Electronic Absorption Spectrum of Nitrate Ion and Boron Trihalides

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Received January 28, 1972

Abstract: The electronic spectrum of the nitrate ion is discussed. We report (i) vapor-absorption spectra of boron trihalides; (ii) absorption spectra of transition metal nitrates in anhydrous methanol; (iii) a phosphorescence of nitrate salts; (iv) a phosphorescence of boron triiodide; and (v) semiempirical Mulliken–Wolfsberg–Helmsholz (MWH), CNDO/s–CI, and spin–orbit coupling calculations. The following conclusions are drawn. (a) The 300-nm absorption band of nitrate ion contains triplet ← singlet character of nature ${}^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ and/or ${}^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$; the singlet ← singlet character of this band arises, most likely, from a ${}^1\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1({}^1E'' \leftarrow {}^1A_1')$ transition. (b) The very weak, but very sharp, absorption lines in the region 320–350 nm are due to triplet ← singlet transitions of the type ${}^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ and/or ${}^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$. (c) The lowest triplet state of the nitrate ion is ${}^3\Gamma_{\pi\pi^*}$ (${}^3E'$) and its energy is $\sim$25,000 cm^{-1}. (d) The low-energy spectra of transition metal nitrato complexes are dominated by charge-transfer transitions.

The electronic absorption spectrum of NO_3^- has been subject to much discussion. Despite this, many state identifications are not convincing, and severe disagreements exist in the literature.

The most distinctive absorption band of NO_3^- solutions occurs at $\lambda_{max} \simeq 190$ nm ($\epsilon_{max} \simeq 7000$). This transition is assigned as $\pi^* \leftarrow \pi$, ${}^1E' \leftarrow {}^1A_1'$ ($a_2'' \leftarrow e''$). General agreement concerning this assignment exists.

The nitrate ion spectrum also contains a much weaker band at $\lambda_{max} \simeq 300$ nm ($\epsilon_{max} \simeq 3$–7, depending upon the solvent). The assignment of this band is controversial.

(i) Sayre[1] measured the absorption spectra of sodium and potassium nitrate single crystals at 4°K and found a series of very weak, very sharp lines starting at $\sim$355 nm and terminating at 321.14 nm in a $Na^{14}NO_3$ crystal. He analyzed the majority of the lines in terms of two vibrational frequencies. He concluded from the polarization, isotope effect, and crystal field splitting that the excited electronic state was E′ (in D_{3h}) and that the two vibrational frequencies belonged to e′ modes. Sayre did not observe the origin band of the series (which, he estimated, should lie at 362.3 nm), nor did he specify the spin multiplicity of the upper state. However, later workers,[2,3] assuming this series to refer to a transition of $S_1 \leftarrow S_0$ type, rejected the Sayre assignment because an ${}^1E' \leftarrow S_0$ excitation should be allowed and should possess high intensity. In view of this, we emphasize the following. Sayre's measurements were limited to $\lambda > 320$ nm. The $\sim$300-nm solution absorption band shifts to the blue in crystal media at low temperatures.[4] Therefore, Sayre's measurements are not pertinent to the 300-nm band. Sayre analyzed all the prominent lines he observed as one electronic transition. Sayre found that most of the lines of sodium nitrate (site symmetry D_{3h}) split into doublets in potassium nitrate (site symmetry C_s). Furthermore, these doublet lines showed no pleochroism with respect to the reflection plane, indicating that they retained a degeneracy not removed by the C_s field. He concluded that the splitting resulted from a removal of an electronic degeneracy of the excited state.

(ii) Friend and Lyons[4] measured sodium nitrate crystals at 77°K in the region 320–240 nm. The entire spectrum was polarized parallel to the plane of the nitrate ions. The solution maximum of 300 nm shifted to 287 nm in the crystal spectrum. They suggested that the transition might be ${}^1A_1'' \leftarrow {}^1A_1'$ ($\pi^* \leftarrow n$).

(iii) Strickler and Kasha[2] concluded that the observed absorption intensity in the 300-nm region was attributable to hydrogen-bonded associates of NO_3^- and solvent, and they assigned this band to the highly forbidden ${}^1A_1'' \leftarrow {}^1A_1'$ transition. They noted that a second-order vibronic coupling involving at least two different vibrational modes was needed to explain the observed absorption intensity. A calculation of the borrowed intensity by perturbational techniques led to $f = 3.0 \times 10^{-7}$. The experimental value is 8.0–15×10^{-5}.

(iv) Rotlevi and Treinin[3] concluded that the oscillator strength of the free ion was not much smaller than $f \sim 7 \times 10^{-5}$. They rejected the Strickler–Kasha[2] assignment; using Sayre's data, they favored an assignment of ${}^1A_2' \leftarrow {}^1A_1'$ ($\sigma^* \leftarrow n$). However, these authors misinterpreted Sayre's work. They assumed that measurements for 350–320 nm in the crystal were relevant to the 300-nm solution band. They assumed that the total (*i.e.*, electronic x vibrational) symmetry of the excited state was E′, whereas Sayre concluded that the electronic symmetry alone was E′.

(v) The absorption of certain metal nitrates in the 300-nm region is greatly intensified in solutions of low polarity.[5,6] It is usually assumed[3] that the enhancement is due to modification of the 300-nm nitrate band caused by metal ion perturbations. However, it has also been suggested[6] that it might be due to charge-transfer effects. We note, in this connection, that the

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(1) E. V. Sayre, *J. Chem. Phys.*, 31, 73 (1959).

