

# Localised vibrations due to pairs and triplet clusters of the $\text{NO}_2^-$ ions in KI single crystals

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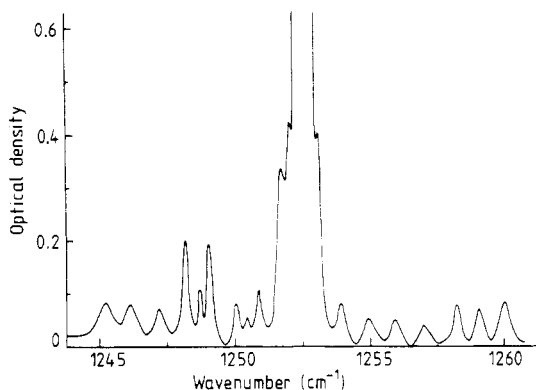
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**Abstract.** We report here high-resolution infrared measurements at 1.7 K on KI single crystals doped with  $\text{NO}_2^-$  ions. At very low concentration of  $\sim 10^{17}$   $\text{NO}_2^-$  ions  $\text{cm}^{-3}$ , we have observed a multiplet structure with the antisymmetric stretching vibration  $\nu_3$  of the  $\text{NO}_2^-$  ion arising due to tunnelling motion of the ion among the twelve equilibrium potential wells in the KI lattice. At relatively higher concentrations of the  $\text{NO}_2^-$  impurities ( $10^{19}$  ions  $\text{cm}^{-3}$ ), several extra sharp and distinct bands have been observed in the region of the antisymmetric stretching vibration of the  $\text{NO}_2^-$  ion in KI at 1.7 K. This structure has been interpreted in terms of mutual interaction effects between the transition dipole moments during the  $\nu_3$  vibrations of the nearby nitrite ions in pairs and triplet clusters. Several ion pairs and triplet clusters were considered and their vibrational spectrum has been calculated using a model of coupled harmonic oscillators. From these studies, we have obtained the magnitude of the transition dipole moment  $\mu_t = 0.248$  D during the  $\nu_3$  vibration of the  $\text{NO}_2^-$  ion doped in KI.

## 1. Introduction

Many atomic or molecular impurities substituted in crystals are known to produce isolated dipoles. Such impurities may have intrinsic dipole moments, i.e. the defect–host combination itself produces an effective dipole moment. Such types of impurities are known as paraelectric defects and are characterised by their dipole orientations in crystals. In some defect–host combinations, the defect ion may lie on the normal lattice site but occupy a new equilibrium position away from the lattice site. These are called off-centred defects. The paraelectric defects may perform tunnelling motion among the various equivalent equilibrium positions in the host lattice. They may also give rise to localised vibrations due to mutually interacting ions for large impurity concentrations.

The  $\text{NO}_2^-$  ion is a dipolar ion. It replaces an  $\text{I}^-$  ion when substituted in the KI lattice with its dipole moment along the [110] direction (Evans and Fitchen 1970). Hence the  $\text{NO}_2^-$  ion has twelve equilibrium orientations in KI. The  $\text{NO}_2^-$  ion performs tunnelling motion among the twelve equilibrium orientations. We have observed a multiplet structure with at least six components with the antisymmetric stretching vibration ( $\nu_3$ ) of the  $\text{NO}_2^-$  ion in KI for low impurity concentrations ( $\sim 10^{17}$  ions  $\text{cm}^{-3}$ ) at 1.7 K in the high-resolution infrared studies. This structure arises due to tunnelling motion of the  $\text{NO}_2^-$  ions (Khatri and Verma 1983a). In this paper we have studied the effects of mutual interactions between the  $\text{NO}_2^-$  ions in KI for large concentrations ( $\sim 10^{18}$  to  $10^{19}$  ions  $\text{cm}^{-3}$ ) of the  $\text{NO}_2^-$  ions in KI.



**Figure 1.** Infrared absorption of a 1 mm thick KI crystal containing approximately  $10^{19}$   $\text{NO}_2^-$  ions  $\text{cm}^{-3}$  at 1.7 K in the  $\nu_3$  fundamental region; spectral resolution is about  $0.05 \text{ cm}^{-1}$ .

When impurity ions are substituted in large concentrations in otherwise pure crystals, the probability of formation of clusters of impurity ions in crystals become quite appreciable. Behringer (1958) has computed the probability of finding an ion in single, double, open-triplet or closed-triplet clusters in a cubic lattice containing two types of ion randomly distributed over the sites. In such situations mutual interaction effects between the impurity ions become important. Such interactions may give rise to localised modes. Such modes due to impurity pairs have been observed previously by several workers in infrared absorption (Templeton and Clayman 1971, de Jong *et al* 1973, Ward and Clayman 1974a, b, Becker and Martin 1972, de Souza and Luty 1973), and Raman scattering experiments (Moller *et al* 1970). The intensity of pair modes shows a quadratic dependence on the concentration of impurity ions in the crystals. For polyatomic impurities such modes can be observed in combination with internal vibrations of the impurity ion in the mid- or near-infrared region where higher resolution can be obtained rather easily compared with the far-infrared region.

