that step 6 is a fast equilibrium, the observed rate constant is $k_{obsd} = K_6k_7$. The transition state of step 7 is similar to that postulated for the first-order oxygen exchange process, but with HCO_3^- as the leaving group instead of water. The rate constant k_7 is thus expected to be somewhat smaller than k_1, the oxygen exchange constant, which is about 50 s^{-1} at 0 °C. Although the numbers are consistent with the proposed mechanism, further discussion must await the results of studies of related systems which are in progress.

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Natural Solid State Optical Activity of Tris(ethylenediamine)metal(II) Nitrates. 4. Optical Activity of Zn(en)$_3$(NO$_3$)$_2$ and Assignment of the Lowest Electronic Transition in NO$_3^-$

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Abstract: The nature of the lowest observed electronic transition of the nitrate ion has been reinvestigated by measurement of the orthoaxial linear dichroism (LD) and axial absorption and circular dichroism (CD) of the enantiomorphous crystals of tris(ethylenediamine)zinc(II) nitrate at temperatures from ambient to 5 K. The data support the assignment of the transition as $^1A_1''\leftarrow{}^1A_1'$ $(a_2''(\pi^*)\leftarrow a_2'(n))$. In-plane intensity in the LD spectrum is analyzed in terms of the C_{3v} symmetry of the excited state and vibronic perturbation by two ϵ modes, consistent with the vibronic structure observed at 5 K. The much stronger out-of-plane intensity is shown to be consistent with interaction between NO$_3^-$ ions to form a dimer of D_3 symmetry.

The spontaneous resolution of tris(ethylenediamine)zinc(II) ion in the hexagonal crystals of the nitrate salt provides a unique opportunity to observe the natural optical activity of the intrinsically achiral nitrate ion. The lowest electronic transition of NO$_3^-$ is observed at ca. 3.3 μm^{-1}, with an absorptivity sufficiently low to be amenable to measurement in single-crystal absorption studies.[1,2] However, with the exception of Zn(en)$_3$(NO$_3$)$_2$ and its nickel(II) and cobalt(II) analogues, no other incidence of enantiomorphous uniaxial or cubic crystals of nitrate salts are known, and the brief description of the circular dichroism of the zinc crystal in the first paper of this series[3] is the only previous mention in the literature of the natural optical activity of the NO$_3^-$ ion.

Although the 3.25 μm^{-1} band of the NO$_3^-$ ion is also observed in the absorption and CD spectra of Ni(en)$_3$(NO$_3$)$_2$[3-5] and Co(en)$_3$(NO$_3$)$_2$,[3,6] ligand field absorption and charge transfer, respectively, partially mask its contours in these crystals. However, Zn(en)$_3$(NO$_2$)$_3$, with its d^{10} metal ion and relatively high energy charge transfer, is devoid of other absorption in the 3.0–4.0 μm^{-1} region, and thus is more suitable than the other members of the series for studying the NO$_3^-$ band. The combination of linear and circular dichroism (LD and CD) measurements of this band at ambient and cryogenic temperatures is reported here along with discussion of its assignment in light of these results.

Experimental Section

Single crystals of Zn(en)$_3$(NO$_3$)$_2$ with dimensions perpendicular to the needle (c) axis of 2–4 mm were grown by slow evaporation of aqueous solutions. For axial spectra, sections (ca. 0.5 mm thick) were cut with a thread saw and polished on a water-dampened fine polishing cloth. The perpendicularity of the polished faces to the c axis was checked by observing the centering and perfection of the uniaxial interference figure from both directions. Orthoaxial (LD) spectra were measured on crystals as grown or polished to appropriate thickness. (ca. 0.3 mm).