(2) S. J. Strickler and M. Kasha, "Molecular Orbitals in Chemistry, Physics, and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 241.

(3) E. Rotlevi and A. Treinin, *J. Phys. Chem.*, 69, 2645 (1965).

(4) J. A. Friend and L. E. Lyons, *J. Chem. Soc.*, 1572 (1959).

(5) L. I. Katzin, *J. Chem. Phys.*, 18, 789 (1950).

(6) C. C. Addison and D. Sutton, *J. Chem. Soc. A*, 1524 (1966).

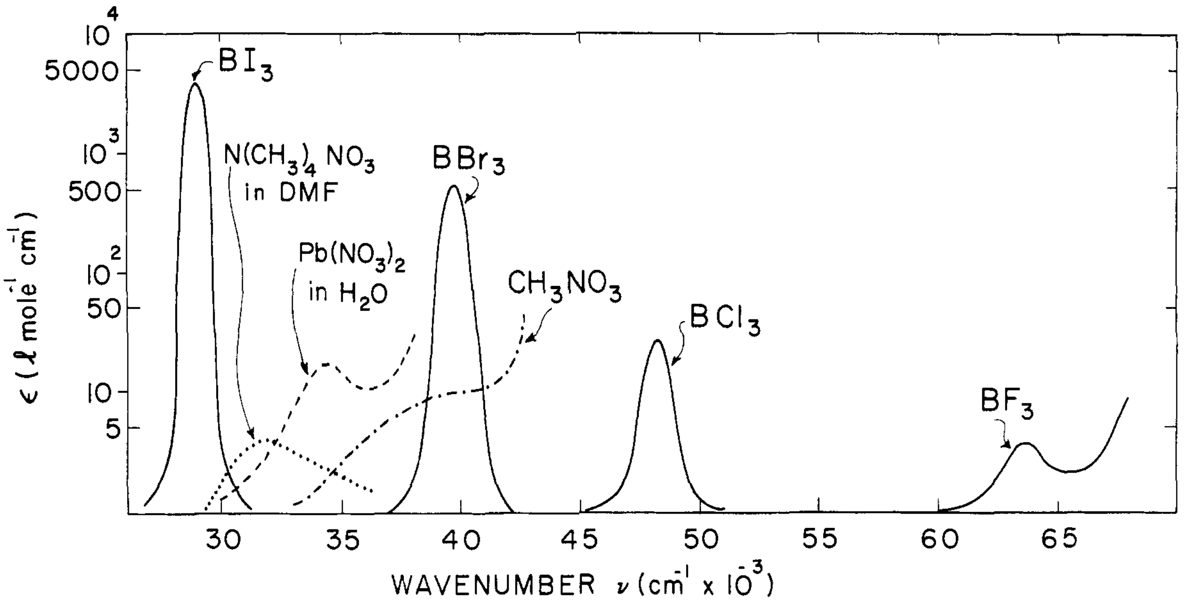

Figure 1. The low-energy absorption bands of boron halides, nitrate ion, and methyl nitrate. All spectra are for the gas phase except as noted on the figure.

intensification is most pronounced with certain transition-metal salts but that it is quite negligible for Al^{3+}, Cd^{2+}, and Zn^{2+} salts even when the nitrate ions are completely covalently bound.[6]

(vi) A phosphorescence of nitrate solutions has been observed[7] at 77°K and assigned to a $T_1 \rightarrow S_0$ luminescence of NO_3^-. This luminescence possesses marginal intensity and exhibits a two-component decay lifetime. The long lifetime of the luminescence, if indeed it be intrinsic to the nitrate ion, requires a $^3\Gamma_{\pi\pi^*} \rightarrow {}^1\Gamma_1$ assignment.

In view of items i–vi, we now ask the following. What is the most viable interpretation of the Sayre band? Which, if any, of the assignments of the 300-nm band is correct? What is the mechanism of the intensification noted in (v) above? Is the emission of item vi intrinsic to the nitrate entity?

In order to attempt answers, we have performed the following experiments.

(a) We have measured the absorption spectra of metal nitrates in anhydrous methanol (a solvent which favors formation of metal–nitrate complexes). The observed spectra reveal a new absorption band which satisfies all criteria for a charge-transfer transition of a nitrate complex. In some instances, this new band occurs in the 300-nm region and provides a rationale for the prior supposition that the metal merely increased the intensity of the 300-nm band.

(b) We have measured vapor-phase absorption spectra of BF_3, BCl_3, BBr_3, BI_3, and CH_3NO_3. All of these molecules are D_{3h} and isoelectronic with NO_3^-.

(c) We have performed calculations of MWH[8] and CNDO/s–CI type[9] in order to obtain insight on the changes which occur in proceeding from NO_3^- to HNO_3 to BF_3 to BCl_3. We have also performed spin–orbit coupling computations.[10]

(d) The luminescences of glassy solutions of NO_3^-, of BBr_3, and of BI_3 single crystal were investigated.

Experimental Section

All nitrate salts were reagent grade and were dried over phosphorus pentoxide in a vacuum desiccator prior to use. Except for tetramethylammonium nitrate and ceric ammonium nitrate, all salts were hydrated. Details of vapor-phase measurements will be given elsewhere.[11]

Results

The first readily observable band in the spectra of the boron halides, nitrate ion, and methyl nitrate is shown in Figure 1. Absorption spectra of nitrate salts in anhydrous methanol are given in Figure 2. Cobalt nitrate shows negligible association in methanol[12] and, therefore, the spectrum of this salt was measured in *tert*-butyl alcohol. Emission and excitation spectra of BI_3 crystals at 77°K are given in Figure 3.

