TABLE VIII

CROSS-SECTIONS AND RATE CONSTANTS FOR THERMAL REACTIONS

Reaction	Extrapolated experimental $f\sigma$ (298°K.) cm.^{2} × 10^{16}	Extrapolated experimental $k_{298°K.}$ (cm.^{3}/molecule-sec.) × 10^9	Theoretical (ref. 13) k (cm.^{3}/molecule-sec.) × 10^9
$C_2H_2^+ + C_2H_2 \rightarrow (C_4H_4^+)$	251	2.1	1.3
$C_2^+ + C_2H_2 \rightarrow C_4H^+ + H$	256	2.1	1.3
$CH^+ + C_2H_2 \rightarrow (C_3H_3^+)$	282	2.5	1.6

previously.[1] In studying reaction rates a Consolidated Electrodynamics Corporation (CEC) Model 21-620 cycloidal focusing mass spectrometer was used. In calibrating the ion source for pressure, the ionization cross section of acetylene was determined as $5.6_0 \times 10^{-16}$ cm.^{2} in reasonably good agreement with the value of 4.98×10^{-16} cm,^{2} reported by Massey and Burhop.[14] Appearance potentials were measured on a Westinghouse Type LV mass spectrometer. The acetylene used in these studies was commercial tank material obtained from Matheson Chemical Company and purified by repeated condensation at liquid nitrogen temperatures. The 1,3-butadiene was Phillips research grade having a stated purity of 99.51% and the 1-butyne was an API standard sample of 99.87% purity. Both were used without further purification. The vinylacetylene was obtained from the du Pont Company and was used without treatment since a mass spectrum indicated it to be of satisfactory purity.

Acknowledgment.—We wish to express our appreciation to Mr. B. L. Clark for his help in making the measurements and calculations.

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[14] H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, p. 265.

BAYTOWN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Electronic and Vibrational States of the Nitrite Ion. I. Electronic States[1]

BY JEROME W. SIDMAN[2]

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The lowest absorption transition of the nitrite ion has been studied in the crystalline state at 77°K. and at 4°K., using single crystals of $NaN^{14}O_2$ and $NaN^{15}O_2$ in polarized light. The corresponding fluorescence transition also has been studied. The spectra are sharp, and can be analyzed in considerable detail to yield vibrational and lattice frequencies for both the ground and excited electronic states. From the intensity dichroism and vibrational structure, it is concluded that the weak absorption transition of $NaN^{14}O_2$ with origin at 25977 cm.$^{-1}$ at 4°K. (25977 cm.$^{-1}$ for $NaN^{15}O_2$ at 4°K.) is allowed by symmetry and is polarized perpendicular to the plane of the NO_2^- ion ($^1B_2 \leftarrow {}^1A_1$). Comparisons with theory and with previous work are made wherever possible. The effect of environment on the electronic spectrum of NO_2^- is discussed. The NO_2^- spectra also are compared with the spectra of other 18-valence electron molecules, such as O_3, SO_2, HCO_2^-, ONCl, etc. The simplest LCAO–MO treatment appears to give a qualitatively correct description of the excited electronic states of NO_2^-

Introduction

Within the last few years, considerable progress has been made toward understanding the electronic spectra of polyatomic molecules. Although much attention has been given to large aromatic hydrocarbons, a survey of the literature reveals that relatively few triatomic molecular electronic spectra have been completely analyzed. The vapor spectra of triatomic molecules are sometimes sharp enough to permit analysis of the rotational fine structure, from which the transition moment direction and the geometry change can be deduced. However, even in such cases, there may be so many closely spaced bands present in the spectrum that the vibrational analysis is made difficult. Furthermore, if the molecule is very different from a symmetric top, the rotational analysis becomes quite difficult. In the cases in which the bands are broadened by predissociation, less information can be obtained.

The study of crystal and mixed crystal spectra has provided exact information about symmetry properties and vibrational structure of the electronic transitions of large, complex molecules. In this paper and in the following one, the results of such a study are reported for the lowest singlet-singlet electronic transition of the NO_2^- molecule-ion. Although it has been known since 1934 that the spectra of crystalline $NaNO_2$ and KNO_2 are sharp at low temperatures,[3] a complete analysis has not yet been given. The recent polarization studies of Trawick and Eberhardt[4] have provided additional information, which, together with the vibrational analysis presented in this work, lead to conclusions about the nature of the ground and lowest excited electronic states of this molecule. These results should also be applicable to other related molecules which possess the same number of valence electrons and similar geometry, and comparisons and predictions will therefore be made where possible.

Experimental

Mallinckrodt Analytical Reagent Grade $NaNO_2$ was further purified by recrystallization from water. Single crystals of suitable thickness were prepared readily by crystallization from molten $NaNO_2$ between quartz disks. The experimental arrangement used to record the absorption and fluorescence spectra of single crystals at low temperature has been described in a previous publication.[5] In this work, a tungsten filament lamp was the source for the absorption experiments, and a medium-pressure Hg arc with a Corning 5860 filter was used to excite the fluorescence of $NaNO_2$. All spectra were recorded on Kodak

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[1] This research was generously supported by the Office of Ordnance Research of the United States Army, under Contract DA-30-115 ORD-728 with the University of Rochester.

[2] Department of Theoretical Chemistry, Cambridge University, England. Post-doctoral fellow, 1955 to 1956, under a grant by the Shell Fellowship Committee to the Department of Chemistry of the University of Rochester.

[3] G. Rodloff, *Z. Physik*, **91**, 511 (1934).

[4] W. G. Trawick and W. H. Eberhardt, *J. Chem. Phys.*, **22**, 1462 (1954).

