is necessary to explicitly consider configurational interaction (CI) in treating the $n \rightarrow \pi$ 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 $n \rightarrow \pi$ 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]

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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 $NaN^{14}O_2$, $\nu_1 = 1325$ cm.$^{-1}$, $\nu_2 = 829$ cm.$^{-1}$, $\nu_3 = 1270$ cm.$^{-1}$, and, for $NaN^{15}O_2$, $\nu_1 = 1306$ cm.$^{-1}$, $\nu_2 = 824$ cm.$^{-1}$, $\nu_3 = 1243$ 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 $NaN^{14}O_2$, $\nu_1 = 1018$ cm.$^{-1}$, $\nu_2 = 632$ cm.$^{-1}$, and, for $NaN^{15}O_2$, $\nu_1 = 1006$ cm.$^{-1}$, $\nu_2 = 621$ 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.

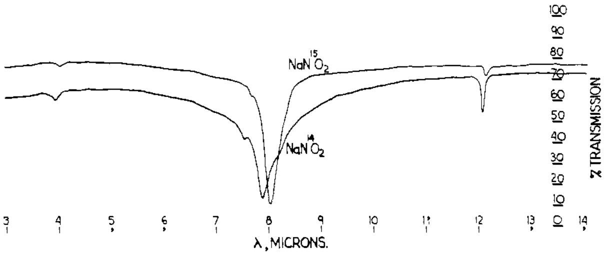

Fig. 1.—Infrared absorption spectra of $NaN^{14}O_2$ and $NaN^{15}O_2$ in KBr pressed pellets. The pure KBr pellet was used as a blank, and absorption due to traces of adsorbed H_2O have been subtracted out of the spectrum. Perkin-Elmer Model 21 Recording Infra-Red Spectrophotometer NaCl prism, linear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

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[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.

TABLE I

ASSIGNMENT OF THE VIBRATIONAL STATES OF NO_2^- [a]

Raman spectrum, $NaN^{14}O_2$ in H_2O [5]				Infrared spectrum, single crystal of $NaN^{14}O_2$ [9]				Infrared spectrum, $NaN^{14}O_2$ and $NaN^{15}O_2$ dispersed in KBr pellet (this work)			
ν, cm.$^{-1}$	Rel. int.	ρ	Assnt.	ν, cm.$^{-1}$	Pol.	Rel. int.	Assnt.[9]	ν, cm.$^{-1}$ $NaN^{14}O_2$	ν, cm.$^{-1}$ $NaN^{11}O_2$	Rel. int.	Assnt.
813	1.0	0.21	ν_2	831	b	s	ν_2	829	824	m	$\nu_2(a_1)$
1240	2.4	.84	ν_3	970	c	w		1270	1243	vs	$\nu_3(b_1)$
1331	12.9	.43	ν_1	1130	a, b	w	(NO_2^-) + (lattice)	1325	1306	m	$\nu_1(a_1)$
				1170–1300	c	ms	(NO_2^-) + (lattice)	2550	2485	w	$2\nu_3$
				1230	a, b	ms					
				1325	b	s	ν_1				
				1360	c	vs	ν_3				
				2120	c	w	$(\nu_2 + \nu_3)$?				
				2670	c	s	$\nu_1 + \nu_3$				

[a] It is suggested that the assignments based on the infrared spectrum of the single crystal are incorrect.

Discussion and Interpretation

(A) Assignment of the Vibrational Frequencies.—The previous data on the vibrational spectrum of NO_2^- are given in Table I, together with results which have been obtained in this work. Literature sources which report more bands than can be attributed to NO_2^- are not included in Table I. A unique vibrational assignment can be proposed from the very careful Raman data due to Langseth and Walles,[5] who have studied the Raman spectra of aqueous $NaN^{14}O_2$. The depolarization ratios of the Raman bands lead to the unexpected conclusion that ν_3, the asymmetric stretching frequency, which is broad and depolarized in the Raman spectrum, is lower than ν_1, the symmetric stretching frequency, which is sharp and polarized in the Raman spectrum. This led Langseth and Walles to propose a structure in which the bond angle was assumed to be nearly 90° and in which a formal bond between the O atoms was assumed. However, such a structure did not agree with the X-ray crystallographic results which were available at that time.[6] Although the more recent structure determinations have led to some revisions, the obtuse-angle model (116°) is considered correct.[7,8]

