302. *The Electronic Spectrum of the Nitrate Ion and Related Molecules.*

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The absorption spectrum of crystalline sodium nitrate has been measured in polarized ultraviolet light. Assigments are given for the two prominent absorption bands.

ALTHOUGH some discussion of the one-electron orbitals of the nitrate ion [1,2] and some determinations [3] of the crystal spectrum of sodium nitrate at room temperature have been reported, we know of no previous consideration of the electronic states in the light of the polarized spectra. This we now give, together with the ultraviolet spectrum of a sodium nitrate single crystal at —186° taken with a continuum of plane-polarized light.

EXPERIMENTAL

The solution spectrum of sodium nitrate was recorded with a " Unicam " S.P. 500 spectrophotometer.

The crystal spectra were obtained on single crystals prepared by melting sodium nitrate between silica discs so that the least possible decomposition occurred. The crystals used were

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[1] Mulliken, *Phys. Rev.*, 1933, **43**, 279.
[2] Walsh, *J.*, 1953, 2301.
[3] Krishnan and Dasgupta, *Nature*, 1930, **126**, 12.

2—4 μ thick, from measurements with an Ehringhaus compensator. They were illuminated with a continuum of plane-polarized light obtained from a hydrogen lamp and polarized by passage through a Wollaston prism which could be rotated through 180° to interchange the two beams. The spectra were recorded photographically, and microphotometer tracings prepared from the plates.

RESULTS

The spectrum of sodium nitrate in aqueous solution shows evidence of two main transitions. The first, for which $\varepsilon_{\max.} = 7{\cdot}3$, and the beginning of the second, were measured, and are shown in Fig. 1. The extinction coefficient at the 2000 Å maximum was measured by Scheibe [5] as 10,000. Microphotometer tracings of sample crystal spectra are also shown in Fig. 1.

There is a close resemblance between the solution and the crystal spectra, although the position of maximum absorption is shifted from 3020 Å in water to 2870 Å in the stronger crystal spectrum.

The value of $\varepsilon_{\max.}$ measured on one crystal spectrum was *ca.* 30 for " parallel " orientation. This corresponds to a value of 10 for random orientation of the absorbing ions, as obtains in solution. This figure is in fair agreement with the experimental $\varepsilon_{\max.}$ in solution.

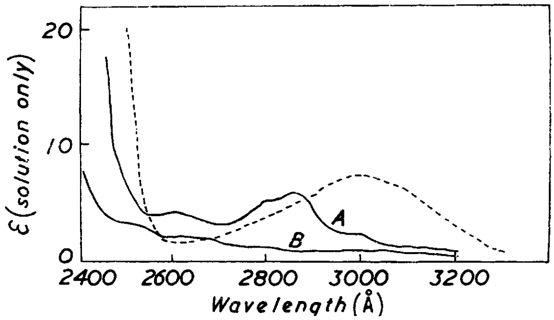

FIG. 1. *Absorption spectra of sodium nitrate solution at* 20° (- - - -) *and crystal at* −186° (——). *The two crystal spectra shown are for light polarized parallel* (*A*) *and perpendicular* (*B*) *to the planes containing the* NO_3^- *ions.*

The crystal structure [4] of sodium nitrate is especially well suited to experiments with polarized light since all the nitrate ions lie with their planes parallel. Our results, in agreement with earlier ones,[3] show that absorption is greater when the electric vector of the light vibrates parallel to the plane of the nitrate ion. It was thought that lowering the temperature to −186° might result in the appearance of some vibrational structure in the bands which at room temperature show none. Only the merest beginnings of structure were in fact apparent. There are some badly defined shoulders on some of the curves at 3010, 2970, and 2935 Å (max.). It is possible that a much lower temperature would reveal more structure but the photodissociation of the nitrate ion is unlikely to allow anything like the well-resolved nitrite-ion spectrum [6] to be obtained.

The orbital description of polyatomic molecules and ions was largely developed by Mulliken.[1] Later, Walsh discussed [2] the orbitals which occur in systems with 24 valence electrons, *e.g.*, CO_3^{2-}, NO_3^-, BF_3, and SO_3, all of which are planar in the ground state and should resemble each other spectroscopically. The orbital description given here differs from that of Walsh in that the bonding orbitals of the oxygen atoms are considered to be *sp* hybrids, with the consequence that each oxygen atom has its second lone-pair also in an *sp* hybrid orbital instead of in a pure *s* orbital. This we consider to be slightly nearer to reality, in view of the nearly similar " radii " of the 2*s* and 2*p* atomic orbitals of oxygen. The final theoretical description will need a full study of configurational interaction.

[4] Wyckoff, *Phys. Rev.*, 1920, **16**, 149.

[5] Scheibe, quoted by Rabinowitch, *Rev. Modern Phys.*, 1942, **14**, 121.

[6] Sidman, *J. Amer. Chem. Soc.*, 1957, **79**, 2669.

The sixteen molecular orbitals constructed from the atomic orbitals with $n = 2$ can be arranged in five groups, *viz.*: σ, n_h, n_p, π, and σ^*. The three σ orbitals bond nitrogen to oxygen and are built from a trigonal hybrid orbital on nitrogen and a digonal hybrid on oxygen. The σ^* antibonding orbitals are built from similar orbitals out-of-phase. Non-bonding orbitals on oxygen are denoted by n_h or n_p and consist either of *sp* hybrid, *h* orbitals or else *p* orbitals with axes in-plane and perpendicular to the N–O bond. Four orbitals with a nodal plane in the plane of the nitrate ion can be built from *p* orbitals on N and O which have axes perpendicular to the plane of the ion. Of all the orbitals, σ orbitals are assumed to have the greatest ionization potential and σ^* the least. Neither type is needed for our interpretation of the nitrate spectrum.

