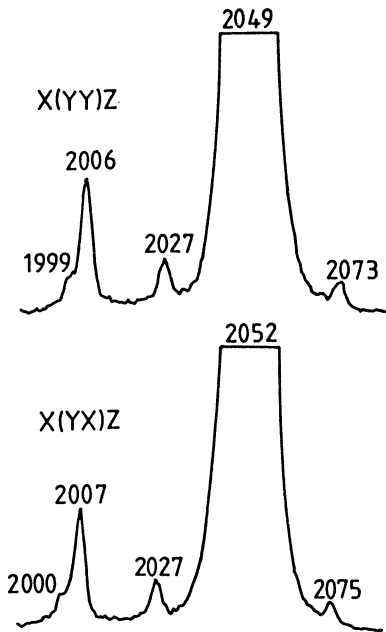
Fig. 5. Weak spectral features near the v_1 internal mode peak, measured at room temperature with 4 cm^{-1} resolution. These are due to isotopes and multiphonon scattering.

Table 4. Observed frequencies of internal modes of isotopes of RbSCN

Frequencies are accurate to ± 2 cm^{-1}. The v_3 mode of N^{13}CS is not resolvable in the room temperature spectrum but can be seen clearly at low temperature

Frequency	Symmetry	N^{13}CS$^-$	^{15}NCS$^-$	NC^{34}S
v_1	A_g	2006	2027	—
	B_{1g}	2007	2027	—
v_3	A_g/B_{1g}	(742)	737	

Several smaller peaks were found to occur at frequencies close to the v_1 and v_3 modes. Those near v_1 are shown in Fig. 5. Most of these have been attributed to the isotopes of S, C and N present. Assuming that the substitution of an isotope does not change the crystal potential significantly, we can predict the expected frequencies of vibrations of the different isotopes. A simple 'valence force' potential (Herzberg 1945) was assumed. This allowed the observed peaks to be matched with particular isotopes, as shown in Table 4.

The other small peaks found near the v_1 mode cannot be explained in terms of isotopes. These peaks were found to drop rapidly in intensity as the temperature decreases, and so are assumed to be due to multiphonon processes involving internal modes and lattice modes. The lattice mode phonons are most likely not at $k = 0$, but arise from critical points in the
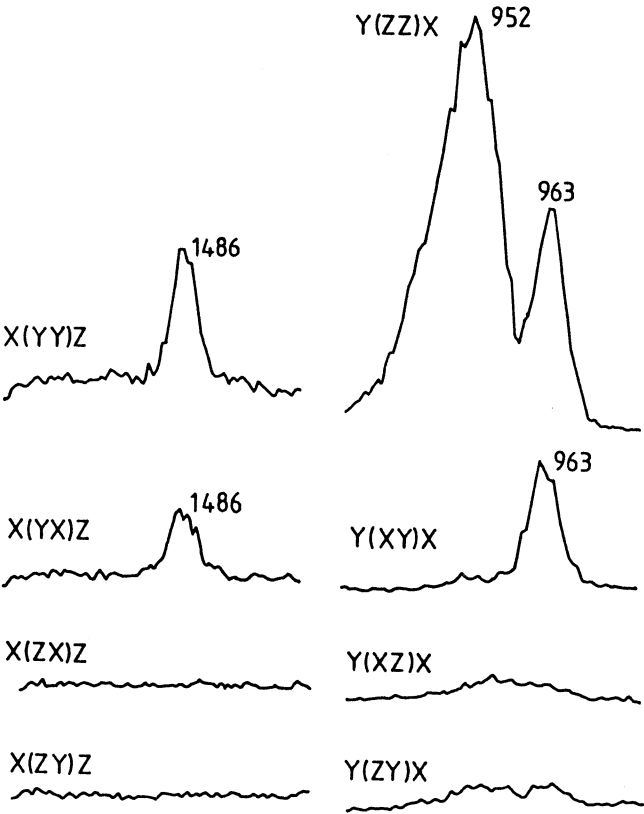
Fig. 6. Two-phonon overtone and combination modes of RbSCN at room temperature, measured with $4\ cm^{-1}$ resolution.

Table 5. Classification of two-phonon modes in RbSCN

All frequencies are accurate to $\pm 2\ cm^{-1}$

Symmetry	Frequency (cm^{-1})	Assignment
A_g	952	$2\nu_2(B_{2g}); 2\nu_2(B_{3g})$
	963	$2\nu_2(A_g); 2\nu_2(B_{1g})$
	1486	$2\nu_3(A_g); 2\nu_3(B_{1g})$
B_{1g}	963	$\nu_2(A_g)+\nu_2(B_{1g})$
	1486	$\nu_3(A_g)+\nu_3(B_{1g})$

Brillouin zone. The peak at $1999\ cm^{-1}$ (A_g) is probably of the type ν_1-L_{cp} where the critical point frequency is $50\ cm^{-1}$, assuming negligible dispersion of the internal mode. The peak at $2000\ cm^{-1}$ (B_{1g}) would correspond to a critical point frequency of $52\ cm^{-1}$. The $2073\ cm^{-1}$ (A_g) and $2075\ cm^{-1}$ (B_{1g}) peaks are believed to be of the type $\nu_1+L_{cp}-L'_{cp}$ since they lose intensity too rapidly to be due simply to a sum of modes.

Internal ± Internal Modes

Fig. 6 shows the internal ± combination and overtone modes for ν_2 and ν_3. The presence of overtone modes for ν_1 was not checked. These peaks were

found to weaken in intensity as the temperature was lowered, as expected for two-phonon processes. From the position of these lines we can assign them tentatively as in Table 5. The results obtained here differ slightly from those of Ti et $al.$ (1976) in that the two-phonon modes were not seen in the B_{2g} orientation.

The ν_2 combination and overtone modes are almost as intense as the fundamentals and this is most likely due to anharmonic effects.

4. Conclusions

The observation of the low temperature Raman spectrum of RbSCN has revealed several new features. Previous interpretations (Ti et $al.$ 1976) of the room temperature spectrum are not consistent with the results obtained in this study, and so several peaks have been reclassified. No multiphonon modes were observed in the external spectrum, and a new peak, believed to be an external mode, has been identified in the B_{2g} orientation.

In view of the assumed isomorphism between RbSCN and KSCN, a new external mode is predicted between 70 and 90 cm^{-1} in the KSCN spectrum under B_{1g} symmetry, and some of the peaks of the KSCN spectrum have been reassigned.

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