Absorption spectra were measured using a Cary 14R spectrophotometer and associated accessories, and CD spectra were obtained on a Durrum-JASCO ORD/CD-5 circular dichroism recorder with SS-20 modification, all as previously described.[7,8]

Values of $\Delta\epsilon$ were derived from the instrumental data by the relationship $\Delta\epsilon = \phi(33cl)^{-1}$, where ϕ is the ellipticity in degrees taken from the chart, c is the molar concentration, and l is the path length (cm). (The output of the JASCO instrument with the SS-20 modification is in degrees ellipticity.) The instrument was standardized against d-10-camphorsulfonic acid, for which the most recent and reliable value for $[\theta] = [\phi]M \times 10^{-2} = 3300\Delta\epsilon$, is given by Wong[9] as +7260 deg cm^2 dmol^{-1}. Formulas used for calculation of I, D, R, and g have been given previously.[6]

Results

Spectral results in terms of the integrated band intensity (I), dipole strength (D), rotational strength (R), and anisotropy factor (g) are given in Tables I and II. The strong temperature dependence of intensity in both absorption and CD should be noted. In addition, all spectra exhibit well-developed progressions of vibronic structure at liquid helium temperature (5 K), as shown in Figures 1 and 2. Table III lists the energies

Table I. Linear Dichroism Data for the Lowest NO_3^- Transition in $Zn(en)_3(NO_3)_2$

Temp, K	$\bar{\nu}_{max}$, μm^{-1}	Polarization	ϵ	$10^5 f$	I	I_π/I_σ
300	3.25	π	10.2	24	1.73	3.6
	3.25	σ	3.7	6.7	0.48	
80	3.25	π	7.0	16	1.14	4.1
	3.25	σ	2.3	4.0	0.28	
5	3.25	π	5.6	12	0.88	4.4
	3.25	σ	1.7	2.8	0.20	

Table II. Axial Absorption and Circular Dichroism Data for the Lowest NO_3^- Transition in $Zn(en)_3(NO_3)_2$

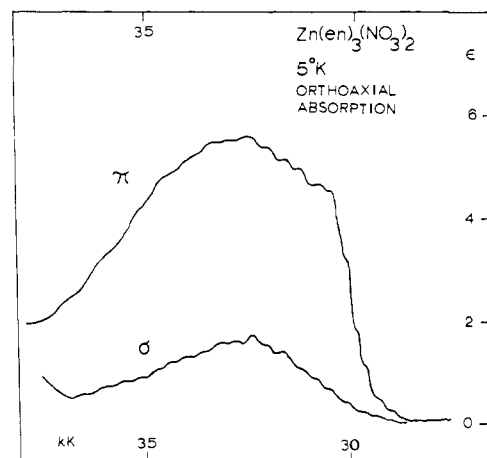| Temp, K	$\bar{\nu}_{max}$, μm^{-1} Abs	$\bar{\nu}_{max}$, μm^{-1} CD	$10^{40}D$, cgs	$10^{40}R$, cgs	g $(4R/D)$
300	3.25	3.25	43.9	0.17	0.015
80	3.25	3.25	26.0	0.10	0.016
5	3.25	3.25	18.2	0.03	0.006

Table III. Energies of Vibronic Absorption and CD Maxima for the Lowest NO_3^- Transition in $Zn(en)_3(NO_3)_2$ at 5 K (cm^{-1})

π	σ and axial	CD
28 985	29 325	30 210
29 286	29 762	30 580
29 656	30 120	31 030
29 850	30 581	31 407
30 166	30 910	31 837
30 506	31 397	32 230
30 960	31 696	32 637
31 269	32 206	33 040
31 625	32 520	33 444
32 102	33 003	33 820
32 520	33 333	34 246
33 333	33 784	34 602
34 013	34 153	35 010
34 843	34 578	35 380
35 765	34 965	
	35 360	
	35 765	
	36 166	
	36 580	

Figure 1. Linear dichroism (LD) spectra of $Zn(en)_3(NO_3)_2$ at 5 K.

of the well-resolved vibronic components obtained from the 5 K spectra. (No fine structure is observed at or above 80 K.) Because of the breadth of these vibronic components, an uncertainty of ±20 cm^{-1} is realistic in the assignment of maxima.