Regarded as molecular orbitals, all types σ, n, and π can be given a symmetry description in the group[7] D_{3h}. Thus, n (*sp*) molecular orbitals are a_1' and a'. If S, T, and U denote the hybrid orbitals on the three oxygen centres, $(1/\sqrt{3})\ (S + T + U)$ denotes an a_1' orbital and $(1/\sqrt{2})\ (S - T)$ or $(1/\sqrt{2})\ (T - U)$ denotes an e' orbital. It follows that the a_1' orbital is the more bonding of the two and will, therefore, have the greater ionization potential. The sequence in energy of the remainder of the orbitals has been given by Walsh and so the ground state can be described, with neglect of crystal perturbation, as

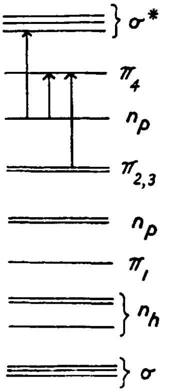

FIG. 2. *Energy levels (schematic) of the nitrate ion.*

$$(\sigma)^6\ (n_h,\ a_1')^2(n_h,\ e')^4(\pi_1,\ a_2'')^2(n_p,\ e')^4(\pi_{2,3},\ e'')^4(n_p,\ a_2)^2 : A_1'$$

The lowest unoccupied orbital is $(\pi_4,\ a_2'')$ and above it lie the σ^* orbitals of which the lowest is $(\sigma^*,\ a_1')$. The sequence of energies is shown in Fig. 2.

Various excited states are possible. Those of lowest energy are likely to be:

$$\ldots\ldots(\pi_{2,3},\ e'')^4\ (n_p,\ a_2')\ (\pi_4,\ a_2'') : A_1''$$
$$\ldots\ldots(\pi_{2,3},\ e'')^4\ (n_p,\ a_2')(\pi_4,\ a_2'') : E'$$
$$\ldots\ldots(\pi_{2,3},\ e'')^4\ (n_p,\ a_2')\ (\sigma^*,\ a_1) : A_2'$$

In each case singlet and triplet levels are possible but we assume that there is no need at present to discuss the triplet levels.

Pure electronic transitions from the ground state to the A_1'' and A_2' upper states are forbidden, but that to the E' state is allowed in xy polarization, where x and y are directions in the plane of the ion. Consideration of the observed extinction coefficients suggests that the long-wavelength transition could be electronically forbidden but that the transition at 2000 Å in solution might well be allowed. An interpretation of the 2000 Å transition as

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[7] The group theory nomenclature is that of Eyring, Walter, and Kimball, " Quantum Chemistry," John Wiley and Sons, New York, 1943.

$E' \longleftarrow A_1'$ is there indicated. The observed polarization agrees with this assignment, although no (0–0) band has been identified. In considering the absorption at longer wavelengths McConnell has suggested [8] on the basis of a study of solvent effects on the solution spectra that a $\pi \longleftarrow n$ transition is present. Such a transition is electronically forbidden. It may therefore be described as $A_1'' \longleftarrow A_1'$. In order to account for the observed (xy) polarization an out-of-plane ε'' vibration must be assumed to be present. This is quite possible. The observed intensity would then be the result of "stealing" from the neighbouring $E' \longleftarrow A_1'$ transition (cf. the spectrum of benzene, where a similar phenomenon occurs).

The spectrum of SO_3 is found in a similar region to that of NO_3^-, but the extinction coefficient is [9] considerably smaller, being only 100 at 2000 Å. For this reason Walsh [2] assumed that there were two forbidden transitions in this region, and associated them with the A_1'' and A_2' upper states. The transition to the E' state of SO_3, then, must occur below 2000 Å. It is possible that the $A_2' \longleftarrow A_1'$ transition is present also in the NO_3^- spectrum, buried beneath other absorption.

The lack of structure in the low-temperature spectrum remains to be discussed. This can be attributed to predissociation. Occupancy of the π_4 orbital is expected [2] to confer anti-bonding character upon the N–O bond. In addition the occurrence of the maximum intensity in the long-wave band at a considerable distance, over 300 Å, from the (0–0) band indicates that the excited state has an equilibrium configuration very different from the ground state. The excited A_1'' state is expected to be pyramidal and the vibrations present in the transition are therefore expected to be out-of-plane motions which carry the planar configuration into the pyramidal. The vibrational interval thought to be present (*ca.* 400 cm.$^{-1}$) is therefore partially identified. There is a similar interval of 430 cm.$^{-1}$ in the SO_3 spectrum.

Nitrites absorb at longer wavelengths than nitrates. The long-wavelength transition in nitrites has been assigned [10] to a $\pi \longleftarrow n_N$ transition, where n_N denotes a non-bonding orbital on the nitrogen centre. Such a transition is impossible with nitrates. Its absence is therefore indirect evidence which confirms the nitrite-ion assignment. The occurrence of absorption near 3100 Å in NO_2Cl, HNO_3, and nitro-alkanes as well as in nitrates and in alkaline nitrite solution was associated by Trawick and Eberhardt with a $\pi \longleftarrow n_O$ transition, where the n_O refers to an oxygen orbital. This assignment was made on the basis of a consideration of intensity of absorption and is seen to be consistent with the fuller orbital descriptions now given.

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[8] McConnell, *J. Chem. Phys.*, 1952, **20**, 700.
[9] Fajans and Goodeve, *Trans. Faraday Soc.*, 1937, **33**, 614.
[10] Trawick and Eberhardt, *J. Chem. Phys.*, 1954, **22**, 1462.