The fluorescence results reported in the previous paper[3] have shown that molecular vibrational frequencies of 829 cm.$^{-1}$ and 1325 cm.$^{-1}$ appear in the $^1B_2 \rightarrow {}^1A_1$ fluorescence transition of $NaN^{14}O_2$. Since the asymmetric stretching frequency, $\nu_3(b_1)$, is forbidden to appear in this transition, the 1325 cm.$^{-1}$ frequency must therefore correspond to the symmetric stretching frequency, $\nu_1(a_1)$, and the 829 cm.$^{-1}$ frequency must correspond to the bending frequency, $\nu_2(a_1)$. The infrared spectrum of $NaN^{14}O_2$ shows, in addition to the bands at 829 and 1325 cm.$^{-1}$, a much more intense band at 1270 cm.$^{-1}$, upon which the 1325 cm.$^{-1}$ band is superimposed (Fig. 1). The fluorescence, infrared and Raman data are in good agreement, and lead to the assignments shown in Table I. The intensity of ν_3 in infrared absorption is greater than that of ν_1, as is usually the case in triatomic molecules.

The numerical value of ν_3 given in this work does not agree with the work of Newman,[9] who has studied the polarized infrared spectrum of single crystals of $NaN^{14}O_2$ at 77°K. For radiation polarized along the *c*-axis in the *ac*-plane, Newman's spectra show total absorption from 1100 to 1400 cm.$^{-1}$, due to the insurmountable difficulties in preparing thin single crystals. Newman has chosen the high frequency peak at 1360 cm.$^{-1}$ as ν_3, but the low frequency peak at 1170 cm.$^{-1}$ has not been satisfactorily assigned. The *center* of the broad band is in the vicinity of 1270 cm.$^{-1}$, which agrees with the single peak observed in this work. The assignment ν_3 = 1270 cm.$^{-1}$ compares more favorably with the Raman spectrum of an aqueous solution of $NaNO_2$ (ν_3 = 1240 cm.$^{-1}$)[5] than does Newman's assignment ν_3 = 1360 cm.$^{-1}$

The polarized infrared crystal spectrum[9] shows incomplete dichroism for the 831 cm.$^{-1}$ band, even when parallel light is used. The appearance of the 831 cm.$^{-1}$ band in the *a*- and *c*-axis spectra may be induced by librations of the NO_2^- ion in the crystal,[10] since otherwise only the *b*-axis spectrum would be expected to show this band.

The assignments of the a_1 vibrational frequencies in the $^1B_2$ electronic state can be made readily, using the results of the previous paper.[3] The assignments are ν_1 = 1018 cm.$^{-1}$, ν_2 = 632 cm.$^{-1}$, for $NaN^{14}O_2$, and ν_1 = 1006 cm.$^{-1}$, ν_2 = 621 cm.$^{-1}$, for $NaN^{15}O_2$.

(B) Calculation of the Force Constants and Normal Coördinates of NO_2^- in the $^1A_1$ (Ground) Electronic State.—The observation that $\nu_3 < \nu_1$ indicates that the interaction constants are not negligible in NO_2^-. Earlier attempts to account for the vibrational potential energy on the basis of the simple valence or central force fields were not successful.[11] Using the observed frequencies for both $N^{14}O_2^-$ and $N^{15}O_2^-$ in $^1A_1$, it is possible to calculate the force constants for the most general potential function. The procedure for doing this has been described in detail by Polo and Wilson in connection with their calculations for SO_2.[12] The vibrational assignments in cm.$^{-1}$ for $N^{14}O_2^-$ are (without anharmonic corrections) $\nu_1 = 1325 \pm 4$, $\nu_2 = 829 \pm 2$, $\nu_3 = 1270 \pm 4$, and the geometrical data are $\alpha = 116 \pm 3°$, $d = 1.23 \pm 0.03$ Å. Using these data, various sets of force constants which reproduce the frequencies of $N^{14}O_2^-$ can be calculated. The best set of force constants is determined by requiring

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(5) A. Langseth and E. Walles, *Z. physik. Chem.*, **B27**, 209 (1934).

