

Optical Spectroscopic Determination of the Zero-Field Splitting in Vibronic Levels of the Triplet State of Nitrite*

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We have used conventional high resolution optical spectroscopic methods to determine the principal values of the fine structure tensor for the lowest triplet state (3B_1 at 18 959 cm^{-1}) of NO_2^- in NaNO_2 single crystals. From the intensities in the Zeeman spectrum we find

$$D-E=0.86\pm 0.04 \text{ cm}^{-1},$$

$$D+E=0.40\pm 0.04 \text{ cm}^{-1},$$

where the z axis is taken as the twofold axis and $E=(Z-X)/2$. From the measurement of line positions in the high-field Zeeman spectrum we find $D-E=0.84\pm 0.05 \text{ cm}^{-1}$, $D+E=0.41\pm 0.05 \text{ cm}^{-1}$. The values of D and E calculated for one-center spin-spin interaction are $D-E=0.42 \text{ cm}^{-1}$ and $D+E=0.24 \text{ cm}^{-1}$. The calculated ordering of the spin states is the same as that observed, but we suggest that there is significant second-order spin-orbit energy associated with the real splittings. Roughly the same splittings are seen for different vibronic levels of 3B_1 associated with ν_2' .

INTRODUCTION

We wish to report on the measurement of the zero-field splitting of the triplet substates of various vibronic levels of the lowest excited triplet level of the nitrite ion (NO_2^-) in sodium nitrite. NO_2^- is an eighteen valence electron triatomic, isostructural with O_3 and SO_2 . The zero-field splittings for triplet states of the neutral molecules can in principle be determined by rotational analysis,¹ but a new approach is needed for ions: We present here two new approaches.

The lowest triplet state of NO_2^- commencing at 18 959 cm^{-1} was previously characterized as 3B_1 by means of high field Zeeman spectra in polarized light² and by pulsed Zeeman measurements.³ The ${}^3B_{1\leftarrow 1}A_1$ transition is polarized along the molecular y -axis (the y -axis is in-plane, perpendicular to the principal (z) axis; \hat{y} is chosen to transform like B_2) and the T_z (a_2 spin component) spin-state is considerably more radiatively active than T_x or T_y .

Crystals of NaNO_2 are orthorhombic $\text{Imm}2_{\cdot 4\cdot 7}$. The NO_2^- site symmetry is C_{2v} . All NO_2^- molecules are equivalently oriented with respect to space fixed axes: The molecular x , y , and z directions coincide with the crystallographic directions a , b , and c , respectively.

THE EXPERIMENTS

The first experiments consisted of precise measurements of the relative intensities of transitions to the low-field magnetic substates of the triplet level. The experiments are similar in principle to those previously presented^{8,9} but the method is especially suited to NO_2^- , and the results can be expected to be more accurate. Since predominantly the T_e (or T_z) spin-state radiates, there are only very weak transitions to the $m_s=0$ state if a magnetic field of any strength is

directed along the a or b axes: Thus a mainly two-line Zeeman spectrum is expected at all field strengths. The relative intensity of transitions to $m_s=\pm 1$ states for each field orientation H_γ ($\gamma=x, y$ or z) provide the sign and magnitude of the zero-field splitting. It is readily shown⁸ that the relative intensity is given by

$$I_{+1}/I_{-1}=[1+\Omega(H_\gamma)/1-\Omega(H_\gamma)]^2,$$

where the $\Omega(H_\gamma)$ are given by

$$\Omega(H_\gamma)=\Delta E_{\gamma}^{zf}/(4g\beta H_0-2\Gamma)$$

where ΔE_{γ}^{zf} is the separation between the zero-field states whose fine structure axes are perpendicular to the field; the indices are to be taken cyclically. Γ is either X , Y , or Z for $\gamma=x, y$, or z , respectively. These relations assume that g is isotropic. A series of spectra for the vibronic band $0+\nu_2'$ ($\nu_2'=644 \text{ cm}^{-1}$) as well as the $0, 0$ band are shown in Fig. 1 for both field orientations. More experimental details are given in the caption to Fig. 1. The other vibronic bands in the ν_2' progression ($0\rightarrow n\nu_2'$, where $n=2, 3, \dots, 6$) still exhibit the same general Zeeman splitting and intensity pattern for both field directions, but the lines get broad (thereby increasing the error to about 20%) and we could detect no variation with vibronic state of the zero-field parameters. The results for $0, 0$ and $0, 1$ are

$$D-E=0.86\pm 0.04 \text{ cm}^{-1},$$

$$D+E=0.40\pm 0.04 \text{ cm}^{-1}.$$

The T_y spin-state lies at lowest energy ($Y=-0.42 \text{ cm}^{-1}$) and T_x lies at highest energy ($X=+0.44 \text{ cm}^{-1}$). The error of ca. 5–9% is a significant improvement over our previous work with less ideal crystals.^{8,9}