Discussion

Electronic Structure of NO_3^-. The nitrate ion has a symmetrical planar structure (D_{3h}) in the ground state with N-O bond lengths of 1.21 Å, in both the $Ni(en)_3(NO_3)_2$ and $NaNO_3$ crystals.[10,11] The electronic structure of NO_3^-, with particular emphasis on the assignment of the weak 300-nm band, has recently been discussed by McGlynn et al.[12] In their review of the previous attempts[1,2,13-18] at a rational analysis of the spectrum, they point out that earlier measurements of the LD of $NaNO_3$ and KNO_3 single crystals[1,2] showing the 300-nm band to be in-plane polarized are consistent with the presumption that its intensity is borrowed by some mechanism from the intense in-plane polarized band at 190 nm. A simple MO model for NO_3^- predicts that the highest filled orbitals will be $e''(\pi)$, $e'(\sigma)$, and $a_2'(n)$, all of which are essentially nonbonding in the sense of having little or no contribution from orbitals on the nitrogen.[19] The lowest empty orbital is clearly the $a_2''(\pi^*)$ (Figure 3). CNDO/S-CI calculations indicate that transitions $^1A_1''\leftarrow^1A_1'$ ($a_2''(\pi^*)\leftarrow a_2'(n)$) and $^1E''\leftarrow^1A_1'$

($a_2''(\pi^*)\leftarrow e'(\sigma)$) are the lowest energy $S\leftarrow S_0$ types, both occurring in the region of 4 eV, and that the $^1E'\leftarrow^1A_1'$ ($a_2''(\pi^*)\leftarrow e''(\pi)$) transition is in the 6-eV range.[17,20] The $^1A_1'\leftarrow^1A_1'$ transition is forbidden in D_{3h} by interaction with the electric and magnetic dipole and the electric quadrupole radiation fields, whereas the $^1E''\leftarrow^1A_1'$ transition is also electric dipole forbidden, though magnetic dipole and electric quadrupole allowed. On the other hand, the $^1E'\leftarrow^1A_1'$ transition is electric dipole (and electric quadrupole) allowed. On this basis, the strong in-plane polarized band at ca. 190 nm is generally agreed to be the $^1E'(\pi\pi^*)\leftarrow^1A_1'$ band. However, assignment of the 300-nm band remains somewhat in doubt. On the strength of the CNDO/S-CI calculation alone, Strickler and Kasha[17] and also Harris[20] favor the $^1A_1''(n\pi^*)\leftarrow^1A_1'$ assignment. The former authors propose that the intensity borrowing mechanism is vibronic with the enabling vibration being a $(a_2'' + \epsilon)$ combination mode. As pointed out by McGlynn, confusion in the interpretation of Sayre's earlier crystal data on $NaNO_3$ and KNO_3[2] led Rotlevi and Treinin[18] to assign the band to a $(\sigma^*\leftarrow n)$ singlet-singlet transition, which, on the basis of the CNDO results,[17-20] seems highly unlikely.

Three additional lines of reasoning have been employed by McGlynn[12] in approaching the assignment of the 300-nm band. First, comparison of the first band of NO_3^- with those of BF_3, BCl_3, BBr_3, and BI_3, along with a spin-orbit calculation for BF_3, BCl_3, and NO_3^-, leads to the conclusion that spin-orbit mixing is a more likely mechanism of intensity borrowing than vibronic mixing since the oscillator strength predicted is ca. 10^{-5}, whereas it is only ca. 10^{-7} for the vibronic model of Strickler and Kasha.[17] The calculated near coincidence of the singlet and triplet transitions involving the configurational excitations $a_2''(\pi^*)\leftarrow e'(\sigma)$, $a_2'(n)$ then suggests either $^{1,3}E''(\sigma\pi^*)$ or $^{1,3}A_1''(n\pi^*)$ as the excited state for the 300-nm band. Secondly, measurement of the solution spectra of various metal nitrates strongly suggests that a separate charge transfer band is responsible for observed increases in intensity in the 300-nm region in many of these cases, rather than any perturbation of the intrinsic NO_3^- 300-nm band.
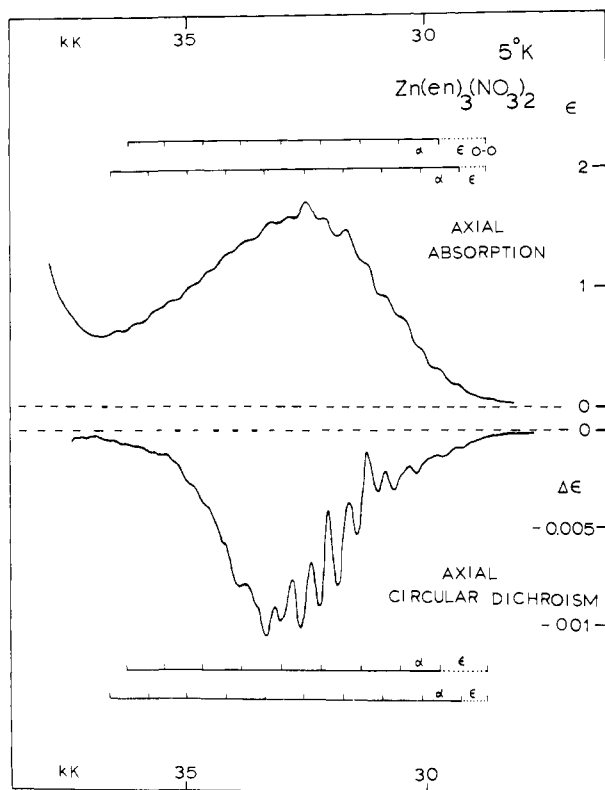
Figure 2. Axial absorption and axial CD spectra of Zn(en)$_3$(NO$_3$)$_2$ at 5 K.