Earlier we have reported a preliminary study of our high-resolution infrared measurements on this system in the region of the antisymmetric stretching vibration ( $\nu_3$ ) of the  $\text{NO}_2^-$  ion doped in KI single crystals (Khatri and Verma 1983b). We have observed several temperature-independent and closely-spaced distinct bands near the  $\nu_3$  fundamental of the ion at  $1252.75 \text{ cm}^{-1}$  (figure 1). The intensities of the bands show a non-linear dependence (roughly quadratic) on the impurity concentration. These extra bands have been explained as arising due to the effects of mutual interactions between the nearby  $\text{NO}_2^-$  ions in pairs and triplet clusters. We have considered several pairs and triplet clusters of the ion which are favoured energetically and have calculated their mode frequencies on the basis of the coupled harmonic oscillator model.

## 2. Experimental procedure and results

Single crystals of potassium iodide doped with potassium nitrite were grown by pulling from the melt using the Kyropolous technique. The crystals were grown under a nitrogen atmosphere to prevent the formation of nitrate ions. The resulting crystals always contain the  $\text{NO}_2^-$  and a small concentration of  $\text{NO}_3^-$  ions. The  $\text{NO}_2^-$  and  $\text{NO}_3^-$  concentrations were determined by a spectrophotometric method. Crystals containing  $\sim 10^{18}$  to  $10^{19}$  ions  $\text{cm}^{-3}$  and 1 mm thick were used in our experiments.

The high-resolution infrared absorption measurements were made on a Perkin-Elmer Ebert-14 spectrometer equipped with a helium-cooled copper-doped germanium bolometer as a detector. The infrared radiation was chopped mechanically and then focused at a sample held in a liquid-helium cryostat after the exit slit of the monochromator. Thus the use of monochromatic radiation reduces the infrared heating of the sample. Low temperatures below 4.2 K were obtained using an immersion cryostat by pumping on the helium gas. Temperature-dependent measurements above 5 K were made with the help of a variable-temperature conduction cryostat of conventional design. The low-temperature measurements were made with an experimental resolution of  $0.05 \text{ cm}^{-1}$ . The position of spectral lines was calibrated with respect to the known water vapour lines.

Here we shall briefly describe the experimental results which have been reported earlier (Khatri and Verma 1983b). The antisymmetric stretching vibration  $\nu_3$  of the  $\text{NO}_2^-$  ion in KI at 1.7 K shows a splitting of this band into six components due to tunnelling of the ion among equivalent potential wells when the concentration of the ions is small ( $\sim 10^{17} \text{ ions cm}^{-3}$ ). The relative intensities of these components were temperature dependent and have been reported elsewhere (Khatri and Verma 1983a). When samples with relatively higher concentrations of the  $\text{NO}_2^-$  ions in KI ( $\sim 10^{18}$  to  $10^{19} \text{ ions cm}^{-3}$ ) were used, we observed several temperature independent and closely-spaced bands near the  $\nu_3$  fundamental vibration of the  $^{14}\text{NO}_2^-$  ion at  $1252.75 \text{ cm}^{-1}$  at 1.7 K while the structure due to tunnelling was completely obscured. The bands on the low-frequency side of the  $\nu_3$  vibration are much stronger than those on the high-frequency side. Temperature-dependent measurements between 1.7 and 10 K show that the relative intensities of these bands are temperature independent. Different crystals containing varying concentrations of the  $\text{NO}_2^-$  ions from  $\sim 10^{18}$  to  $10^{19} \text{ ions cm}^{-3}$  were used to check the concentration dependence of these features. All the results were reproducible. The intensities of these bands relative to the intensity of the  $\nu_3$  fundamental band at  $1227 \text{ cm}^{-1}$  due to the  $^{15}\text{NO}_2^-$  ions in natural abundance in the same crystal showed a non-linear, roughly quadratic, dependence on the  $\text{NO}_2^-$  ion concentration. No structure was observed near the  $\nu_3$  band due to the  $^{15}\text{NO}_2^-$  isotropic species in KI although the concentration of the  $^{15}\text{NO}_2^-$  impurity was enough to give a strong  $\nu_3$  band. The measurements were made with the instrumental resolution of  $\sim 0.05 \text{ cm}^{-1}$ . Figure 1 shows the spectrum of the  $^{14}\text{NO}_2^-$  ion in KI in the  $\nu_3$  fundamental region at 1.7 K.