(6) G. E. Ziegler, *Phys. Rev.*, **38**, 1040 (1931).

(7) G. B. Carpenter, *Acta Cryst.*, **5**, 132 (1952).

(8) M. R. Truter, *ibid.*, **7**, 73 (1954).

(9) R. Newman, *J. Chem. Phys.*, **20**, 444 (1952).

(10) R. M. Hexter and D. A. Dows, *ibid.*, **25**, 504 (1956). I am grateful to the authors for a preprint of this paper.

(11) D. Williams, THIS JOURNAL, **61**, 2987 (1939).

(12) S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **22**, 900 (1954).

that the force constants reproduce the observed frequencies for $N^{15}O_2^-$: $\nu_1 = 1306 \pm 4$, $\nu_2 = 824 \pm 2$, $\nu_3 = 1243 \pm 4$. The experimental frequencies are in satisfactory agreement with the Teller–Redlich product rule. The best set of force constants, in units of 10^5 dyne/cm., is $f_d = 8.1_0$, $f_{dd} = 2.3_5$, $f_\alpha/d^2 = 2._5$, $f_{d\alpha}/d = 0._9$.

The normal coördinates readily can be determined, and will be important in connection with the calculations described in the next section. The internal coördinates of the A_1 class which have been used in this calculation are S_1, the symmetric stretching of the two N–O bonds, and S_2, the deformation of the O–N–O angle. The normal coordinates Q_1 and Q_2, which are associated, respectively, with the vibrations ν_1 and ν_2, are related to the symmetry coördinates S_1 and S_2 through the transformation $S_t = L_{kt}Q_k$. The results are $S_1 = 0.3_2Q_1 + 0.0_4Q_2$, $S_2 = -0.2_8Q_1 + 0.3_7Q_2$. The relative contribution of each symmetry coördinate S_t to a given normal coördinate Q_k is given by the ratio of the coefficients in the *t* column of the matrix whose elements are L_{kt}, inasmuch as $(\partial S_t/\partial Q_k)_{Q_{k'}} = L_{kt}$, where all other normal coördinates $Q_k'(k' \neq k)$ are held constant in the partial differentiation. It is thus seen that the normal coördinate Q_1 contains nearly equal amounts of the symmetric stretching of the N–O bonds (S_1) and the angle deformation (S_2). In Q_1, the stretching of the N–O bonds is accompanied by a decrease in the O–N–O angle. The normal coördinate Q_2 contains very little S_1, and may be described adequately as a deformation of the O–N–O angle (S_2).

(C) **The Geometry and Bonding of NO_2^- in the $^1B_2$ (Excited) Electronic State.**—Craig[13] has shown that it is possible to calculate the dimensions of the excited state of a polyatomic molecule if the intensity distribution in the vibrational structure of the electronic transition is known. The intensity distribution is very sensitive to the change of the molecular dimensions when the molecule undergoes an electronic transition, but it is much less sensitive to changes in the force constants.