[5] J. W. Sidman, THIS JOURNAL, **78**, 4217 (1956).

103-0 or 103-a-F plates. Fe arc spectra were used to calibrate the wave lengths.

The $NaN^{15}O_2$ was prepared by reducing fused $NaN^{15}O_3$ with powdered Pb.[6,7]

Results

The polarized absorption and fluoresence spectra of crystalline $NaNO_2$ at 77°K. and at 4°K. are shown in Figs. 1 and 2. A summary of the results of the vibrational analyses, which are further discussed in section (B), is given in Table I.

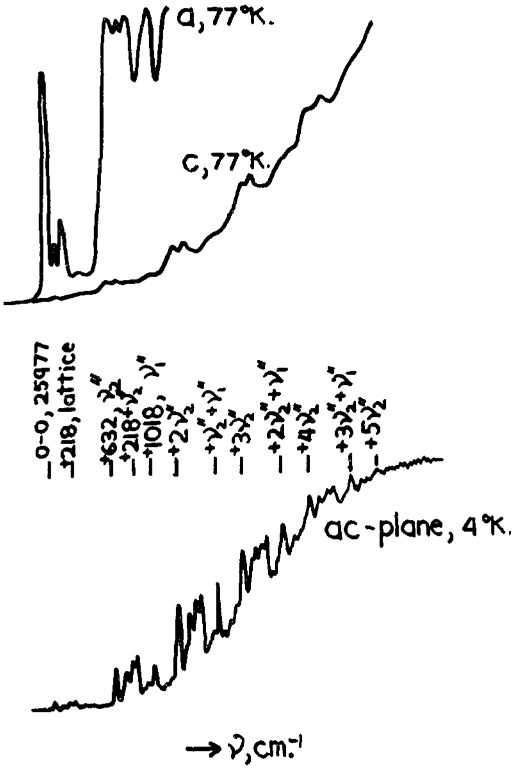

Fig. 1.—Microphotometer tracing of the absorption spectrum of $NaN^{14}O_2$, tungsten strip filament lamp source: top, polarized spectrum of single crystal, 77°K., *ac*-plane; bottom, *ac*-plane, 4°K.

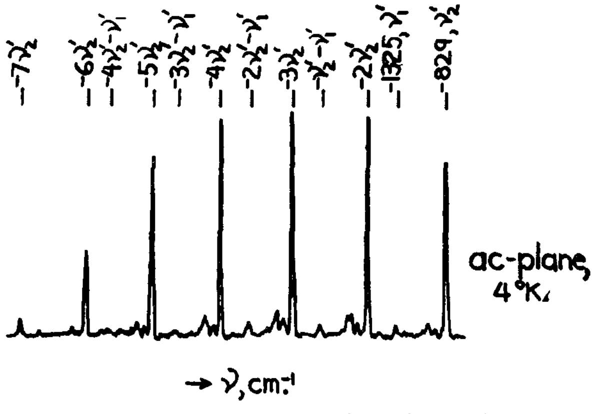

Fig. 2.—Microphotometer tracing of the fluorescence spectrum of $NaN^{14}O_2$, *ac*-plane, 4°K. Lines in the source obscure the 0–0 band.

TABLE I

SUMMARY OF THE RESULTS OF THE VIBRATIONAL ANALYSES OF THE $^1B_2 \leftarrow {}^1A_1$ ABSORPTION AND FLUORESCENCE TRANSITIONS OF $NaN^{14}O_2$ AND $NaN^{15}O_2$ AT 77 AND AT 4°K.

Frequencies are in $cm.^{-1}$.

	$NaN^{14}O_2$	$NaN^{15}O_2$
0–0, $^1B_2 \leftarrow {}^1A_1$, 77°K.	25960 ± 8	25960 ± 8
0–0, $^1B_2 \leftarrow {}^1A_1$, 4°K.	25977 ± 3	25977 ± 3
Vibrational frequencies in $^1A_1$, 4°K.	$\nu_1 = 1325 \pm 4$ $\nu_2 = 829 \pm 2$	$\nu_1 = 1306 \pm 4$ $\nu_2 = 824 \pm 2$
Vibrational frequencies in $^1B_2$, 4°K.	$\nu_1 = 1018 \pm 4$ $\nu_2 = 632 \pm 4$	$\nu_1 = 1006 \pm 4$ $\nu_2 = 621 \pm 4$
Lattice frequencies in $^1A_1$, 4°K. (± 15 $cm.^{-1}$)	45, 105, 165, 205, 270	45, 80(?), 105, 165, 205, 270
Lattice frequencies in $^1B_2$, 4°K. (± 15 $cm.^{-1}$)	65, 110, 155, 180, 218	65, 110, 155, 180, 218

Discussion and Interpretation

(A) Assignment of the Electronic Transitions.—The determination of the symmetry properties of the combining states in an electronic transition of a polyatomic molecule is as important as the determination of the energy and transition probability. Until recently, the direct determination of this property has been quite difficult. It has often been difficult or impossible to determine correctly the electronic symmetry properties from polarized spectra of single crystals, due to intermolecular coupling between identical molecules in the crystal.[8,9] Such effects are absent in the polarized absorption spectra of dilute mixed crystals, and considerable data are now available for the electronic assignments of the aromatic hydrocarbons from mixed crystal studies.[10]

The crystals which have been studied previously are molecular crystals, in which the molecule and its nearest neighbors are identical. $NaNO_2$ is an ionic crystal, and the nearest neighbors of the NO_2^- ions are Na^+ ions, which shield the NO_2^- ions from each other. Consequently, effects due to intermolecular coupling, such as dichroic splitting of the 0–0 band and/or formation of trapped excitons,[9,11] should be much less prominent in $NaNO_2$, which may be regarded as a concentrated (50%) mixed crystal in which there is order with respect to the position and orientation of both the solute (NO_2^-) and solvent (Na^+).