### 3. Discussion

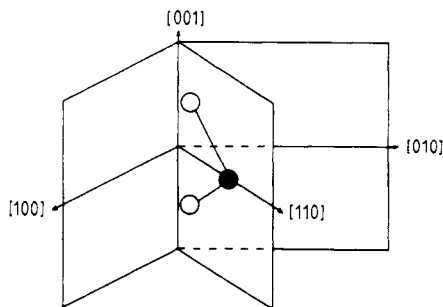
Narayanamurti *et al* (1966) reported some bands near the  $\nu_3$  band of the  $\text{NO}_2^-$  ion in KI for fairly high concentration of  $\sim 10^{18} \text{ ions cm}^{-3}$ . They interpreted the origin of these bands as due to either free rotation or libration of the ion which is incorrect from our findings. At such high concentrations used by Narayanamurti *et al* (1966) mutual interactions between the ions in the KI lattice cannot be neglected. We have made observations in KI crystals containing  $\sim 10^{18}$  to  $10^{19} \text{ ions cm}^{-3}$ , and have observed several distinct features on both the higher and lower side of the  $\nu_3$  band of the  $^{14}\text{NO}_2^-$  ions. As mentioned in the experimental section, we did not observe any structure near the  $\nu_3$  band of the  $^{15}\text{NO}_2^-$  species in KI, though the  $\nu_3$  ( $^{15}\text{NO}_2^-$ ) band was quite strong in some of the samples. Therefore the possibility of the structure near the  $\nu_3$  band of the  $^{14}\text{NO}_2^-$  ions arising from site effects can be ruled out (Decius *et al* 1965). Moreover, the concentration of the  $^{15}\text{NO}_2^-$  ions in natural abundance is much smaller than that of the

$^{14}\text{NO}_2^-$  ions thereby making the possibility of finding nearby  $^{15}\text{NO}_2^-$  ions in the KI lattice very small. Therefore the dynamical coupling between the  $^{15}\text{NO}_2^-$  ions would be negligible which explains the absence of structure near the  $\nu_3$  band of the  $^{15}\text{NO}_2^-$  ions.

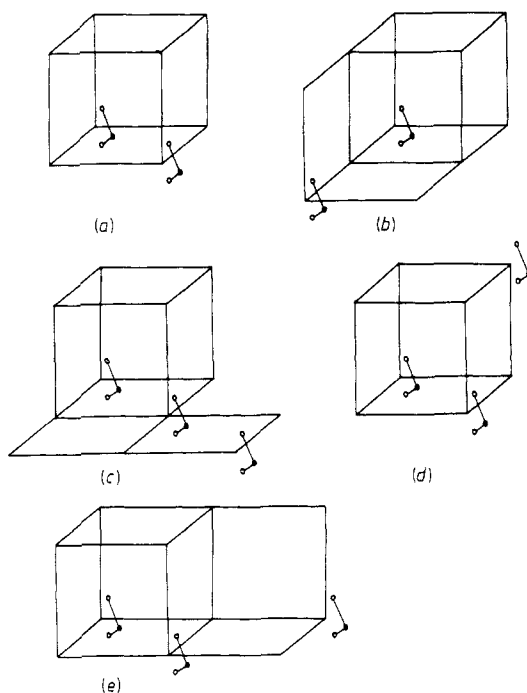
The non-linear, roughly quadratic, dependence of the intensities of these satellite bands on the concentration of the  $^{14}\text{NO}_2^-$  ions suggests that these bands arise from dynamical coupling between the ions in pairs and triplet clusters. At such concentrations the probability of formation of pairs and triplet clusters of the  $\text{NO}_2^-$  ions in KI becomes appreciable (Behringer 1958) and mutual interactions become important. We have explained the origin of the satellites observed near the  $\nu_3$  band in terms of dynamical coupling between nearby ions. The coupling between the two localised oscillators is provided by the interaction between the transition dipole moments during the  $\nu_3$  vibration of the  $\text{NO}_2^-$  ions in KI. We have considered nearest-neighbour pairs, second-nearest-neighbour pairs, open triplets, closed triplets and another type of triplets which will be referred to as triplet clusters of the third type.