In the case of NO_2^-, long progressions of ν_2 appear both in absorption and in fluorescence in the $^1B_2$—$^1A_1$ transition. The intensity maximum is in the 0–3 (and 3–0) band in the ν_2 progression. The ν_1 frequency does not form long progressions, and only a single quantum of it can be detected. In the $^1A_1$ state, the normal coördinate analysis described in the previous section indicates that the normal coördinate Q_2 is composed almost entirely of bending (S_2). Assuming[13] that k_α/ν_2 is approximately the same in $^1B_2$ and in $^1A_1$, the quantitative application of the Franck–Condon principle leads to the result that the bond angle has changed by about 9 ± 4° in the $^1B_2$-$^1A_1$ transition. Lacking rotational structure, it is not possible to directly determine the sign of the change. Excitation of an electron from the n_N orbital to the π_3 orbital leads to an increase of electronic charge in the vicinity of the O atoms. This should cause an increase in the bond angle, due to increased electronic repulsion between the O atoms. If a 9° increase in the bond angle is accepted, then the results of this work tend to confirm many of Walsh's predictions for the lowest electronic transition in this class of molecules.[14] The appearance of ν_1 in the electronic–vibrational transition is attributed to the fact that Q_1 contains an appreciable fraction of S_2. It is thus reasonable to conclude that the principal geometry change in $^1B_2$ is a small increase of the bond angle, and that the bond distance changes slightly, if at all.

(D) **The Bonding in the A_1 (Ground) Electronic State of NO_2^-; Comparison with Other Molecules.**—The interpretation of the vibrational frequencies and force constants can provide useful information about the nature of the bonding in a molecule.[15] Such data are especially valuable if comparisons can be made with other molecules. Fortunately, accurate vibrational assignments have been proposed for O_3,[16,17] SO_2[12,18] and HCO_2^-.[19] Since these molecules are isovalent with respect to NO_2^-, a comparison can be of value. The pertinent data are shown in Table II.

TABLE II

VIBRATIONAL FREQUENCIES AND FORCE CONSTANTS OF MOLECULES RELATED TO NO_2^-

	$N^{14}O_2^-$	O_3	SO_2	HCO_2^-
d, Å.	1.23	1.276	1.432	$d_{C-O} = 1.27$
α,°	116	117	119.5	α(oco) = 124°
ν_1, cm.$^{-1}$	1325	1110	1122	symm. C–O stretch = 1377
ν_2, cm.$^{-1}$	829	705	507	O–C–O bend = 784
ν_3, cm.$^{-1}$	1270	1043	1341	asymm. C–O stretch = 1584
$f_d \times 10^5$, dyne/cm.	8.1_0	5.70	10.02	....
$f_{dd} \times 10^5$, dyne/cm.	2.3_5	1.52	0.03	....
$f_\alpha/d^2 \times 10^5$, dyne/cm.	$2._5$	1.28	0.793	....
$f_{d\alpha}/d \times 10^5$, dyne/cm.	$0._9$	0.332	0.20	....

The molecules which are most similar are O_3 and NO_2^-. It is possible to relate the differences in their force constants to their molecular structure. The stretching and bending force constants are appreciably higher in NO_2^- than in O_3. This is related to the fact that the bond distance is shorter in NO_2^- (1.23 Å.) than in O_3 (1.276 Å.). The difference in electronegativity between O and N would give the bonds in NO_2^- higher ionic character, shorter bond distance, and higher stretching and bending force constants than the bonds in O_3, due to the possibility of increased ionic-covalent resonance in NO_2^-. The higher positive values of the interaction constants in NO_2^- are attributed to greater repulsion between the end oxygen atoms,[20] due both to the shorter distance between them and to the greater electronic charge on them relative to the end oxygen atoms in O_3.

Although the bond angle is very similar in all four molecules, it is seen that O_3 and NO_2^- differ

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(13) D. P. Craig, *J. Chem. Soc.*, 2146 (1950).

(14) A. D. Walsh, *ibid.*, 2266 (1953).

(15) See, for example, G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945.

(16) R. M. Badger and M. K. Wilson, *J. Chem. Phys.*, **18**, 998 (1950).

(17) L. Pierce, *ibid.*, **24**, 139 (1956).

(18) D. Kivelson, *ibid.*, **22**, 904 (1954).

(19) R. Newman, *ibid.*, **20**, 1663 (1952).