A check on these indirectly measured fine-structure constants is available because the T_y spin state is in

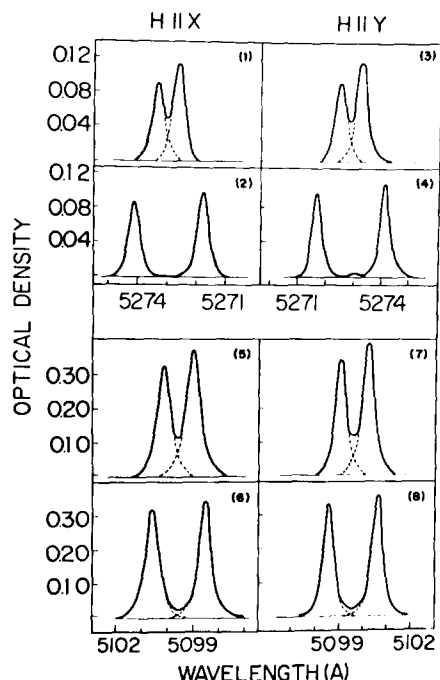


FIG. 1. Absorption spectra for 0, 0 band (1-4) and 0, 1 (ν_2') band (5-8) of NO_2^- in NaNO_2 , at 4.2°K. The 0, 0-band spectra are for $H=19.25$ kG (1, 3) and $H=49.5$ kG (2, 4). The 0, 1 band spectra are for $H=27.5$ kG (5, 7) and $H=49.5$ kG (6, 8). The crystal is mounted with the c axis perpendicular to H and could be rotated about the c axis. The spectra are all polarized parallel to the b axis (y axis) of the crystal.

fact very weakly radiatively active.¹⁰ This means that with the field along the y axis (b -crystal axis) a very weak center line is observed in the Zeeman pattern. This result is shown in Fig. 2. The optical resolution is ≈ 0.05 cm^{-1} , and the value of Y is given directly from the spectral line positions (without knowing the field strength!): We find $Y = -0.43$ cm^{-1} . The values of X and Y can also be obtained from the line positions and the value of $g\beta H$: In that case we find $X = +0.43$ cm^{-1} , $Y = -0.42$ cm^{-1} . These values compare well with those obtained from the intensities, and indeed provide a confirmation of the general applicability of the indirect method.

DISCUSSION

In order to investigate the contributions to D and E from spin-spin interaction and spin-orbit interaction we have calculated the one-center contribution to the spin-spin interaction. The following four integrals were calculated using the Fourier convolution method, Slater-type orbitals and exponents¹¹ (μ_2) of 1.95 and 2.275 for $a = \text{N}$ and O , respectively:

$$A_a = \left(-\frac{1}{2}g^2\beta^2/hc\right) \iint 2p_{xa}(1)2p_{ya}(2) \left(r_{12}^2 - 3x_{12}^2/r_{12}^5\right) \\ \times 2p_{xa}(1)2p_{ya}(2) d\tau_1 d\tau_2, \\ B_a = \left(-\frac{1}{2}g^2\beta^2/hc\right) \iint 2s(1)2p_{xa}(2) \left(r_{12}^2 - 3x_{12}^2/r_{12}^5\right) \\ \times 2s(1)2p_{xa}(2) d\tau_1 d\tau_2.$$

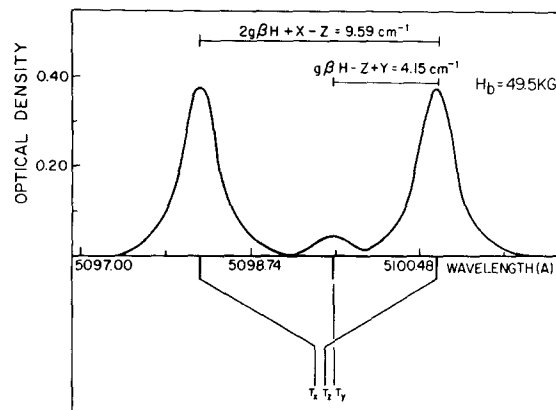


FIG. 2. High resolution absorption spectrum of 0, 1 band. The crystal is mounted and the light is polarized as described in the caption to Fig. 1. The field is directed along the b axis. One can clearly see the asymmetry of the Zeeman pattern, from which the fine-structure constants can be derived directly.