The  $\text{NO}_2^-$  ion is a bent dipolar molecule of  $C_{2v}$  point group symmetry. In KI it replaces the  $\text{I}^-$  ion with its dipolar axis (which is also its  $C_2$  axis) along the  $[110]$  direction and  $\text{O}-\text{O}$  axis along the  $[001]$  direction (Evans and Fitchen 1970). Owing to its large dipole moment of 0.97 D (Sack and Moriarty 1965) in KI it takes an off-centred position displaced along the  $[110]$  direction (figure 2). During the antisymmetric stretching vibration ( $\nu_3$ ) of the  $\text{NO}_2^-$  ion in KI its transition dipole moment lies along its  $\text{O}-\text{O}$  axis, i.e. the  $[001]$  direction in KI. The  $\text{NO}_2^-$  ion is displaced from the normal lattice site in the direction of its  $C_2$  axis in KI along the  $\langle 110 \rangle$  directions. The displacement is  $2d = 0.346 \text{ \AA}$  (Khatri and Verma 1983a). Therefore the centre of mass of one of the  $\text{NO}_2^-$  ions in the nearest-neighbour pairs may be near the origin, which is taken as one of the normal anion sites, and the centre of mass of the other ion may be near the  $(a/2, a/2, 0)$  position in the lattice (figure 3(a)) where  $a = 6.994 \text{ \AA}$  is the lattice constant at 1.7 K, taken from *Landolt-Börnstein* (1973). In the case of second-nearest-neighbour pairs, the position of one of the ions will be near the origin and the other ion will be near  $(a, 0, 0)$  (figure 3(b)). The position of the ion in the open triplets will be near the origin,  $(a/2, a/2, 0)$  and near  $(a, a, 0)$  (figure 3(c)); in the closed triplets they will be near  $(0, 0, 0)$ ,  $(a/2, a/2, 0)$  and  $(0, a/2, a/2)$  (figure 3(d)) and in the triplet cluster of the third type they will be near  $(0, 0, 0)$ ,  $(a/2, a/2, 0)$  and  $(0, a, 0)$  (figure 3(e)).

Since the dipole interaction varies as  $R^{-3}$ , the interaction effect will be negligible for dipoles situated at larger distance from each other. Therefore, we have considered only the pairs and triplet clusters. Moreover, for large distances ( $R \gg a$ ), there should be a



**Figure 2.** Equilibrium orientation of the off-centre  $\text{NO}_2^-$  ion in KI at low temperatures. The  $\text{NO}_2^-$  ion is displaced towards the  $\text{I}^-$  ion nearest to the nitrogen atom.



**Figure 3.** Different types of pair and triplet clusters of the  $\text{NO}_2^-$  ion in KI single crystal. (a) nearest-neighbour pair, (b) second-nearest-neighbour pair, (c) open-triplet cluster, (d) closed-triplet cluster and (e) triplet cluster of third type.

correction factor in the dipole-dipole interaction but it is close to unity for smaller distances (de Souza and Luty 1973).

The interaction between the permanent dipoles of the ions will determine the relative orientations of the  $\text{NO}_2^-$  dipoles. Because of the twelve equilibrium orientations possible for the  $\text{NO}_2^-$  ion in KI lattice, there will be various configurations of pairs and triplet clusters. For pairs there are  $12^2 = 144$  possible possibilities and for triplet clusters there are  $12^3 = 1728$  possibilities and hence for dipole-dipole interactions. But the number of distinct possibilities is not so large. There will be positive and negative interaction energies between permanent dipoles. Because of the finite possibility of tunnelling (Khatri and Verma 1983a) the ions will align preferentially in those configurations in which the pair or triplet cluster will have large negative interaction energy between permanent dipoles. The pairs and triplet clusters with positive interaction energies are very unlikely energetically and their population would be negligible. We have therefore considered the mutual interaction between the transition dipole moments of only those pairs and triplets which have large negative interaction energies between permanent dipoles. We have calculated the interaction energies for permanent dipole moments of the  $\text{NO}_2^-$  ions in pairs using equation (1) and for the triplet clusters using equation (2)

$$W_{\text{pair}} = \frac{R_{ij}^2(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) - 3(\boldsymbol{\mu}_i \cdot \mathbf{R}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{R}_{ij})}{R_{ij}^5} \quad (1)$$

$$W_{\text{trip}} = \sum_{\substack{i,j=1 \\ j>i}}^3 \frac{R_{ij}^2(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) - 3(\boldsymbol{\mu}_i \cdot \mathbf{R}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{R}_{ij})}{R_{ij}^5} \quad (2)$$

**Table 1.** Interaction energies of permanent dipoles and transition dipoles of the NO<sub>2</sub> ions in nearest-neighbour pairs. The types of pairs giving the same interaction energy are given in the last column. The pairs are characterised by the directions of the permanent dipoles near (0, 0, 0) and (a/2, a/2, 0) positions.