Discussion

The molecules NO_3^-, CH_3NO_3, BF_3, BCl_3, BBr_3, and BI_3 are isoelectronic. It would be expected that their spectra might be more or less identical, the total spectrum of any one molecule merely being displaced energetically with respect to that of any other. Insofar as data are available,[11] this supposition is confirmed.

The dominant instance in which the parallelism of the various spectra does not exist concerns that band which we suppose to be the analog of the 300-nm absorption band of NO_3^-. The most striking effects are an abnormal increase of extinction and a fairly normal decrease of energy as one proceeds from BF_3 to BI_3, an expected displacement toward higher energies as one progresses from NO_3^- to CH_3NO_3, and

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[7] H. J. Maria, B. N. Srinivasan, and S. P. McGlynn, "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y. 1969, p 787.

[8] D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, **44**, 1865 (1966).

[9] J. Del Bene and H. H. Jaffé, *ibid.*, **48**, 1807 (1968).

[10] D. G. Carroll, L. G. Vanquickenborne, and S. P. McGlynn, *ibid.*, **45**, 2777 (1966).

[11] J. R. McDonald, H. J. Maria, and S. P. McGlynn, in preparation for publication.

[12] L. I. Katzin and E. Gebert, *J. Amer. Chem. Soc.*, **72**, 5455 (1950).

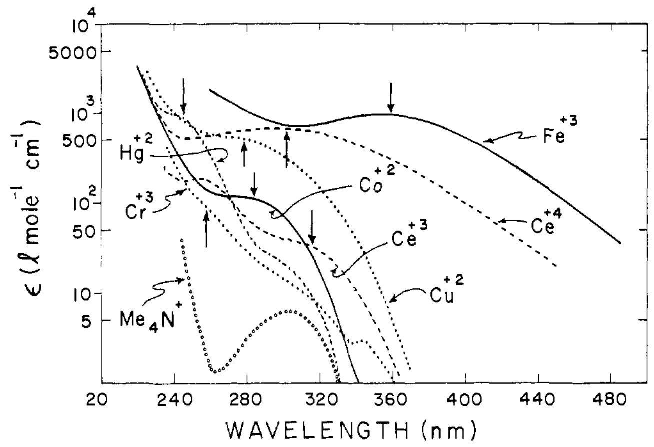

Figure 2. Absorption spectra of nitrate salts in anhydrous methanol (for a discussion of the meaning of ε, see footnote *b*, Table IV). In the case of cobaltous nitrate, the solvent is *tert*-butyl alcohol. Solutions of ferric nitrate were acidified with nitric acid to prevent hydrolysis. Charge-transfer absorption bands are indicated by a vertical arrow. The band at 256 nm in the spectrum of cerous nitrate is due to an internal transition of the cerous ion. The weak band ($\epsilon \simeq 3$) at 344 nm in the spectrum of chromic nitrate is not present in the spectrum of an aqueous solution of this salt; it may be due to an enhanced singlet–triplet transition of the nitrate ion.

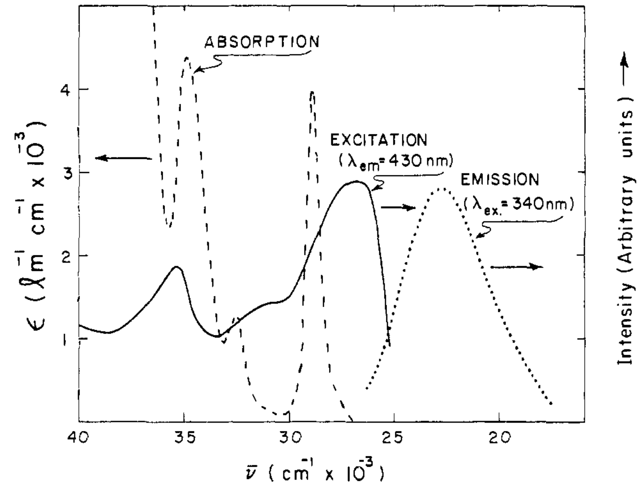

Figure 3. Excitation and emission spectra as corrected for instrument parameters of a BI_3 single crystal at 77°K. The absorption spectrum of BI_3 vapor is sketched in a dash-line representation in order to illustrate the correspondence of peaks between absorption and excitation and the long-wavelength sensitivity of the latter. Horizontal arrows refer spectra to appropriate ordinates.

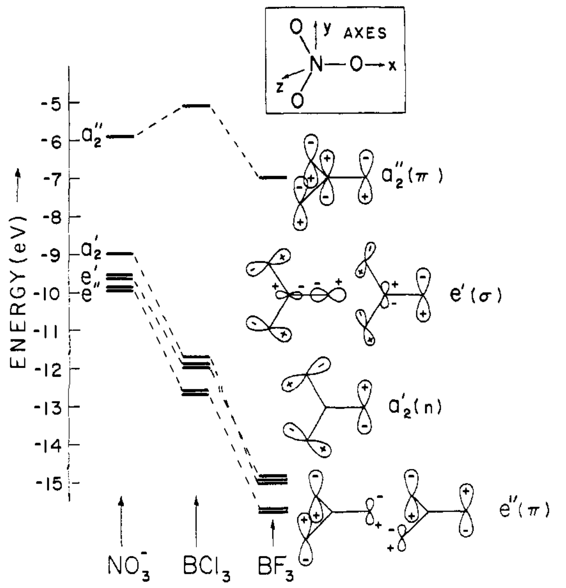

Figure 4. Molecular orbital energy diagram for NO_3^-, BCl_3, and BF_3. The form of the MO's are represented roughly in pictorial form on the right of the diagram. Axes are also designated.