(20) C. A. Coulson, J. Duchesne and C. Manneback, *Nature*, **160**, 793 (1947). See also "Vol. Comm. Victor Henri, Contribution à l'Etude de la Structure Moleculaire," Desoer, Liege, 1948, p. 33.

markedly from SO_2 and from HCO_2^- in one important respect. The asymmetric stretching frequency (ν_3) in O_3 and in NO_2^- is lower than the symmetric stretching frequency (ν_1), whereas in SO_2 and in HCO_2^- the reverse is true. As Bernstein and Powling have shown,[21] the ratio $(\nu_1/\nu_3)^2$ depends approximately on the relative magnitudes of the stretching force constant and the bond–bond interaction constant, and also on a term which involves the atomic masses and the bond angle. In the molecules NO_2^-, O_3, SO_2 and HCO_2^-, the latter term which involves the molecular geometry is less than unity. The geometrical term becomes close to unity only when the bond angle is nearly 90°. For obtuse angle AB_2 molecules in which the bond–bond interaction constant is negligible in comparison with the stretching force constant, the value of ν_1 is then lower than the value of ν_3. This is the usual case in most AB_2 molecules.[22] Although the data are not sufficiently complete to permit a force constant calculation for HCO_2^-, it is reasonable to expect that the bond–bond interaction constant for the C–O bonds will not be as large relative to the C–O stretching force constant as the corresponding interaction constant in NO_2^- and in O_3. The cases in which $\nu_3 < \nu_1$ are relatively few in number. Thus far, NO_2^-, O_3 and OF_2[21] appear to be definitely established cases of this sort. In NO_2^- and in O_3, the complete force constant analyses have indeed verified that the bond–bond interaction constant is large and positive, and presumably the same would be true for OF_2.

The origin of the interaction terms in the vibrational potential function has been discussed by Coulson, Duchesne and Manneback.[20] According to these authors, the resonance effect is expected to lead to a positive value of the bond–bond interaction constant in AB_2 molecules. However, it appears to be necessary to consider other features of the electronic structure in order to explain why NO_2^- and O_3 should behave differently from HCO_2^- and SO_2. One feature in which NO_2^- and O_3 differ from HCO_2^- is in the nature of the orbitals on the central atom. Whereas the central atom in NO_2^- and in O_3 possesses a non-bonding orbital, the carbon atom in HCO_2^- does not have such a non-bonding orbital. In addition, the C–H bending mode (b_1) could influence the frequency of the asymmetric C–O stretching mode (b_1). In SO_2, Moffitt[23] has shown that the sulfur atom employs the 3d atomic orbitals in building the molecular orbitals, so that the sulfur atom can form a full double bond with each oxygen atom. The observed force constants (Table II) are in agreement with this. A full double bond between the central atom and both end atoms cannot occur in O_3 or in NO_2^-, since the oxygen and nitrogen atoms can employ only the 2s and the three 2p AOs in building the MOs. The bonding in SO_2 may therefore be quite different from the other molecules in which the central atom is C, O or N. It is possible that the electrons in the non-bonding orbital on the central atom in O_3 and in NO_2^- may actually make some contribution to the bonding. SCF–MO calculations would be needed to test this hypothesis. In OF_2, an additional important effect contributing to f_{dd} may be the repulsion of the non-bonding electrons on the F atoms. Electrostatic repulsions between non-bonded atoms should lead to a positive contribution to f_{dd}.[20]

In conclusion, it does not appear possible at the present time to explain the wide variation of f_{dd} in NO_2^- and O_3 relative to SO_2 and, presumably, HCO_2^-. Other similarities and differences can be reasonably well accounted for in terms of valence theory. As additional complete force constant data for simple molecules become available, through the use of isotopes of C, N and O and through analysis of the centrifugal distortion coefficients from microwave spectroscopy, it is hoped that a clearer account of the details of the bonding in simple molecules and the relation of the force constants and interaction constants to the molecular structure will eventually emerge.

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(21) H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 685 (1950).

(22) W. G. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc. (London)*, **A156**, 654 (1936).

(23) W. Moffitt, *ibid*, **A200**, 409 (1950).