Interaction energy (cm <sup>-1</sup> ) (permanent dipoles)	Interaction energy (cm <sup>-1</sup> ) (transition dipoles)	Orientation of permanent dipole moments in the nearest-neighbour pairs
-15.37	±0.20	[1̄10] [011], [1̄10] [01̄1], [1̄10] [101], [1̄10] [10̄1], [1̄10] [1̄10], [1̄10] [1̄10], [01̄1] [1̄10], [01̄1] [1̄10]
-34.16	±0.24	[1̄10] [1̄10], [1̄10] [1̄10], [1̄10] [01̄1], [1̄10] [01̄1], [1̄10] [01̄1], [101] [110], [10̄1] [110], [011] [110], [01̄1], [110]
-44.46	±0.30	[110] [101], [110] [10̄1], [110] [011], [110] [01̄1], [101] [1̄10], [1̄10] [1̄10], [01̄1] [1̄10], [01̄1] [1̄10]
-23.52	±0.33	[1̄10] [1̄10], [1̄10] [1̄10], [1̄10] [01̄1], [1̄10] [01̄1], [101] [1̄10], [10̄1] [1̄10], [01̄1] [110], [01̄1] [1̄10]
-29.03	-1.22	[101] [10̄1], [10̄1] [101], [1̄10] [1̄10], [1̄10] [1̄10], [1̄10] [1̄10], [01̄1] [01̄1], [01̄1] [01̄1], [01̄1] [01̄1]
-17.64	+2.19	[101] [1̄10], [10̄1] [1̄10], [011] [01̄1], [01̄1] [01̄1]
-48.21	±3.67	[101] [01̄1], [10̄1] [011], [1̄10] [01̄1], [1̄10] [01̄1], [011] [10̄1], [01̄1] [101], [01̄1] [101], [01̄1] [1̄10], [01̄1] [1̄10]
-38.27	+2.48	[1̄10] [1̄10], [1̄10] [1̄10]
-78.67	+2.55	[110] [110], [1̄10] [1̄10]

**Table 2.** Interaction energies of permanent dipoles and transition dipoles of the NO<sub>2</sub><sup>-</sup> ions in open-triplet clusters. Types of the triplet cluster giving the same interaction energy are given in the last column. The triplet clusters are characterised by the directions of the permanent dipoles near (0, 0, 0) (a/2, a/2, 0) and (a, a, 0) positions. Each triplet cluster gives four interaction energies between transition dipole moments as given in this table.

Interaction energy (cm <sup>-1</sup> ) (permanent dipoles)	Interaction energy (cm <sup>-1</sup> ) (transition dipoles)				Orientation of permanent dipole moments in the open-triplet clusters
-95.21	-7.50	0.16	7.18	0.16	[01̄1] [1̄10] [01̄1], [01̄1] [1̄10] [01̄1], [01̄1] [101] [01̄1], [011] [10̄1] [011], [10̄1] [01̄1] [1̄10], [1̄10] [01̄1] [1̄10], [10̄1] [01̄1] [101], [101] [01̄1] [101]
-97.90	-3.39	-3.95	3.36	3.98	[011] [1̄10] [1̄10], [01̄1] [1̄10] [1̄10], [1̄10] [01̄1] [1̄10], [1̄10] [01̄1] [1̄10], [1̄10] [01̄1] [1̄10], [110] [10̄1] [011], [110] [101] [01̄1]
-127.95	2.87	2.24	-2.83	-2.27	[01̄1] [1̄10] [1̄10], [01̄1] [1̄10] [1̄10], [1̄10] [01̄1] [1̄10], [1̄10] [01̄1] [1̄10], [1̄10] [01̄1] [1̄10], [101] [110] [01̄1], [110] [110] [011], [110] [110] [10̄1], [110] [110] [101]
-117.00	2.3	-2.78	-2.33	2.81	[01̄1] [110] [110], [011] [110] [110], [10̄1] [110] [110], [101] [110] [110], [1̄10] [1̄10] [01̄1], [1̄10] [1̄10] [01̄1], [1̄10] [1̄10] [1̄10], [1̄10] [1̄10] [1̄10]
-166.31	5.42	-0.32	-4.78	-0.32	[1̄10] [1̄10] [1̄10], [110] [110] [110]

**Table 3.** Observed and calculated satellite bands due to nearby interacting transition dipoles during  $\nu_3$  vibration of the  $\text{NO}_2^-$  ions in KI on the low-frequency side of the  $\nu_3$  band.