Table I. Spin–Orbit Coupling Model Applied to Spectroscopic Data for the First Distinctive Absorption Bands of the Boron Halides and Nitrate Ion[a,b]

Molecule	ϵ_m, l./(mol cm)	$\bar{\nu}_m$, cm^{-1}	ζ, cm^{-1}	ζ^2/ζ_{Cl}^2	$\frac{\epsilon_m/\bar{\nu}_m}{(\epsilon_m/\bar{\nu}_m)_{BCl_3}}$
BF_3	3.6	63600	272	0.215	0.101
BCl_3	27.3	48200	587	≡1	≡1
BBr_3	560	39700	2460	17.56	24.9
BI_3	3940	28900	5060	74.30	241
NO_3^-	4.0	31900	152	0.067	0.22

[a] The subscript m denotes "maximum"; ζ is the atomic spin–orbit coupling constant for halogen atom or for oxygen atom; all data are normalized to the BCl_3 data because the absorption data in this instance are more secure than those for BF_3. The BF_3 tends to react with almost everything and the data here for BF_3 are conceivably not entirely free of error in the ϵ_{max} measurements; since the absorption bands are situated at different energies, the absorption data are rendered independent of $\bar{\nu}_m$ (see column 6) in order to achieve proper comparison with the ζ^2 expectations (see column 5).
[b] A discussion of the simple spin-orbit coupling mode used here is available in Chapter 7 of S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

a slight enhancement of absorptivity in $Pb(NO_3)_2$ relative to $N(CH_3)_4NO_3$.

The first conclusion relates to the boron halide spectra of Figure 1. While the transition may be considered forbidden in BF_3 and BCl_3, it is rather difficult to posit such for BBr_3 and BI_3. It is also obvious that the intensifications conform rather well to that expected for a spin–orbit enhancement of a triplet ← singlet act. In order to validate this latter hypothesis, the data are correlated in Table I with a simple spin–orbit model.

Table I indicates that intensity data which vary over a range of 10^3 are correlatable by a simple spin–orbit model. On this basis, it would seem that the 300-nm absorption band of nitrate may be represented as T ← S. In any event, no second-order vibronic phenomenon can account for the observations on the boron halides and it is, therefore, doubtful that such an interpretation retains validity for nitrate ion.

We now inquire into the excitation energies of this transition. Toward this end, we have used MWH techniques[8] to generate Figure 4. The first point is that the π, n, and σ MO's are all more or less nonbonding (in the sense that the MO amplitudes on the central atom (*i.e.*, B or N) are either zero or very small). Consequently, the transition energy associated with configurational excitations $a_2'' \leftarrow e''$, e', a_2' is largely determined by the VOIE of the np peripheral-atom valence orbital. Thus, the transition energies should decrease as $BF_3 > BCl_3 > NO_3^- \simeq BBr_3 > BI_3$, which is the precise order observed.

Transition energies and oscillator strengths are compared with experiment in Table II for nitrate ion. The second point is inherent in Table II. It implies that no excited states involving σ* orbitals should contrib-

Table II. Electronic Transitions of Nitrate Ion

State symmetry	MWH calculation Energy, eV		CNDO/s-CI Energy, eV		McEwen Energy, eV		Observed Energy, eV	
		f		f		f		f
$^1A_1''$ ($^1\Gamma_{n\pi^*}$)	3.10	0	3.62	0	4.95	0		
							3.97[a]	$(8\text{–}15) \times 10^{-5}$
$^1E''$ ($^1\Gamma_{\sigma\pi^*}$)	3.70	0	4.54	0	4.86	0		
$^1E'$ ($\Gamma_{\pi\pi^*}$)	4.01	0.20	6.42	0.19	6.22	0.34	6.07[a]	0.36
$^1E'$ ($^1\Gamma_{n\sigma^*}$)	20.4	7.5×10^{-3}	13.8					
$^3A_1''$ ($^3\Gamma_{n\pi^*}$)			3.62		4.95			
							3.6[b]	$\sim 10^{-7}$ [c]
$^3E''$ ($^3\Gamma_{\sigma\pi^*}$)			4.54		4.85			
$^3E'$ ($^3\Gamma_{\pi\pi^*}$)			3.61		4.40			

[a] S. J. Strickler and M. Kasha, "Molecular Orbitals in Chemistry, Physics and Biology," P. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 241. [b] E. V. Sayre, *J. Chem. Phys.*, **31**, 73 (1959). [c] Estimated from Sayre's experimental conditions.