Trawick and Eberhardt[4] have studied the polarization properties of the electronic transitions of single crystals of $NaNO_2$ at 77°K. They have found that the origin of the lowest absorption band at λ 3851.4 Å. is polarized perpendicular to the plane of the NO_2^- ion. The results of this investigation are in agreement with Trawick and Eberhardt's work. However, thicker crystals at wave lengths shorter than λ 3851.4 Å. show that there is weak but definite absorption for light polarized in the plane of the NO_2^- ion (Fig. 1). This will be discussed in further detail in section (C).

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(6) J. Turner, *J. Soc. Chem. Ind.*, **34**, 585 (1915).

(7) $HN^{15}O_3$ was obtained from the Isomet Corporation, 118 Union Street, Palisades Park, N. J. The isotopic concentration of N^{15} was 99.5%.

(8) D. S. McClure and O. Schnepp, *J. Chem. Phys.*, **23**, 1575 (1955).

(9) J. W. Sidman, *Phys. Rev.*, **102**, 96 (1956).

(10) J. W. Sidman and D. S. McClure, *J. Chem. Phys.*, **24**, 757 (1956); J. W. Sidman, *ibid.*, **25**, 115, 122 (1956).

(11) J. W. Sidman, THIS JOURNAL, **79**, 305 (1957).

The polarization of the crystal absorption spectrum does not in itself lead to an unambiguous electronic assignment, since it is possible that the electronic transition might be forbidden by symmetry and that its appearance might be due to a vibrational or to a lattice perturbation, or both. However, an unambiguous determination often can be made if the same electronic transition appears in fluorescence. Excitation of crystalline $NaNO_2$ with the λ 3660 Å. Hg group produces a weak but detectable fluorescence spectrum, which nearly is the mirror image of the absorption spectrum.[12] Although lines from the Hg arc interfere in the region near λ 3851.4 Å., the vibrational analyses of the absorption and the fluorescence spectra leave no doubt that the lowest absorption band at λ 3851.4 Å. is the 0–0 band of an electronic transition which is allowed by symmetry and which is polarized perpendicular to the plane of the NO_2^- ion. Since the molecular point group, molecular site group in the crystal, and crystallographic space group are all C_{2v}, the polarization results of the crystal spectra should be directly applicable to the free ion.

The crystal structure of $NaNO_2$ has been extensively and carefully investigated.[13–15] A diagram of the crystal and molecular structure is shown in Fig. 3. The crystallographic axes are labeled according to Ziegler's notation.[13]

If a totally-symmetric electronic ground state is assumed, ($^1A_1$), the polarization results lead to the $^1B_2 \leftarrow {}^1A_1$ electronic assignment for the lowest absorption transition of NO_2^-.[16] The orbital assignment proposed by Trawick and Eberhardt is $n_N \rightarrow \pi_3$, which is in agreement with the fact that the transition is allowed by symmetry but is nevertheless weak ($\epsilon_{max} \cong 25$, $\lambda_{max} \cong 3550$ Å.[17]). The $n_O \rightarrow \pi^*$ transitions of carbonyl compounds are also weak, even though the transition may be formally allowed by symmetry, as in glyoxal[18] and biacetyl.[19] This is to be expected, since the n- and π-orbitals do not simultaneously possess large amplitude in the same regions of space, so that the integrand in the transition moment integral $\int(n)^*R(\pi)d\tau$ is everywhere small, and consequently leads to low intensity for $n \rightarrow \pi^*$ transitions. Furthermore, $n \rightarrow \pi^*$ transitions which are allowed by symmetry possess a transition moment which is necessarily perpendicular to the nodal plane of the π-orbitals, since the n-orbitals and the π-orbitals are, respectively, symmetric and antisymmetric with respect to reflection in the plane of the molecule. This has been verified experimentally in glyoxal from the analysis of the rotational structure.[18] Thus, the $^1B_2 \leftarrow {}^1A_1$, $n_N \rightarrow \pi_3$ assignment for the lowest transition of NO_2^- appears to be reasonable.

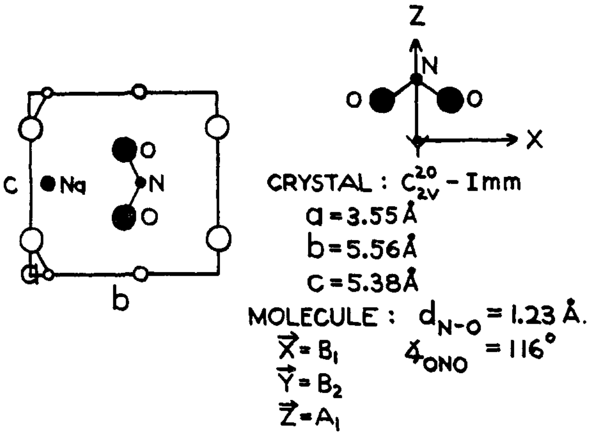

Fig. 3.—Crystal structure of $NaNO_2$ and molecular structure of NO_2^-. The clear circles are at $a = 0$, whereas the dark circles are displaced by $a/2$. The crystallographic axes are labelled according to Ziegler's notation.[13] The bond distance and bond angle of NO_2^- are from Carpenter's work.[14]