Observed ( $\text{cm}^{-1}$ )	Calculated ( $\text{cm}^{-1}$ )	Corresponding interaction energy ( $\text{cm}^{-1}$ )		Type of cluster	
		Transition dipoles	Permanent dipoles		
1252.06	1252.09	-0.66	-109.04	triplet (3rd type)	
1251.78	1251.94	-0.81	-109.04	triplet (3rd type)	
	1251.71	-1.04	-110.53	triplet (3rd type)	
	1251.56	-1.19	-110.53	triplet (3rd type)	
	1251.53	-1.22	-29.03	NN pair <sup>†</sup>	
	1251.00	-1.75	-13.68	2nd NN pair	
1250.97	1250.97	-1.78	-110.31	closed triplet	
1250.56	1250.48	-2.27	-127.95	open triplet	
	1250.42	-2.33	-117.00	open triplet	
	1250.51	-2.24	-102.04	triplet (3rd type)	
	1250.45	-2.30	-107.29	triplet (3rd type)	
1250.12	1250.10	-2.65	-102.04	triplet (3rd type)	
	1250.29	-2.46	-102.04	triplet (3rd type)	
1249.14	1249.08	-3.67	-48.21	NN pair	
	1249.08	-3.67	-144.64	closed triplet	
1248.76	1248.80	-3.95	-97.90	open triplet	
	1248.83	-3.92	-110.53	triplet (3rd type)	
1248.25	1247.97	-4.78	-166.31	open triplet	
	1248.54	-4.21	-126.84	closed triplet	
	1247.95	-4.80	-103.67	triplet (3rd type)	
	1248.45	-4.32	-109.04	triplet (3rd type)	
	1247.19	-5.56	-110.31	closed triplet	
1247.23					
1246.15					
1245.25	1245.25	-7.5	-95.21	open triplet	
	1252.64	-0.11	-8.41	2nd NN pair	
	1252.55	-0.20	-15.37	NN pair	
	1252.51	-0.24	-34.16	NN pair	
	1252.45	-0.30	-44.46	NN pair	
	1252.42	-0.33	-23.53	NN pair	
	1252.43	-0.32	-166.31	open triplet	
	—	1251.26	-1.49	-103.67	triplet (3rd type)
	—	1249.92	-2.83	-127.95	open triplet
	—	1249.97	-2.78	-117.00	open triplet
—	1249.95	-2.80	-107.29	triplet (3rd type)	
—	1249.36	-3.39	-97.90	open triplet	
—	1249.62	-3.13	-126.84	closed triplet	

<sup>†</sup> NN pairs refer to nearest neighbour.

Here  $\mu_i$  and  $\mu_j$  are the two permanent dipoles at lattice sites  $i$  and  $j$  and  $R_{ij}$  is the distance between them. The permanent dipolar interaction energies are given in tables 1–4 along with the interaction energies between the transition dipole moments of the ions in those configurations.

The  $\nu_3$  vibration of the ion is equivalent to a localised harmonic oscillator. In pairs, two such harmonic oscillators are coupled to each other. The equation of motion for such a coupled harmonic oscillator is given by

$$H = \frac{1}{2}m(\dot{q}_i^2 + \dot{q}_j^2 + q_i^2\omega^2 + q_j^2\omega^2) + Bq_iq_j. \quad (3)$$

**Table 4.** Observed and calculated satellite bands due to nearby interacting transition dipoles  $\nu_3$  vibration of the  $\text{NO}_2^-$  ions in KI on the high-frequency side of the  $\nu_3$  bands.

Observed ( $\text{cm}^{-1}$ )	Calculated ( $\text{cm}^{-1}$ )	Corresponding interaction energy ( $\text{cm}^{-1}$ )		Type of cluster
		Transition dipoles	Permanent dipoles	
1253.01	1252.95	0.20	-15.37	NN pair
	1252.99	0.24	-34.16	NN pair
	1253.05	0.30	-44.46	NN pair
	1252.91	0.16	-95.21	open triplet
1254.00	1253.94	1.19	-110.31	closed triplet
1255.06	1255.23	2.48	-38.27	NN pair
	1255.30	2.55	-78.67	NN pair
	1254.94	2.19	-17.64	NN pair
	1254.99	2.24	-127.95	open triplet
	1255.05	2.30	-117.00	open triplet
	1254.89	2.14	-107.29	triplet (3rd type)
1256.07	1256.11	3.36	-97.90	open triplet
1257.16				
1258.97	1258.90	6.15	-110.31	closed triplet
	1259.34	6.59	-103.67	triplet (3rd type)
	1258.89	6.14	-110.53	triplet (3rd type)
1259.92	1259.93	7.18	-95.21	open triplet
—	1252.86	0.11	-8.41	2nd NN pair
—	1253.65	0.90	-20.66	2nd NN pair
	1253.65	0.90	-6.92	2nd NN pair
—	1255.62	2.87	-127.95	open triplet
	1255.56	2.81	117.00	open triplet
—	1255.61	2.86	-102.04	triplet (3rd type)
	1255.71	2.96	-107.29	triplet (3rd type)
—	1256.42	3.67	-48.21	NN pair
	1256.36	3.61	-126.84	closed triplet
	1256.48	3.73	-126.84	closed triplet
—	1258.17	5.42	-166.31	open triplet
—	1258.51	5.76	-109.04	triplet (3rd type)
—	1263.76	11.01†	-144.64	closed triplet

† Observed by Narayanamurti *et al* (1966) at  $1265 \text{ cm}^{-1}$ .