Table III. Oscillator Strengths in Different Polarizations for Various $^3\Gamma_i \leftarrow {}^1\Gamma_1$ Transitions of NO_3^-, BF_3, and BCl_3[a]

Transition	Molecule	Oscillator strength f_x	f_y	f_z
$^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$	BF_3	1.49×10^{-4}	1.51×10^{-4}	2.15×10^{-7}
	BCl_3	5.6×10^{-4}	5.6×10^{-4}	4.8×10^{-6}
	NO_3^-	2.4×10^{-5}	2.4×10^{-5}	2.4×10^{-8}
$^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$	BF_3	6×10^{-7}	6×10^{-7}	4.9×10^{-4}
	BCl_3	1.7×10^{-6}	1.7×10^{-6}	2.0×10^{-5}
	NO_3^-	1.9×10^{-5}	1.9×10^{-5}	1.3×10^{-7}
$^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$	BF_3	0	0	1.9×10^{-7}
	BCl_3	0	0	5.1×10^{-6}
	NO_3^-	0	0	2.2×10^{-8}

[a] The energies and wave functions used were those of Figure 4. The procedural spin–orbit computational route followed along lines outlined by Carroll, *et al.*[10]

ute to the low-energy spectrum of nitate ion. Our calculations lead us to reject any such prior assignments.[3,13]

The third point refers to the fact that all calculations predict two forbidden singlet ← singlet transitions to occur at energies lower than the allowed $\pi^* \leftarrow \pi$ transition. However, aside from the Sayre bands, only one other weak absorption band, namely that in the 300-nm region, appears at low energies and all observations[1,4] on the 300-nm band indicate that it is in-plane (*i.e.*, *xy*) polarized. Let us now consider the $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ assignment for this 300-nm band. A $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition should be forbidden by electric dipole, magnetic dipole, electric quadruple, and all first-order vibronic effects; therefore, the source of the observed intensity of the 300-nm band is problematic. The obvious ploy is to suppose that the $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition borrows intensity from the in-plane polarized, strongly allowed $^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition at 190 nm. Such a mechanism was devised by Kasha and Strickler. Their calculations yielded in-plane polarization with $f = 3.0 \times 10^{-7}$. The experimental value, at $8.0\text{–}15 \times 10^{-5}$, is considerably larger.

Let us now suppose that the 300-nm band is best assigned to a triplet ← singlet event. Let us further suppose, per Table II, that the designation of the excited state might be any of $^3\Gamma_{n\pi^*}$, $^3\Gamma_{\sigma\pi^*}$, or $^3\Gamma_{\pi\pi^*}$. A first-order spin–orbit mechanism would enable either of the transitions $^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ or $^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ to borrow in-plane intensity from the intense $^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition and must be investigated. Such an investigation is reported in Table III. The results indicate that transitions $^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ or $^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ can account for the intensity of the 300-nm nitrate band. In fact, both transitions are computed to have $10^{-5} < f < 10^{-4}$ and to be in-plane polarized, in exact coincidence with experiment.

Granted the vagaries of any semiempirical route, it is proper to make the following judgments.

(i) Second-order vibronic effects cannot account for the intensities of Figure 1 for the lowest energy distinctive transitions in BCl_3, BBr_3, or BI_3. Spin–orbit coupling can account for the observed effects if the transition is assigned as either $^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ or $^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$.

(ii) Spin–orbit coupling can account for the observed intensities in BF_3 and NO_3^- if a similar assignment obtains as in (i) above. It is not clear that any second-order vibronic mechanism coupled with a $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ assignment can provide comparable rationalization.

(iii) In any event, it is now clear that the point of debate relates to the identification of the excited state as either spin singlet or spin triplet. In the case of BI_3 and BBr_3, where strong *j–j* coupling exists, this point is redundant and in the case of BCl_3, NO_3^-, and BF_3 it may very well be academic. This claim will be illustrated now for $^1\Gamma_{n\pi^*}$ and $^3\Gamma_{n\pi^*}$ states. The two $^1\Gamma_{n\pi^*}$ and $^3\Gamma_{n\pi^*}$ states are closely degenerate, the exchange integral $K_{n\pi^*}$ being approximately 1000 cm^{-1}, and $E\,(^1\Gamma_{n\pi^*}) - E\,(^3\Gamma_{n\pi^*}) \geq 2000$ cm^{-1}. Thus, the two transitions $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ and $^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$ should be encompassed within the same single broad absorption band. Under these circumstances, a spin–orbit perturbation would cause enhancement of T ← S character and make this absorption band behave as if it were $^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$; such effects could be held responsible for the boron halide enhancement phenomenon and for the intensification observed in $Pb(NO_3)_2$ (see Figure 1). Similarly, another type of perturbation might elicit dominance of the $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ character and make the band appear to be of S ← S type. Thus, we conclude that the 300-nm band could be assigned as $^{1,3}\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$. Since the characteristics discussed also apply in identical fashion to a $^{1,3}\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ possibility, these latter two designations must be retained as equally valid assignment candidates.

(iv) With regard to the eliciting of a S ← S character referred to in (iii) above, we emphasize that we

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(13) K. L. McEwen, *J. Chem. Phys.*, 24, 547 (1961); the McEwen computations assumed zero-differential overlap and included configuration interaction with doubly excited configurations; however, the inclusion of the σ-electron system was quite limited.

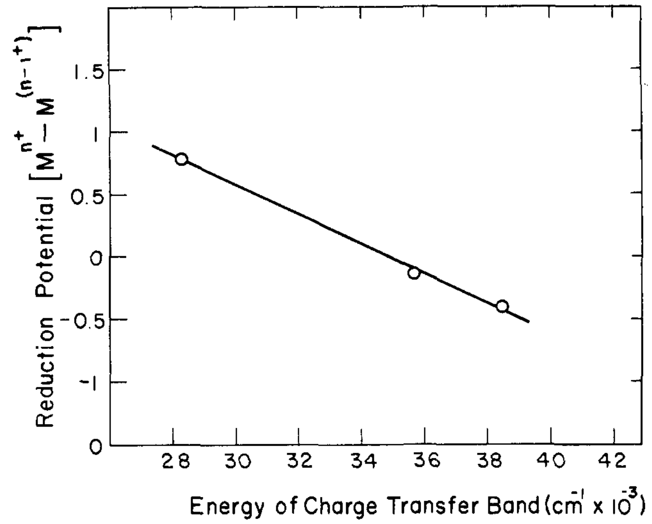

Figure 5. Energy of the charge-transfer band of nitrate salts in methanol plotted against the reduction potential of the positive ion.