Figure 3. 0001 projection of adjacent NO$_3^-$ groups in Ni(en)$_3$(NO$_3$)$_2$[10] showing potential for interaction between O$_{pz}$ and O$_{py}$ orbitals.

Table IV. Correlation Table for Group D_{3h}

D_{3h}	D_3	C_{3v}	C_3
A$_1'$	A$_1$	A$_1$	A
A$_2'$	A$_2$	A$_2$	A
E$'$	E	E	E
A$_1''$	A$_1$	A$_2$	A
A$_2''$	A$_2$	A$_1$	A
E$''$	E	E	E

And, finally, observation of weak luminescence at ca. 450 nm excited at ca. 320 nm in frozen glassy solutions of nitrates leads to the conclusion that Sayre's band may be due to a ^{3}E$'(\pi\pi^*)\leftarrow^1$A$_1'$ process, with the observed luminescence being the reverse process.

Thus, all evidence up to now seems clearly to point to the assignment of the 300-nm band to a transition to either ^{1,3}E$''$-($\sigma\pi^*$) or ^{1,3}A$_1''$(nπ^*), or perhaps both. However, which of the two configurational excitations, $\sigma\pi^*$ or nπ^*, is correct and whether the borrowing mechanism is vibronic or spin–orbit coupling remains in doubt.

The new data presented in this paper which bear on the question of the assignment of the 300-nm band are the following: (1) strong temperature dependence of both the dipole and rotational strengths; (2) extensive vibronic structure in both the LD and CD spectra not apparently related to that observed by Sayre; (3) unusual, out-of-plane polarization in the LD spectrum. These will now be discussed in turn.

Temperature Dependence. As shown in Tables I and II, σ,π and axial absorption and axial CD intensity of the 3.25 μm^{-1} (308 nm) band in Zn(en)$_3$(NO$_3$)$_2$ decrease by 50, 60, and 80%, respectively, as the temperature is decreased from 300 to 5 K. Such a decrease is characteristic of a band which borrows both electric and magnetic dipole strength by a vibronic mechanism. This behavior is not usually associated with spin–orbit coupling unless the intensity of the "allowed" band from which intensity is borrowed is itself vibronic. The intense σ-polarized 190-nm band ^{1}E$'(\pi\pi^*)$ is electric dipole allowed and does not appear to fit this description. The greater decrease of intensity in the σ than the π polarization for the 3.25 μm^{-1} band suggests that vibronic coupling to the ^{1}E$'(\pi\pi^*)$ state is a more important mechanism for the in-plane (σ) polarization.

Vibronic Analysis. Extensive vibronic structure in the 3.25 μm^{-1} band is observed in both the CD and LD spectra at 5 K. Analysis of this fine structure requires knowledge of the position of the 0–0 transition and the frequencies of normal vi-
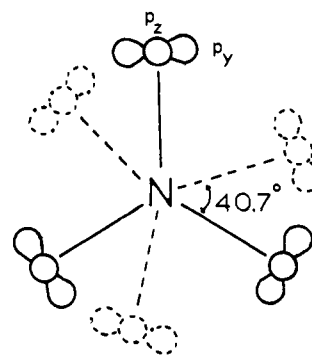
brational modes. The envelope of an allowed band should be composed of a progression that has equal spacing of totally symmetric vibrational modes following the 0–0 band, but in a vibronically allowed band the progression begins with a component involving one quantum of an asymmetric mode added to the forbidden and thus missing 0–0 band. This is then followed by an equally spaced progression in the totally symmetric vibrational mode. However, it has been found[21-23] in some instances that several non-totally symmetric quanta can be excited simultaneously. In such a case the envelope of the band will be the sum of several progressions.[21] This is apparently the case in the spectra of Zn(en)$_3$(NO$_3$)$_2$. (See below.)