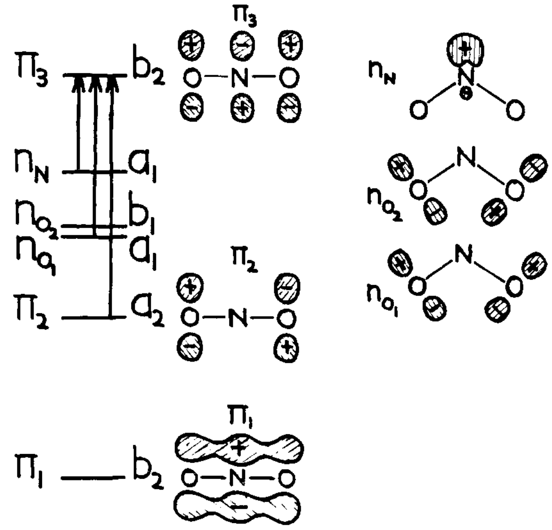

Fig. 4.—Schematic diagram of the one-electron n- and π-molecular orbitals of NO_2^-. The orbital transitions which may correspond to the observed electronic transitions of NO_2^- are shown in the diagram.

A qualitative orbital energy level diagram for the n- and π-orbitals of the NO_2^- molecule is shown in Fig. 4, and orbital assignments of the three electronic transitions which are observed at wave lengths longer than 2000 Å. are also shown in the diagram.[17] It is assumed that the σ-bonding orbitals are lower than π_1, and the σ*-antibonding orbitals are higher than π_3. This is reasonable, since the hybridized AOs which form the σ-MOs overlap with each other more than the p-AOs which form the π-MOs, so that the energy difference between the σ- and σ*-MOs is greater than the energy difference between the π- and π*-MOs. The n-MOs are essentially AOs (which may be hybridized), since they are formed from orbitals which overlap very little with the σ-orbitals. Since O is more electronegative than N, the n_O orbitals are placed slightly below the n_N orbital[4]. The two n_O orbitals should

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[12] J. W. Sidman, THIS JOURNAL, **78**, 2911 (1956).

[13] G. E. Ziegler, *Phys. Rev.*, **38**, 1040 (1931).

[14] G. B. Carpenter, *Acta Cryst.*, **5**, 132 (1952).

[15] M. R. Truter, *ibid.*, **7**, 73 (1954).

[16] The group-theoretical notation is that of H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1943.

[17] H. L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953).

[18] J. C. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954).

[19] J. W. Sidman and D. S. McClure, THIS JOURNAL, **77**, 6461, 6471 (1955).

be nearly degenerate, since the overlap of the AOs from which they are formed is so small.

The $n_O \rightarrow \pi_3$ transition(s) of NO_2^- has been previously assigned[4] to the $\lambda_{max} \cong 3000$ Å., $\epsilon_{max} \cong 15$ band.[17] The present work has not studied wave lengths shorter than 3300 Å., due to the complete absorption by the double Pyrex glass Dewar vessels at the shorter wave lengths. An examination of Rodloff's spectral tracings[3] reveals that the bands which are observed near 3200 Å. are broader than the bands near 3800 Å., but there is no definite evidence that they belong to another electronic transition. The broadening of the bands which correspond to higher vibrational transition may be due to perturbations by the $n_O \rightarrow \pi_3$, ${}^1B_2 \leftarrow {}^1A_1$ transition, as Trawick and Eberhardt have suggested.[4] The absence of the $n_O \rightarrow \pi_3$ transition in the crystal spectrum is difficult to understand, but possibly it could be explained if the upper state were unstable. Absorption due to this transition would then be nearly continuous, and would not appear unless the crystal thickness were much greater than that which is necessary for detecting the very sharp $n_N \rightarrow \pi_3$ transition. The intensity due to a very diffuse transition at any individual wave length would thus be very much less than the intensity due to a sharp transition in the same region, even though the integrated intensities over the corresponding regions of absorption are similar, as the solution spectra suggest.[17] This interpretation must be considered tentative.

At shorter wave lengths, a more intense band of NO_2^- is found, both in aqueous solution ($\lambda_{max} \cong 2100$ Å., $\epsilon_{max} \cong 5500$[17]) and in crystalline $NaNO_2$[4]. The polarization studies and the moderately high intensity are in agreement with the $\pi_2 \rightarrow \pi_3$, ${}^1B_1 \leftarrow {}^1A_1$ assignment suggested by Trawick and Eberhardt.[4] Friedman[17] considers this transition to be due to an intermolecular electron-transfer transition from NO_2^- to H_2O. The fact that the energy of this transition is only slightly different in the crystal from the value observed in aqueous solution is strong evidence against Friedman's interpretation.

The simple orbital diagram in Fig. 4 thus appears to be successful in accounting for the polarization properties and the order of the excited singlet states of NO_2^-. In section (D) of this paper, comparisons between the spectra of NO_2^- and other isovalent molecules will be given.

(B) Analysis of the Vibrational and Lattice Structure.—In an electronic transition of a polyatomic molecule in the crystalline state, fine structure due to transitions involving simultaneous changes in the vibrational and lattice states usually appears in the spectrum. In order to resolve this structure, it is desirable to study the spectra at very low temperatures. If the vibrational fine structure can be analyzed, it is sometimes possible to determine how the arrangement of the nuclei and the bonding between them differs in the upper and lower electronic states. This leads to an understanding of valence and molecular structure which is deeper than that obtained either from the study of the vibrational spectrum of the ground electronic state alone or from the study of an electronic spectrum which is broad because of perturbations by the environment. The full power of the vibrational fine structure analysis in elucidating the molecular and electronic structure can be felt if the molecule is small and if isotopically substituted species are available. The recent availability[20] of isotopically pure N^{15} has enabled such a study to be performed for NO_2^-.