know of no perturbation which effects such for NO_3^- ion. The intensity enhancement in HNO_3 (C_s point group) and CH_3NO_3 (approximate C_s point group), where both ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ and ${}^1\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ transitions are formally electric dipole allowed, are quite negligible experimentally. Indeed, the computed intensities of these two transitions for HNO_3 are smaller than the observed values in NO_3^- ion! And the intensity enhancement of the 300-nm band in covalently bound nitrate salts in which the metal ion does not function as a significant electron acceptor (*e.g.*, Cd^{2+} and Zn^{2+}; *vide infra*), and in which both ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ and ${}^1\Gamma_{\sigma n^*} \leftarrow {}^1\Gamma_1$ transitions should be allowed, is also quite negligible.

Charge-Transfer Spectra of Nitrato Complexes. Nonetheless, gross changes do occur in the nitrate spectrum when its transition metal salts are investigated under conditions favorable to the presence of metal–nitrate covalencies. These changes, previously adduced as evidence for intensity enhancement of the 300-nm band, are caused by entirely new band systems appropriate to a nitrate–metal entity.

We have measured the absorption spectra of several nitrate salts. The results, in Figure 2 and Table IV, indicate the occurrence of an absorption band whose energy is strongly dependent upon the metal counterion. In the case of Cu^{2+} and Co^{2+}, this band occurs at about the same wavelength as the 300-nm band of the nitrate ion and makes it seem as if this latter band is intensified. On the other hand, in the case of Cr^{3+} and Hg^{2+}, both bands (the 300-nm and the charge-transfer band) are clearly observed.

We identify the new band as a charge-transfer band which moves electronic charge from the nitrate group to the metal ion.

The band is observable only in nonaqueous solvents (except in the case of ceric ammonium nitrate) in which covalency effects are strong.

The energy correlates with the one-electron reduction potential of first-row transition elements, as shown in Figure 5. Such a correlation should hold[14] for charge-transfer transitions. Unfortunately, the number of first-row transition metals for which the one-electron reduction potentials are known and which form well-characterized nitrato complexes is limited. In fact, we know only of the three represented in Figure 5. However, we also note that those ions which possess high reduction potentials [*e.g.*, Co^{3+} (1.82), Mn^{3+} (1.51)] do not form stable simple nitrate salts. Similarly, the Ce^{4+} (1.61) ion is rapidly reduced to Ce^{3+} in solutions of ceric ammonium nitrate.[15]

Table IV. Absorption Bands of Nitrate Salts[a]

	300-nm band		Charge-transfer band	
Counterion	λ_{max}, nm	ϵ_{max}, l. $mol^{-1}\,cm^{-1}$ [b]	λ_{max}, nm	ϵ_{max}, l. $mol^{-1}\,cm^{-1}$ [b]
Hg^{2+}	300	21	244	900
Co^{2+} [c]			280	120
Cr^{3+}	300	15	260	82
Cu^{2+}			280	510
Ce^{4+}			297	660
Ce^{3+}			310	34
Fe^{3+}			353	950
NMe_4^+	303	6.2		
Mg^{2+} [d]	294	7.5		
Zn^{2+} [d]	290	7.7		
Cd^{2+} [d]	297	4.1		

[a] Solvent is anhydrous methanol except as noted. [b] Extinction coefficient is per nitrate group. The extinction coefficient of the 300-nm band, as quoted for Hg^{2+} and Cr^{3+} nitrates, refers to the total absorption at this wavelength; the large value of ϵ does not necessarily imply intensification of the 300-nm band because, in these cases, the band in question is overlapped by more intense absorption at shorter wavelengths (Figure 2). The extinction coefficient of the charge transfer band is calculated on the basis of the total concentration of nitrate present; and, therefore, it is not a true measure of the intensity of this band. The large variations in ϵ reflect differences in formation constants of the nitrato complexes. [c] In *tert*-butyl alcohol. [d] These data are for the anhydrous nitrates in ethanol and are taken from ref 6.

The dependence of the absorption band on solvent polarity is consistent with its assignment to a charge-transfer transition. An increase in solvent polarity should stabilize the energy of the ground state more than that of the excited state and cause an increase in the energy of the charge transfer transition. For anhydrous cupric nitrate,[16] the transition occurs at 33.8, 34, and 37 kK in the three solvents dioxane, ethyl acetate, and ethanol, respectively. The dielectric constants of these solvents, in the same order, are 2.2, 6.0, and 24.3. Acetonitrile does not fit in this pattern probably because of its own strong tendency to coordinate with metal ions. The absorption band of ceric ammonium nitrate also shows a solvent dependence consistent with its assignment to a charge-transfer transition. It occurs at 297 nm (33.6 kK) in methanol (Table IV) and at 305 nm (32.8 kK) in the less polar glacial acetic acid.[17]

190-nm Absorption Band of NO_3^-. The 190-nm absorption band is assigned as ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$. The evidence for this assignment resides in the high intensity of the observed transition: $f = 0.36$, which is in excellent agreement with the computed value; $0.19 \leq f \leq 0.34$ (see Table II). Indeed, all computations predict that the ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ should be the lowest energy transition of relatively high oscillator strength.