The six normal vibrational modes of the NO$_3^-$ ion in D_{3h} are a totally symmetrical stretching vibration α_1', a vibration perpendicular to the plane, α_2'', and two pairs of asymmetric vibrations in the plane of the ion, both belonging to the ϵ' representation.[24] The frequencies associated with these modes of vibration have been determined in Raman and infrared absorption studies of many nitrate crystals and in solution. The values are $\nu_1(\alpha_1')$, 1068 cm^{-1}; $\nu_2(\alpha_2'')$, 845 cm^{-1}; $\nu_3(\epsilon')$, 720 cm^{-1}; $\nu_4(\epsilon')$, 1385 cm^{-1}, for the sodium nitrate crystal.[25] It should be noted that none of these six normal modes alone can make the transition A$_1''\leftarrow$A$_1'$ vibronically allowed in the isolated NO$_3^-$ ion of D_{3h} symmetry.

As stated above, the strong temperature dependence of the band supports the assumption of vibronic intensity borrowing. However, it is not necessary to presume that a combination mode of $\epsilon' + \alpha_2''$ symmetry must be excited in order to induce intensity into the A$_1''\leftarrow$A$_1'$ transition.[17] Excitation of an electron into the a$_2''$ orbital produces an excited state with pyramidal geometry. Thus, the selection rules for the transition must be those of the point group C_{3v}, which spans those symmetry elements that are common to both the ground and excited states.[26] The pertinent correlation table and the selection rules are given in Tables IV and V. The A$_1''\leftarrow$A$_1'$ transition (which becomes A$_2\leftarrow$A$_1$ in C_{3v}) is vibronically allowed in the σ spectrum by coupling with either of the two ϵ normal vibrational modes. The predicted σ polarization is in accord with the results of Friend and Lyons,[1] who found that the LD spectra of sodium nitrate crystal exhibit strong dichroism for this transition, with absorption only when the electric vector

Table V. Selection Rules for NO_3^-

Point group	Excited state	Polarization	$\langle \psi_e^* Me \psi_g \rangle^{a,b}$ symmetry	Electric[c] dipole intensity	Vibronic[d] intensity
D_{3h}	A_1''	π	A_2'	x	x
		σ	E''	x	x
	E'	π	E''	x	ϵ_a', ϵ_b'
		σ	$A_1' + A_2' + E'$		$(\epsilon_a', \epsilon_b')$
	E''	π	E'	x	ϵ_a, ϵ_b
		σ	$A_1'' + A_2'' + E''$	x	x
C_{3v}	A_2	π	A_2	x	x
		σ	E	x	ϵ_a, ϵ_b
	E	π	E	x	ϵ_a, ϵ_b
		σ	$A_1 + A_2 + E$		(ϵ_a, ϵ_b)
D_3 $(NO_3^-)_2$	A_1	π	A_2	x	x
		σ	E	x	ϵ_a, ϵ_b
	A_2	π	A_1		x
		σ	E	x	ϵ_a, ϵ_b
	E	π	E	x	ϵ_a, ϵ_b
		σ	$A_1 + A_2 + E$		(ϵ_a, ϵ_b)

^{a} Symmetry of electric dipole transition moment. ^{b} Ground state symmetry: A_1' (D_{3h}), A_1 (C_{3v}), A_1 (D_3). ^{c} Allowed (blank); forbidden (x). ^{d} Forbidden (x); if allowed, allowing modes indicated.

of the light is parallel to the plane of the nitrate ion.[27] Thus, this interpretation can well account for the intensity and the polarization of this transition in sodium nitrate and other crystals *in which the nitrate ions are isolated from one another.*