The zero-field splitting parameters can be expressed in terms of these four integrals: Using the calculated values $A_N = 0.44$, $A_O = 0.69$, $B_N = 0.35$, $B_O = 0.57$ cm^{-1} we have obtained the following one-center contributions to the spin-spin interaction, based on the 3B_1 wavefunction given by McEwan¹²:

$$D^{(1)} - E^{(1)} = 0.42 \text{ cm}^{-1},$$

$$D^{(1)} + E^{(1)} = 0.24 \text{ cm}^{-1}.$$

The simple one-center calculation gives the correct ordering of the spin-substates, but the fine structure constants are much too small. Perhaps the two-center spin-spin interaction would improve the agreement. We have tried including *spin-orbit interaction* in a simple way: If the total spin-orbit coupling energy of 3B_1 with 1B_2 states via T_z was ≈ 35 cm^{-1} , then the resulting interaction between 3B_1 and 3B_2 would shift the T_x and T_y states down by ≈ 0.2 cm^{-1} . When this correction is applied, the calculated results become $D + E = 0.44$ cm^{-1} $D - E = 0.82$ cm^{-1} and these are encouragingly close to the experimental values considering that 35 cm^{-1} is about the spin-orbit coupling needed between 3B_1 and 1B_2 to explain the singlet-triplet absorption intensity.² Spin-orbit interactions with 3A_2 states, that would not be derivable from singlet-triplet absorption spectra because ${}^1A_2 \leftarrow {}^1A_1$ is forbidden, would lower the energies of T_y and T_z . This is contrary to experiment if the one-center approximation for the spin-spin interaction is reliable.

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¹⁰ With first-order spin-orbit coupling selection rules, the 3B_1 state can connect with the ground state in dipole radiation via

the T_z spin state resulting in \hat{y} polarization; or via the T_y spin state resulting in \hat{z} polarization. We showed previously² that the former effect dominates. The observed transition to the T_y spin state (with $H \parallel Y$) is not obviously \hat{z} -polarized, and so its intensification mechanism is not certain at this time.

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Kinetics of Diffusion-Controlled Reaction between Chemically Asymmetric Molecules.* I. General Theory

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The treatment of diffusion-controlled bimolecular chemical reactions is extended to molecules with axially symmetrical distributions of reactivity on their spherical surfaces. Whereas an explicit solution exists for the time-dependent effective rate constant at small times, the physically more interesting solution at large times can be obtained only approximately (though to any required degree of accuracy) by solving sets of linear equations.

INTRODUCTION

Much attention has been paid in the past to the kinetics of diffusion-controlled bimolecular reactions of spherical, chemically homogeneous molecules, the reactivities of which are the same all over their surfaces. A critical review of papers published until 1960 was given by Noyes¹; some of the more recent papers²⁻⁶ take into account correlations among individual particles in the system^{4,5} and hydrodynamic interaction between pairs of diffusing particles.⁶ However, no attempt has been made, as far as we know, to analyze the effect of heterogeneity of surface reactivity. Although the assumption of uniform reactivity is sometimes justified, there are many cases (e.g., fluorescence quenching by highly asymmetric molecules, recombination of protein subunits, etc.) for which the reactive loci on the molecules are sharply specified and a steric factor should be considered. In this paper the Steinberg-Katchalski³ statistical method is generalized and applied to hydrodynamically spherical molecules with axially symmetric distributions of chemical reactivity. In a second paper, the results obtained will be compared with some simple approximate relations following from a quasi-chemical treatment of the diffusion.

We shall examine the kinetics of a diffusion-limited bimolecular irreversible reaction $A+B \rightarrow AB$. The molecules of both reactants are approximated as spheres of radii r_A and r_B , and no interaction is assumed between them unless the distance r between their centers is $r = a = r_A + r_B$. Since the reactive group represents in general only a small fraction of the total surface of the molecule, the surface should be described as chemically heterogeneous. A successful encounter resulting in

chemical reaction requires not only sufficiently close approach of the two spheres but also their specific mutual orientation. If their position is such that at least one molecule is completely unreactive at the place of contact, no reaction can occur and the spheres may diffuse apart from each other. On the other hand, only if contact is made between strongly reactive spots on *both* spheres is success assured. In all intermediate cases a positive outcome of an encounter is only more or less probable. In many cases of practical interest the surface reactivity of A and B shows axial symmetry, and the distribution of the probability of reaction at a single encounter $W(\theta_1, \theta_2)$ can be described in terms of the polar angles θ_1 and θ_2 , respectively, of the contact point with respect to the symmetry axes of both molecules. In this model, the state of each molecule is described sufficiently by giving the positional coordinates of its center and the orientation of the vector of its symmetry axis.

Following the approach of Steinberg and Katchalski,³ we shall estimate successively the probability of reaction between a single pair of A and B, between an A and one of many surrounding B's, and finally the probability of reaction in the system composed of many A's and B's.

PROBABILITY OF REACTION BETWEEN A SINGLE PAIR OF MOLECULES A AND B

Starting from their initial positions, both molecules undergo Brownian motion characterized by two translational diffusion coefficients D_A , D_B and two rotational diffusion coefficients D_A^{rot} , D_B^{rot} . Because translational and rotational motions are independent of each other