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$^3\Gamma_{\pi\pi^*}$ State of NO_3^-. We now inquire into the whereabouts of the $^3\Gamma_{\pi\pi^*}$ state. Granted the 190-nm $^1\Gamma_{\pi\pi^*}$ assignment and a computed value of 2.8 eV for the exchange energy $2K_{\pi\pi^*}$, we expect the $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ excitation to lie at $(6.1 - 2.8)$ eV $= 3.3$ eV $=$ 370 nm. This prediction is in the energy region of the sharp Sayre bands. Consequently, some temptation exists to assign the Sayre bands to a $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition. However, two considerations militate against such. Firstly, the computed value of 370 nm for the $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ event refers, more properly, to an absorption maximum; thus, this event origin should lie at quite longer wavelengths than 370 nm (*i.e.*, to the red of the Sayre band origin). Secondly, the oscillator strength of the $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition is computed, as given in Table III, to be entirely out-of-plane polarized. Thus, the Sayre bands should exhibit no electronic degeneracy. Indeed, the intensity resident in these bands, given the $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ assignment, should arise by stealing from a $^1\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ event calculated to occur at 9.7 eV with $f = 4.6 \times 10^{-2}$ and the resultant polarization and absence of electronic degeneracy discord with Sayre's experimental observations.

Unfortunately, Sayre was unable to observe the origin band and since his data may refer, in their entirety, to vibronic effects, his results are not unambiguously interpretable. Thus, the $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ assignment for the Sayre bands cannot be entirely discounted. Indeed, a $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition can readily borrow in-plane intensity by a variety of second-order spin–orbit vibronic means. Nonetheless, granted the validity of Sayre's observations and deductions, the $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ assignment is not a probable designation for the Sayre band system.

At this point, we note two further observations. A phosphorescence of metal nitrate salts has been reported[7] and all computations (see Table II) predict that the lowest energy transition of NO_3^- should be $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$. We now consider each of these in turn.

(a) The reported phosphorescences are very weak and, in dilute glassy solutions, usually contain two decay components whose mean lifetimes are $\sim$0.1 and $\sim$1 sec, respectively. We have found that an increase of concentration produces a dominance of the decay kinetics by the long-lived component. In view of this, we assume that the $\sim$1 sec component refers to a nitrate entity. Thus, we must include in our considerations a phosphorescence with $\lambda_{\max} \simeq$ 460 nm and $\tau_m \simeq 1$ sec. The long lifetime of this emission dictates a $^3\Gamma_{\pi\pi^*}$ ($^3E'$) $\rightarrow {}^1\Gamma_1$ assignment.

(b) If the lowest triplet state of NO_3^- is indeed $^3\Gamma_{\pi\pi^*}$, then comparison with the spectra of the boron halides suggests that these molecules may have triplet states which were not observable in gas-phase absorption studies. In this regard, since the boron halide absorption work was restricted to the gas phase because of chemical stability difficulties, low-intensity absorption bands might not have been detected. Consequently, we have searched for a luminescence from boron tribromide and triiodide compounds. In both cases, a very weak luminescence was observed. Boron tribromide was not entirely free of bromine and, for that reason, will not be discussed further. On the other hand, boron triiodide was obtained in a very pure form by growing crystals over a 9-month period from the room-temperature vapor in a sealed quartz tube containing inert gas. One of the larger single crystals was isolated in this tube, without breaking any seals, and all emission experiments were performed on this crystal. The phosphorescence emission and phosphorescence excitation spectra of single crystal BI_3 as well as the absorption spectrum of gaseous BI_3 are shown in Figure 3. Apart from some broadening in the crystal phase and a slight red shift of the lowest energy excitation peak relative to the first absorption peak, the excitation appears to be more or less replicative of the absorption spectrum. The following suppositions appear reasonable.

(a) The excitation spectrum, which pertains to the condensed phase, exhibits weak $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ events which could not be detected in the dilute gas-phase absorption experiments. It is this extra absorptivity which is held responsible for the red shift of the first excitation peak in the solid BI_3 sample. Indeed, one might go further and assume, as seems reasonable, that a $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ absorption should be particularly effective in exciting a $^3\Gamma_{\pi\pi^*} \rightarrow {}^1\Gamma_1$ emission. In this sense, the $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ event would dominate the excitation spectrum, would produce the apparent red shift, and would yield a good mirror-image relationship to the phosphorescence act. In this sense also, the luminescence is interpreted as intrinsic to BI_3 and as a $^3\Gamma_{\pi\pi^*}$–$^1\Gamma_1$ process.

(b) The luminescence is a phosphorescence with $10^{-4} < \tau_p < 10^{-1}$ sec. Exact lifetime measurements were impeded by low-emission intensities.

(c) The NO_3^- phosphorescence excitation spectrum consists essentially of one band with $\lambda_{\max}$ 350 nm. Thus, the experimental results on NO_3^- and BI_3 indicate that the Sayre absorption region of NO_3^- ion and the corresponding "Sayre counterpart region" of BI_3 are particularly effective insofar as phosphorescence excitation is concerned. Whether this indicates that the Sayre absorption region and the phosphorescence of NO_3^- ion are inverse electronic processes is, perhaps, debatable. However, given the correctness of our assertions concerning BI_3, it does appear that the Sayre bands must be associated with an $T \leftarrow S$ process.