In the 5 K spectra, the structure in the π spectrum (Figure 1) is rather more complicated than that of σ and axial CD spectra (Figure 2). Since the latter are better resolved, they are analyzed first. The σ and axial absorption spectra are completely identical indicating an electric dipole mechanism. The correspondence of the vibronic structure in the axial absorption and CD is of great interest. For a vibronic band, the envelope should exhibit a progression of equal spacing due to multiple quanta of the totally symmetric vibrational mode (without the Jahn–Teller effect). In the σ spectrum two overlapping progressions with spacing about 800 ± 20 cm^{-1} can be discerned. It is expected that the frequencies of vibrational modes in the excited state should be decreased compared to those of the ground state, since the excitation involves taking an electron from an essentially nonbonding orbital to antibonding orbital and thus would weaken the N–O bond. Therefore, a value of 800 cm^{-1}, about 75% of that in the ground-state value for ν_1, might be reasonable. These two progressions begin with false origins ($1\leftarrow0$ transitions) at 29 325 and 29 762 cm^{-1} representing excitations of single quanta of the two ϵ vibrations (ϵ' in D_{3h}), which make this transition vibronically allowed in the σ and axial spectra. The progression can be fit by assuming that the two ϵ modes have energies in the excited state which differ by ~500 cm^{-1}. Presuming that the energies of these asymmetric modes will be 25% less in the excited state than in the ground state, as appears to be the case for the symmetric stretch (see above), leads to values of 540 and 1030 cm^{-1} for these modes—a ~500-cm^{-1} difference, as required to fit the pregressions (see Table III). This assumption would lead to the position for the forbidden (and unobserved) 0–0 components of 2.87 μm^{-1} (348 nm).[32] The correspondence of the absorption and CD spectra, not only in the positions of vibronic components, but also in the relative intensities (i.e., ϵ and $\Delta\epsilon$), is in agreement with the earlier theoretical prediction by Moffitt and Moscowitz.[28] This band may be classified as case III in Weigang's scheme,[29] in which both electric and magnetic dipole strengths are induced by vibronic coupling. A similar correspondence in the lowest ligand field band in the axial crystal spectra of tris(ethylenediamine)cobalt(III) ion was also found by Denning.[22] This
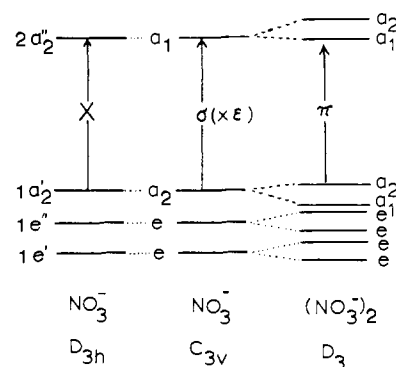

Figure 4. Qualitative MO diagram and allowed polarization of lowest spin allowed transition in NO_3^- for effective electronic symmetry of D_{3h} and C_{3v} and for $(NO_3^-)_2$ with symmetry D_3.

has been classified as case II (in which the transition of electric dipole forbidden but magnetic dipole allowed) with the vibronic contribution corresponding to case III.[30]

In contrast to the σ absorption spectrum at 5 K, the π spectrum is rather complicated and the progressions less distinct. Since, as discussed below, the π polarization is weakly allowed owing to the intermolecular perturbation, we expect that additional totally symmetric mode progressions (both the A_1' and the A_2'' representations in D_{3h} transform as A_1 in D_3) might occur, and that considerable overlap of these structures would result in the spectrum.

Out of Plane Polarization. The fact that the 3.25 μm^{-1} band in $Zn(en)_3(NO_3)_2$ is strongly polarized parallel to the C_3 axis of the nitrate ion is in direct contrast to the results noted for $NaNO_3$.[1,31] Although, as discussed above, vibronic perturbation and excited state distortion may reasonably be invoked to explain the in-plane intensity, there is no vibration in either D_{3h} or C_{3v} which will promote out-of-plane polarization. However, the packing of the NO_3^- ions in $Zn(en)_3(NO_3)_2$ suggests that an interionic interaction may be the source of this apparent anomaly.

The packing of two nitrate groups in the unit cell is such that one is stacked above the other with a separation of 3.17 Å along the c axis.[12] This is in contrast to the packing in $NaNO_3$ where the NO_3^- ions are separated by intervening Na^+ ions. It is reasonable to assume that in $Zn(en)_3(NO_3)_2$ through-space interaction of the nonbonding p_y and p_z orbitals of the oxygens

on the two nitrate groups will be significant in determining the intensity distribution (Figure 3). The closest O–O distance between adjacent NO_3^- ions is 3.3 Å.