Here  $m$  is the mass of the  $\text{NO}_2^-$  ion,  $\omega$  is the frequency of the  $\nu_3$  vibration,  $q_i$  and  $q_j$  are the normal coordinates of the two  $\text{NO}_2^-$  ions during their  $\nu_3$  vibrations and  $B$  is the coupling term which can be written in terms of the dipole-dipole interaction as

$$Bq_i q_j = \frac{\mu_i^2}{r_{ij}^3} [\hat{\mu}_i \cdot \hat{\mu}_j - 3(\hat{\mu}_i \cdot \hat{r}_{ij})(\hat{\mu}_j \cdot \hat{r}_{ij})] \quad (4)$$

where  $\mu_i$  and  $\mu_j$  are the transition dipole moments of the two ions,  $|r_{ij}|$  is the distance between the centres of two dipoles and  $\mu_i^2 = |\mu_i| \cdot |\mu_j|$ , since  $|\mu_i| = |\mu_j| = \mu$ ,  $\hat{\mu}_i$ ,  $\hat{\mu}_j$  and  $\hat{r}_{ij}$  are the unit vectors along  $\mu_i$ ,  $\mu_j$  and  $r_{ij}$  respectively. A triplet cluster is equivalent to three pairs of coupled harmonic oscillators. The coupling term  $C$  is the sum of the interactions of transition dipoles of the three pairs which can be written as

$$C = \mu_t^2 \sum_{\substack{i,j=1 \\ j>i}}^3 \frac{\hat{\mu}_{ti} \cdot \hat{\mu}_{tj} - 3(\hat{\mu}_{ti} \cdot \hat{r}_{ij})(\hat{\mu}_{tj} \cdot \hat{r}_{ij})}{r_{ij}^3} \quad (5)$$

The distances between the centres of two dipoles can be calculated from the coordinates of the centre of mass of the two ions which in turn can be obtained from the displacement ( $2d = 0.346 \text{ \AA}$ ) of the ion in KI and the direction of displacement.

We have calculated the interaction energies between the transition dipole moments using expressions (4) and (5) for all possible orientations of the  $\text{NO}_2^-$  ions having negative interaction energies between the permanent dipoles. For a particular pair, for instance the nearest-neighbour pair, whose  $C_2$  axes are along the [110] and [101] directions;  $\mu_t$  can be in either the [001] or  $[00\bar{1}]$  direction for the first ion and in the [010] or  $[0\bar{1}0]$  direction for the second ion. Therefore there are  $2^2 = 4$  possibilities for such interactions which can be schematically represented as (1)  $\uparrow \uparrow$ , (2)  $\downarrow \downarrow$ , (3)  $\uparrow \downarrow$  and (4)  $\downarrow \uparrow$ . These can be grouped into two sets depending on the values of the interaction energies between the induced dipole moments (transition dipole)  $\mu_t$  of the ions. The first and second configurations are identical and the third and fourth configurations are identical as far as the interactions between the induced dipoles are concerned. Therefore there are only two distinct possibilities for interaction between the induced dipole moments of the  $\text{NO}_2^-$  ions in a pair. To illustrate this point, we have given the interaction energies between the transition dipole moments and the corresponding interaction energies between the permanent dipole moments in table 1 for the nearest-neighbour pairs. The orientations of the  $C_2$  axes of the  $\text{NO}_2^-$  ions in the pairs are also given in table 1. Similar calculations have also been done for the second-nearest-neighbour pairs but they are not shown separately and are included in tables 3 and 4. For the pairs whose transition dipoles  $\mu_t$  are along the same direction, for instance pairs with their  $C_2$  axes along the [110] and  $[1\bar{1}0]$  directions, the configuration in which the induced dipole moments are in opposite phase will not show any infrared absorption because of the total cancellation of the varying dipole moments. They may, however, show up in Raman scattering due to the changing polarisability of the system. There are no such possibilities for triplet clusters, for which there are  $2^3 = 8$  possibilities for interaction between the induced dipoles for the same reasons as mentioned above. These eight possibilities can be schematically represented as (1)  $\uparrow \uparrow \uparrow$ , (2)  $\downarrow \downarrow \downarrow$ , (3)  $\uparrow \uparrow \downarrow$ , (4)  $\downarrow \downarrow \uparrow$ , (5)  $\uparrow \downarrow \uparrow$ , (6)  $\downarrow \uparrow \downarrow$ , (7)  $\uparrow \downarrow \downarrow$  and (8)  $\downarrow \uparrow \uparrow$ . These can be grouped into four sets depending on the values of the interaction energies between the three induced dipole moments. The first and second configurations are identical, the third and fourth are identical, the fifth and sixth are identical and the seventh and eight configurations are identical as far as the interactions between the induced dipole moments are concerned. Therefore there are only four distinct possibilities for the interaction between the induced dipole moments of the  $\text{NO}_2^-$  ions in a triplet cluster. We have calculated the interaction energies and have given four distinct possibilities in table 2 for the induced dipolar interactions corresponding to permanent dipolar interactions for the  $\text{NO}_2^-$  ions in the open-triplet clusters. The orientation of  $C_2$  axes of the  $\text{NO}_2^-$  ions in the open-triplet clusters are also given in table 2. Similar interaction energies for other types of triplet clusters are not shown separately but are included in tables 3 and 4. Interactions with negative sign give satellite bands on the low-frequency side of the  $\nu_3$  band and those with a positive sign give satellite bands on the higher-frequency side. Here the transition dipole moment  $\mu_t$  is the adjustable parameter. We have calculated the interaction energies for various values of  $\mu_t$ , but the value of  $\mu_t = 0.248 \text{ D}$  gave best agreement with the experimental