The lattice fine structure which appears in the electronic transitions of molecules in crystals and mixed crystals provides information about lattice oscillations, and should be valuable in understanding intermolecular forces in the solid state. So far, extensive interpretation of the lattice structure has not been made, although lattice frequencies in many molecular crystals and mixed crystals have been determined from the analysis of the electronic transitions.[10]

The analysis of the fine structure of the $n_N \rightarrow \pi_3$, ${}^1B_2 \leftarrow {}^1A_1$ absorption transition of NO_2^- in crystalline $NaN^{14}O_2$ and $NaN^{15}O_2$ at 4°K. is quite straightforward. At 77°K., the 0–0 band in both $NaN^{14}O_2$ and $NaN^{15}O_2$ is 25960 ± 8 cm.$^{-1}$, whereas at 4°K. the 0–0 band has shifted slightly to 25977 ± 3 cm.$^{-1}$ in both cases. It is possible that there is a calibration error in Rodloff's work,[3] since the work of Trawick and Eberhardt and of the present author are in agreement with respect to the 0–0 frequency at 77°K. The most prominent feature of the absorption transition in $NaN^{14}O_2$ is the progression of a single frequency of 632 ± 4 cm.$^{-1}$ (621 ± 4 cm.$^{-1}$ in $NaN^{15}O_2$) in which the intensity maximum is in the fourth band of the progression. This is seen most readily in the microphotometer tracings in Figs. 2 and 5 of ref. 3, in which the source is a hydrogen discharge tube, which provides a more uniform background than the tungsten filament lamp employed in this research. Besides the main progression, additions of a frequency of 1018 ± 4 cm.$^{-1}$ (1006 ± 4 cm.$^{-1}$ in $NaN^{15}O_2$) to each of the bands in the main progression are also seen in the spectrum. Rodloff has previously identified the main progression (A_1, B_1, C_1, D_1, etc., in Fig. 2, ref. 3), but he has not identified the 1018 cm.$^{-1}$ interval. It is clearly seen in his tracing, however (A_1, B_5; B_1, C_5; C_1, D_5; etc., in Fig. 2 of ref. 3). It is clear that this identification is correct, and that B_5 represents a vibrational addition to A_1 and not to B_1, since there is no band between A_1 and B_1 which corresponds to band B_5 between B_1 and C_1.

The analysis of the lattice structure in the absorption spectrum yields the values 65, 110, 155, 180 and 218 cm.$^{-1}$ for the lattice frequencies of $NaNO_2$ in ${}^1B_2$ at 4°K. Due to the greater diffuseness of the lattice additions, the lattice frequencies may be uncertain by ±15 cm.$^{-1}$. Within this limit of error, the lattice frequencies are indistinguishable in $NaN^{14}O_2$ and in $NaN^{15}O_2$.

The analysis of the fluorescence transition is also quite straightforward. The main progression in $NaN^{14}O_2$ is 829 ± 2 cm.$^{-1}$ (823 ± 2 cm.$^{-1}$ in $NaN^{15}O_2$). The 1325 ± 4 cm.$^{-1}$ frequency in ${}^1A_1$ of $NaN^{14}O_2$ corresponds to 1018 ± 4 cm.$^{-1}$ in ${}^1B_2$. Virtually all of the intensity in the fluorescence transition is contained in the bands of the 829

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(20) W. Spindel and T. I. Taylor, *J. Chem. Phys.*, **24**, 626 (1956).

cm.$^{-1}$ progression, in which the intensity maximum is in the fourth band. The bands corresponding to the 1325 cm.$^{-1}$ frequency and the lattice additions appear only very weakly in fluorescence. A correspondence between lattice frequencies in $^1A_1$ and $^1B_2$ is also found. The lattice frequencies (± 15 cm.$^{-1}$) in $^1A_1$ of $NaN^{14}O_2$ and $NaN^{15}O_2$ at 4°K. are 45, 105, 165, 205 and 270 cm.$^{-1}$. In addition, a lattice frequency of 80 cm.$^{-1}$ possibly appears in $NaN^{15}O_2$. It is interesting to observe that the highest frequency lattice mode in $^1B_2$ and in $^1A_1$ is different by an amount which far exceeds the experimental error.

The absorption and fluorescence spectra, although very similar, do show some differences, so that they are not quite "mirror images" of each other. The lattice structure is much more prominent in absorption than in fluorescence, as can be seen from an examination of Figs. 1 and 2. It is interesting to note that the bands of the 632 cm.$^{-1}$ progression (in absorption) are accompanied by very pronounced lattice structure, but that the lattice structure is far less pronounced, or is even absent, in the 1018 cm.$^{-1}$ additions to the bands of the 632 cm.$^{-1}$ progression.

The detailed assignments of the vibrational states of $NaNO_2$ and the calculation of the force constants of NO_2^- are discussed in detail in the following paper.[21] A summary of the analyses of the absorption and fluorescence spectra is given in Table I. Anharmonic corrections in the ν_2 progression are negligible (<3 cm.$^{-1}$) for the first few members of the progression. In fluorescence, the anharmonic correction to $6\nu_2$ is approximately 20 cm.$^{-1}$.

(C) The Effect of the Environment on the Electronic Transition.—Since the lowest absorption transition of NO_2^- can be studied under a variety of conditions, it is possible to determine the relationship between the environment and the nature of the spectrum.

(1) **The Effect of Temperature.**—The increase in sharpness of the spectrum with decrease in temperature is seen in Fig. 1 of ref. 3. This is due to a decrease in the population of the excited lattice states. Even at 77°K., absorption due to molecules in the first excited state of the 110 cm.$^{-1}$ lattice mode can be detected in the spectrum. With the same crystal at 4°K., the bands corresponding to the "hot" lattice transition of the 110 cm.$^{-1}$ frequency are absent. The small shift of the bands when the temperature is decreased from 77 to 4°K. probably is due to further contraction of the lattice.