If the two interacting nitrate ions are considered as a single (dimeric) unit, then the symmetry of this unit is D_3. A qualitative MO diagram including this dimer interaction is shown in Figure 4. The dimer HOMO has a_2 symmetry and the LUMO a_1, for the a_2' (p_y) and a_2'' (p_z) single ion orbital interactions. Therefore, the lowest energy allowed transition ($A_2 \leftarrow A_1$) is $\pi(\|C_3)$ polarized on the basis of D_3 electric dipole selection rules. It is worth noting that the adjacent transition ($A_1 \leftarrow A_1$) is strictly forbidden by the electric dipole selection rules. It is also forbidden vibronically since there is no α_2 normal vibrational mode.

However, the fact that the $A_1 \leftarrow A_1$ component is forbidden is consistent with the fact that we see no clear evidence of splitting (into two components) in either the absorption or CD spectra. Thus, the polarization difference between Zn-$(en)_3(NO_3)_2$ and $NaNO_3$ can be explained satisfactorily on this basis. The prediction that in this case the energy of this transition will be smaller than the single ion model because of the splitting due to the perturbation is also consistent with observation. The position of this absorption in solution is around 3.33 μm^{-1} (300 nm) depending on the polarity of solvents[17] and 3.48 μm^{-1} (287 nm) in the crystal spectrum of $NaNO_3$.[1] All these values are larger than the result of 3.25 μm^{-1} in $Zn(en)_3(NO_3)_2$. This difference in the energy is of the right order of magnitude expected for the splitting of orbitals as shown in Figure 4. The $A_2 \leftarrow A_1$ transition arising from the transfer of an electron from the lower (a_1) component from $1a_2'$ to the upper (a_2) component from $2a_2''$ is not seen. This is plausibly attributed to the expected unsymmetrical splitting of the $1a_2'$ and $2a_2''$ components due to configuration interaction (Figure 4). This should place the upper A_2 state further above the unperturbed A_1'' state than the lower A_2 is below it. Therefore, the upper $A_2 \leftarrow A_1$ transition is likely in the 3.8–4.0 μm^{-1} region and lost beneath the intense allowed band. Taken together, these considerations support strongly the model of the interionic perturbation described above.

The Cotton Effect and the Chirality of Crystal Lattices. Finally, it is obvious that the Cotton effect of the NO_3^- transition is due to the chiral crystal lattice and that it is a manifestation of enantiomorphism of $Zn(en)_3(NO_3)_2$ crystals. The chirality of the crystal lattices and the complex ions has been correlated to the sign of the Cotton effect of this transition by reference to the ligand field Cotton effects of the $Ru(en)_3^{2+}$ complex. It is interesting to note that in the axial CD the sign of R for the NO_3^- band is invariably opposite to that of the ligand field bands for all the transition metal ions observed (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Ru^{2+}).[3,6]

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Excited state		$10^{40}R$, cgs		g, $4R/D$	
O_h	D_3	300 K	80 K	300 K	80 K
$^4T_{2g}(F)$	^4E	5.58	7.19	0.29	0.37
$^2T_{1g}(P)$	^2E		0.30		0.43
$^4T_{1g}(P)$	^4E	2.75	3.1	0.09	0.17

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(32) As observed by one of the referees, a strong progression in even quanta of the out-of-plane bending mode (α_2'' in D_{3h}), which carries the isolated molecule ground state into C_{3v}, might also be expected. This mode should have an energy of ca. 630 cm^{-1} in the excited state (by analogy to the other modes). References to Figure 2 shows that the $0\rightarrow0$, $0\rightarrow2$, $0\rightarrow4$, etc., components of progressions in this mode built on the same false origins as illustrated would come into approximate phase with the more obvious progressions in the 3.2–3.3 μm^{-1} region. This may account for the more clearly defined structure in this part of the axial CD band. However, a similar effect is not observed in the axial absorption spectrum, casting some doubt on this interpretation. The resolution in these spectra is relatively poor compared to possible analogies in gas-phase spectra, and consequently a clear conclusion cannot be made on this point.