In sum, it appears that the observed luminescences are intrinsic to the molecules being investigated and that, in the case of NO_3^-, this luminescence is of $^3\Gamma_{\pi\pi^*} \rightarrow {}^1\Gamma_1$ type. It also seems that the Sayre absorption bands of NO_3^- are of $T \leftarrow S$ nature. However, the precise character of the Sayre bands is open to debate. A $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ attribution provides wrong degeneracies and polarizations unless a second-order coupling is invoked. A more rational attribution for the Sayre bands is either $^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ or $^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ because first-order coupling considerations provide the right electronic degeneracies and polarizations in both instances.

Conclusions

A "most probable" energy-level scheme for NO_3^- is schematized in Figure 6. This level diagram is a synopsis of all the conclusions and speculations of the preceding text.

The analog of the 300-nm band in BCl_3, BBr_3, and BI_3 cannot be interpreted as a vibronically induced

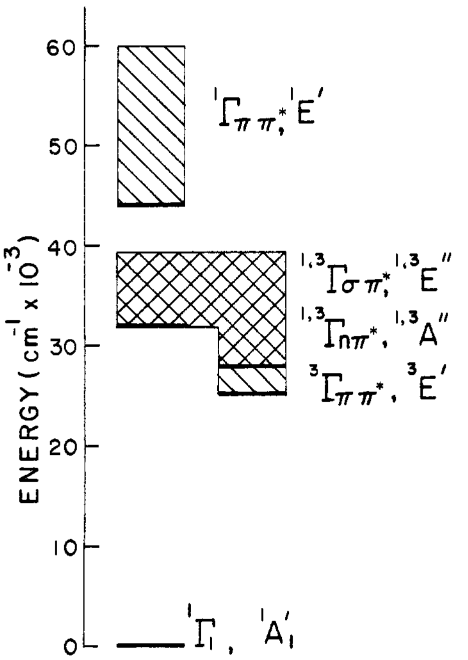

Figure 6. An energy level diagram for nitrate ion. Character notation refers to the D_{3h} point group tables. In view of the MO diagram of Figure 4, it is expected that low-energy transitions of type $\pi^* \leftarrow \sigma$ (*i.e.*, $a_2'' \leftarrow e'$) should also occur at low energies; the corresponding transitions, $^{1,3}E'' \leftarrow {}^1A_1'$, are orbitally forbidden and more or less degenerate. Some authors[18] predict the $^1E'' \leftarrow {}^1A_1'$ excitation to be the lowest energy transition in the singlet manifold and, indeed, the arguments indulged in this present paper are not adequate to distinguish $^{1,3}A_1''$ from $^{1,3}E''$ pair states (*cf.* Figure 4 and Table III).

$S_1 \leftarrow S_0$ transition whereas a $T_i \leftarrow S_0$ transition is in accord with all the data in these instances. It is not clear, however, that the 33,000-cm^{-1} band of NO_3^- or the 63,000-cm^{-1} band of BF_3 can be similarly assigned.

The Sayre bands observed in KNO_3 and $NaNO_3$ are interpreted as triplet ← singlet transitions with the upper state being, most probably, $^3E''$ ($\sigma\pi^*$) or $^3A_1''$ ($n\pi^*$). We emphasize that there are four excited states, $^{1,3}E''$ and $^{1,3}A_1''$, which are expected to be energetically close and the transitions to which are forbidden. The transition to any of these states must acquire intensity, by whatever mechanism, from the allowed $^1E'$ ($\pi\pi^*$) $\leftarrow {}^1\Gamma_1$ excitation and, therefore, they will all be in-plane polarized. In addition, the $^3E'$ state which is of $\pi\pi^*$ type and which is also expected to lie in this same wavelength region may couple vibronically with $^3E''$ and thereby obtain allowedness by spin–orbit coupling of $^3E''$ with $^1E'$. The resultant polarization of this transition would then exhibit in-plane intensity also. Thus, polarization alone may not be adequate to distinguish experimentally between these five states. All available evidence indicates that the lowest triplet state is $^3\Gamma_{\pi\pi^*}$ and, consequently, we assign the luminescence of nitrate solutions to an intrinsic $^3E' \rightarrow {}^1A_1'$ emissive process.

We have presented evidence, both experimental and computational, which indicates that the 300-nm band of NO_3^- may be of $^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ or $^2\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ type. However, we note that the observed oscillator strength ($f \simeq 10^{-4}$) is unexpectedly large for a transition of this type and is too large by a factor of $\sim$3 compared to the oscillator strength which might be adduced by comparison to the analogous transitions in the boron halides (Table I). It is probable that a large part (perhaps even the largest part) of the intensity of the 300-nm band is contributed by transition to a forbidden singlet state. We think it is unlikely that this state is the highly forbidden $^1A_1''$ and favor instead the $^1E''$ ($\sigma\pi^*$) state. The energies of these two states are calculated to be quite close (Table II), and in one instance[11] the E'' state is calculated to have lower energy. Moreover, the E'' state can acquire intensity by coupling to the allowed E' ($\pi\pi^*$) state *via* one vibrational mode of e' or a_2'' symmetry. The resulting polarization will be in-plane and in agreement with experiment.

We raise no questions concerning the 190-nm absorption band of NO_3^-. It is clearly of $^1\Gamma_{\pi\pi^*} \rightarrow {}^1\Gamma_1$ type.

Acknowledgment. We wish to thank Professors M. Kasha (Tallahassee) and R. Hochstrasser (Philadelphia) for helpful discussion and comments. This work was supported by contract between the U. S. Atomic Energy Commission–Biology Branch and The Louisiana State University.