(2) **The Effect of Other Ions.**—The environment of the NO_2^- ion can be altered by changing the positive ion in the lattice or by dissolving it in the lattice of another crystal. In KNO_2, the bands at 77°K. are much broader than the bands in $NaNO_2$ at the same temperature. Even at 4°K., the KNO_2 bands are more diffuse than the $NaNO_2$ bands. The results found in this research for KNO_2 are in good agreement with the results of Rodloff,[3] who has given photographs and tracings of the KNO_2 absorption spectrum at low temperature. The fluorescence bands of KNO_2 are correspondingly broader than the fluorescence bands of $NaNO_2$. The 0–0 band in KNO_2 at 4°K. is 25412 ± 10 cm.$^{-1}$, which constitutes a shift of 565 cm.$^{-1}$ to lower frequencies relative to $NaNO_2$ at 4°K. The vibrational frequencies in $^1B_2$ of KNO_2 are 616 and 1015 cm.$^{-1}$, in good agreement with the frequencies in $^1B_2$ of $NaNO_2$. The lattice structure is partially resolved at 4°K., and a lattice frequency of 120 cm.$^{-1}$ (in $^1B_2$) can be detected. The vibrational envelope of the $^1B_2 \leftarrow {}^1A_1$ transition is very similar in $NaNO_2$ and in KNO_2, the principal difference being a shift of the 0–0 band and a decrease in sharpness in KNO_2.

In the environment of a still larger positive ion, the bands become so broad that the vibrational structure appears diffuse. At 77°K., it is not possible to resolve any vibrational structure in the $^1B_2 \leftarrow {}^1A_1$ transition in $CsNO_2$. Rodloff found no structure in the corresponding absorption transition of barium nitrite at 20°K.[3] In dilute mixed crystals of NO_2^- in KBr or in KCl,[22] the $^1B_2 \leftarrow {}^1A_1$ transition is shifted to lower frequencies (0–0 band = 25100 ± 100 cm.$^{-1}$ at 77°K.), and the bands are broader than in crystalline $NaNO_2$ at the same temperature.

The red shift and increase in diffuseness in the case of the larger positive ions can be understood on the basis of the MO description of the $n_N \rightarrow \pi_3$, $^1B_2 \leftarrow {}^1A_1$ transition. The $n_N \rightarrow \pi_3$ electronic transition transfers electronic charge from the nitrogen atom to the N–O bonds, and therefore leads to increased electronic charge near the O atoms. The dipole moment in the excited $^1B_2$ state is therefore expected to be higher than in the ground $^1A_1$ state. Since the larger positive ions are more polarizable than the smaller ones, they will preferentially stabilize the electronic state with the higher dipole moment. Therefore, the more polarizable positive ions should decrease the energy of the $^1B_2$ state relative to the $^1A_1$ state, as is observed. Greater coupling of the low frequency lattice vibrations of the positive ion with the electronic transition of the NO_2^- ion is also expected to occur in the case of the more polarizable positive ions, which might possibly account for the greater diffuseness of the bands of the $^1B_2 \leftarrow {}^1A_1$ transition in lattices containing K^+, Cs^+ and Ba^{++} ions.

(3) **Anomalies in the Polarization of the Absorption and Fluorescence Bands.**—An examination of Fig. 1 reveals that the vibrational and lattice structure of the $^1B_2 \leftarrow {}^1A_1$ transition shows a weak but definite intensity in the *c*-axis component of the crystal spectrum. A careful examination of the plate revealed that the 0–0 band appeared to be completely *a*-axis polarized, but that the lattice additions to the 0–0 band, which are weaker than the 0–0 band in the *a*-axis spectrum, did appear weakly in the *c*-axis spectrum. The lattice additions to the 0–0 band therefore lead to a partial depolarization of the absorption spectrum. Some of the intensity of the higher, more intense vibrational bands in the *c*-axis spectrum may be due to unavoidable errors involved in the optical

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[21] J. W. Sidman, THIS JOURNAL, **79**, 2675 (1957).

[22] E. Hutchinson and P. Pringsheim, *J. Chem. Phys.*, **23**, 1113 (1955).

arrangement. However, in the regoin near the 0-0 band, the *c*-axis component of the lattice structure cannot be due to experimental error. Since the *c*-axis corresponds to a direction in the plane of the NO_2^- molecule, the excitation of lattice quanta in the electronic transition must therefore be accompanied by oscillations of the NO_2^- molecule about the molecular symmetry axis. Hexter and Dows[23] have discussed the effect upon the dichroic ratios, in the vibrational spectra of molecular crystals, of libration of molecules about axes perpendicular to that of the transition moment of the molecular vibration. These results are in qualitative agreement with Hexter and Dows' explanation.

The fluorescence spectrum of single crystals of $NaNO_2$ also shows anomalous polarization. Both spectroscopic examination and direct visual observation indicate that the fluorescence spectrum at 77°K. is strongly depolarized relative to the absorption spectrum. (The 0-0 band itself could not be observed in fluorescence, due to the presence of source lines in the same region of the spectrum.) The *c*-axis fluorescence is approximately 50% as intense as the *a*-axis fluorescence. The degree of depolarization of the fluorescence spectrum is so much greater than the degree of depolarization of the absorption spectrum that it appears necessary to explain it in a different way. In previous studies of the polarized absorption and fluorescence spectra of crystals and mixed crystals, it has been found that the fluorescence spectrum at low temperatures may be partially or completely depolarized with respect to the corresponding absorption spectrum.[9,24] The detailed explanation of this puzzling phenomenon has not yet been proposed, and additional work appears necessary.