observations. Since there are numerous possibilities of interaction energies, several calculated line positions correspond to a single observed line. We have given the calculated and observed lines in tables 3 and 4. The agreement between the calculated and observed band positions is quite satisfactory. The band calculated at  $1263.76\text{ cm}^{-1}$  ( $11.01\text{ cm}^{-1}$  higher satellite) was not observed by us since our observations did not extend beyond  $1261\text{ cm}^{-1}$ . But Narayanamurti *et al* (1966) have reported a line at  $1265\text{ cm}^{-1}$  which may correspond to our calculated value.

For comparison purposes we have calculated the induced dipole moments for the  $\text{NO}_3^-$  ions in  $\text{KNO}_3$  and  $\text{CO}_3^{2-}$  ions in  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$  during the out-of-plane bending vibration of these ions. Decius (1955) had also calculated the dipole derivatives for these systems. He considered the coupling between the nearest-neighbour  $\text{NO}_3^-$  ions in  $\text{KNO}_3$  and  $\text{CO}_3^{2-}$  ions in  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$  during the out-of-plane bending modes of these ions. He considered the interaction between the induced dipole moments of the ions in the plane of the ions. From these data the induced dipole moment of the  $\text{NO}_3^-$  ion in  $\text{KNO}_3$  comes out to be 1.43 D while for the  $\text{CO}_3^{2-}$  ions in  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{BaCO}_3$ , the induced dipole moments come out to be 1.48, 1.69 and 1.90 D respectively. For the  $\text{NO}_2^-$  ion in KI it is 0.248 D which is small compared with those obtained for the  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  ions in the above-mentioned systems. The small value of the transition dipole (induced dipole) moment for the  $\text{NO}_2^-$  ion in KI can be correlated with the weaker intensity of the  $\nu_3$  fundamental vibration of the  $\text{NO}_2^-$  ion compared with the other ions quoted above. The small value of  $\mu_t$  for the  $\text{NO}_2^-$  ions in KI would also provide rather weaker coupling between nearby ions in pairs and triplet clusters, giving rise to closely-spaced lines.

#### 4. Conclusions

In this study we have seen the effect of increasing the concentration of the  $\text{NO}_2^-$  ions in KI. Many sharp and distinct bands appear near the  $\nu_3$  fundamental of the  $\text{NO}_2^-$  ion in KI. The origin of these bands has been explained satisfactorily on the basis of a model of coupled harmonic oscillators where the coupling is brought about by the interaction between the transition dipole moments of the ions during their  $\nu_3$  vibration. From this study we could estimate the magnitude of the transition dipole moment of the  $\text{NO}_2^-$  ion during its  $\nu_3$  vibration to be  $\mu_t = 0.248\text{ D}$ .

In earlier studies on the KI: $\text{NO}_2^-$  system with large concentrations of the  $\text{NO}_2^-$  ions in KI ( $\sim 10^{19}$  ions  $\text{cm}^{-3}$ ) Narayanamurti *et al* (1966) were not able to observe these bands. However, they observed few broad bands at higher frequencies but could not understand their origin satisfactorily. From the present study, it is evident that the closely-spaced and well-resolved bands observed by us arise from the mutually interacting ions in pairs and triplet clusters. From this study the importance of high-resolution work is evident for a proper understanding of the often observed broad bands and complicated structures near fundamental vibrations of molecular ions in solids.

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