(D) **Comparison with the Electronic Spectra of Other Molecules.**—Mulliken[25] and, more recently, Walsh[26] have discussed the orbitals and spectra of AB_2-type molecules. The results of this work on NO_2^- are in agreement with Walsh's $^1B_2 \leftarrow {}^1A_1$ assignment[27] for the lowest electronic absorption transition of other isovalent molecules, such as SO_2. However, the higher excited singlet states do not appear to correspond in all cases. In section (A), reasons were given for assigning the second transition of NO_2^- as $n_O \rightarrow \pi_3$, $^1B_2 \leftarrow {}^1A_1$. In SO_2, there is strong evidence, based on the appearance of both a_1 and b_1 vibrations in the electronic transition, that the second transition is of the $\pi \rightarrow \pi^*$ (or $n \rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$) type, and that the upper state is either $^1A_1$ or$^1B_1$.[28]

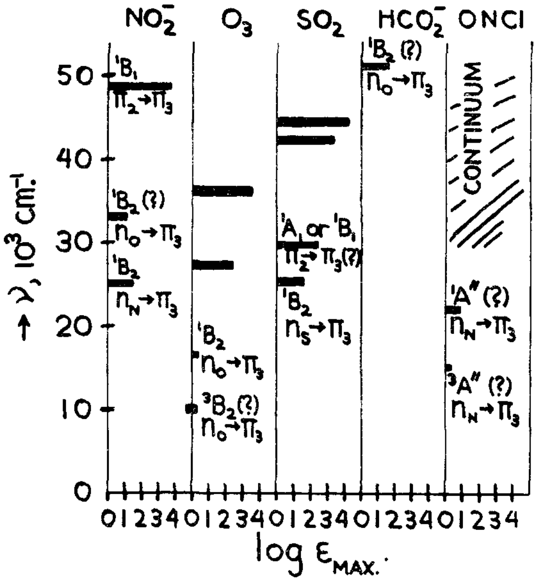

Fig. 5.—Excited electronic states of molecules which are isovalent with NO_2^-. References to the experimental data for O_3, SO_2 and ONCl are to be found in Walsh's paper.[26] The data for HCO_2^- are from Bielecki and Henri.[30] Some of the more certain assignments are shown, and others are given by Walsh.[26]

The qualitative orbital energy level diagram for NO_2^- which is shown in Fig. 4 gives a reasonable description of the NO_2^- spectrum, although it differs in several respects from the diagram given by Walsh.[26] It is likely that the relative orbital energies will vary from one molecule to another, and that appreciable differences may occur within this isovalent series. In the sequence HCO_2^-, NO_2^-, O_3, it is seen that the corresponding excited electronic states are lowered as the central atom becomes more electronegative. It is quite reasonable to expect that excited states derived from the $\pi_2 \rightarrow \pi_3$ configuration should decrease in energy when the central atom is more highly electronegative, since this will decrease the orbital energy of π_3 but will not affect the orbital energy of π_2. The $\pi_2 \rightarrow \pi_3$ transition has not been observed below 50000 cm.$^{-1}$ in HCO_2^-. In HCOOH[29] the strong absorption in the vicinity of 64500 cm.$^{-1}$ may be due to the $\pi \rightarrow \pi$ transition. The $\pi_2 \rightarrow \pi_3$ transition moves down to 49000 cm.$^{-1}$ in NO_2^-, and moves down still further to either 27000 cm.$^{-1}$ or to 36000 cm.$^{-1}$, more probably the latter, in O_3. It is more difficult to predict the behavior of the $n \rightarrow \pi$ transitions, since the non-bonding orbital of the central atom and the antibonding π_3 orbital are both lowered in energy by an increase in the electronegativity of the central atom. However, the $n_O \rightarrow \pi_3$ transition involving the non-bonding orbitals of the end oxygen atoms should decrease in energy in the sequence HCO_2^-, NO_2^-, O_3. These simple considerations appear to be qualitatively capable of accounting for many of the spectral differences in Fig. 5. The molecules SO_2 and ONCl are included for completeness, but the bonding in these molecules is considerably different than in HCO_2^-, NO_2^- and O_3, inasmuch as S can employ 3d AOs whereas ONCl is asymmetric.

It should be emphasized that the simple one-electron LCAO-MO description of the electronic transitions is at best rather crude. In particular, it

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[23] R. M. Hexter and D. A. Dows, *J. Chem. Phys.*, **25**, 504 (1956). I am grateful to the authors for a preprint of this paper.

[24] J. W. Sidman, *ibid.*, **25**, 115 (1956).

[25] R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 204 (1942).

[26] A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

[27] Since Walsh and the present author have employed different labelling schemes for the axes in NO_2^-, it is necessary to interchange B_1 and B_2 when comparing results.

[28] N. Metropolis, *Phys. Rev.*, **60**, 295 (1941).

[29] W. C. Price and W. M. Evans, *Proc. Roy. Soc. (London)*, **A162**, 110 (1937).

[30] J. Bielecki and V. Henri, *Chem. Ber.*, **46**, 3627, 3650 (1913).

is necessary to explicitly consider configurational interaction (CI) in treating the n → π transitions, since in NO_2^- both the $n_N \rightarrow \pi_3$ configuration and one of the $n_O \rightarrow \pi_3$ configurations belong to the B_2 representation of C_{2v}. The extent of CI will in general vary from molecule to molecule, and it is possible that this may be a prime consideration in determining the energies of the n → π transitions in these molecules.

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ROCHESTER, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Electronic and Vibrational States of the Nitrite Ion. II. Vibrational States[1]

BY JEROME W. SIDMAN[2]

RECEIVED AUGUST 16, 1956

The infrared absorption spectra of $NaN^{14}O_2$ and $NaN^{15}O_2$ have been examined. The vibrational frequencies and assignments deduced from the infrared absorption spectrum agree with the results of the fluorescence and Raman spectra. The vibrational assignments for the lowest ($^1A_1$) state are, for $NaN^{14}O_2$, ν_1 = 1325 cm.$^{-1}$, ν_2 = 829 cm.$^{-1}$, ν_3 = 1270 cm.$^{-1}$, and, for $NaN^{15}O_2$, ν_1 = 1306 cm.$^{-1}$, ν_2 = 824 cm.$^{-1}$, ν_3 = 1243 cm.$^{-1}$. A complete force constant calculation has been performed for NO_2^-, with the results, $f_d = 8.1_0$, $f_{dd} = 2.3_5$, $f_\alpha/d^2 = 2._5$, $f_{d\alpha}/d = 0._9$, in units of 10^5 dyne cm.$^{-1}$. The partial vibrational assignments in the first excited singlet electronic state ($^1B_2$) are, for $NaN^{14}O_2$, ν_1 = 1018 cm.$^{-1}$, ν_2 = 632 cm.$^{-1}$, and, for $NaN^{15}O_2$, ν_1 = 1006 cm.$^{-1}$, ν_2 = 621 cm.$^{-1}$. From a quantitative application of the Franck-Condon principle, the bond angle in the excited state is calculated to change by approximately 9° for the 0–0 transition. The bond distance in the excited state changes little, if at all. The geometry and bonding are discussed. The vibrational frequencies and force constants are compared with the values in related molecules, such as O_3, HCO_2^- and SO_2. Some of the similarities and differences can be explained in terms of valence theory. However, the large value of f_{dd} in O_3 and in NO_2^-, but not in SO_2 or, presumably, in HCO_2^-, cannot be explained completely at the present time.

Introduction

The vibrational spectra of triatomic molecules have received considerable study during recent years. Although it might at first sight appear to be simple to identify and to assign the three fundamental vibrational frequencies of a triatomic molecule, a few molecules, of which O_3 is possibly the best known example, have tenaciously resisted analysis until very recently. A survey of the literature reveals that NO_2^-, which is iso-electronic with O_3 and geometrically very similar to it, is another triatomic molecule for which the vibrational assignment is uncertain.

In the previous paper,[3] the analysis of the vibrational fine structure of the $^1B_2$—$^1A_1$ electronic transition has been given for the absorption and fluorescence spectra of crystalline $NaN^{14}O_2$ and $NaN^{15}O_2$ at 4°K. In this paper, the infrared spectra, vibrational assignments and force constants of NO_2^- will be discussed.

Experimental

The preparation of $NaN^{15}O_2$ has been described in the previous paper.[3] Infrared absorption spectra were recorded on a Perkin-Elmer Double Beam Recording Spectrophotometer, Model 21, using a NaCl prism. Atmospheric H_2O and CO_2 absorption bands were used to calibrate the wave lengths.

The most convenient method for studying the infrared spectra was the KBr-pressed pellet. The $NaNO_2$ was ground in an agate mortar with Harshaw Chemical Company's Spectroscopic Grade KBr. Pressed pellets of 1 mm. thickness which contained 0.3% $NaNO_2$ were suitable. Comparison of the spectrum of the pressed pellet with the spectrum of the dilute mixed crystal of NO_2^- in KBr showed numerous differences between the spectra, indicating that the pressed pellet spectrum is due to $NaNO_2$ dispersed in KBr, and not to a solid solution of NO_2^- in KBr.[4] Furthermore, the infrared spectra of pressed KBr pellets of other nitrite salts showed differences between themselves, which is additional evidence that the spectra are not due to a solid solution of the nitrite salt in KBr, but are due to physically dispersed microcrystals.

A single recrystallization from H_2O yielded a sample of $NaNO_2$ which showed no trace of the intense NO_3^- band at 1300 cm.$^{-1}$.

Results

The infrared spectra of $NaN^{14}O_2$ and $NaN^{15}O_2$ are shown in Fig. 1. The assignments of the bands are given in Table I.

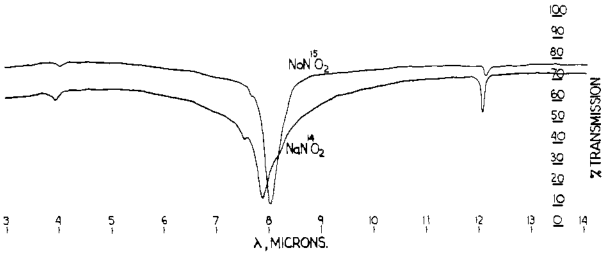

Fig. 1.—Infrared absorption spectra of $NaN^{14}O_2$ and $NaN^{15}O_2$ in KBr pressed pellets. The pure KBr pellet was used as a blank, and absorption due to traces of adsorbed H_2O have been subtracted out of the spectrum. Perkin-Elmer Model 21 Recording Infra-Red Spectrophotometer NaCl prism, linear wave length scale. The spectra were calibrated against atmospheric H_2O and CO_2 absorption bands.

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[2] Department of Theoretical Chemistry, Cambridge University, England. Post-doctoral fellow, 1955–1956, under a grant by the Shell Fellowship Committee to the Department of Chemistry of the University of Rochester.

[3] J. W. Sidman, THIS JOURNAL, **79**, 2669 (1957).

[4] I am grateful to Dr. P. Yuster of the Argonne National Laboratory for a gift of the mixed crystals of NO_2^- with KBr. Since the infrared spectrum of the mixed crystal is currently under investigation at the Argonne Laboratory, further data will not be reported here.