(5) The value of the enthalpy of activation $(\Delta H^{\ddagger})^{*}$ in the photochemical reaction is very small compared with that $(\Delta H^{\ddagger})$ in the thermal reaction. For the entropy of activation, the value $(\Delta S^{\ddagger})^{*}$ in the former is more negative than that $(\Delta S^{\ddagger})$ in the latter. On the basis of experimental results, the isotope-exchange mechanism of α-RH can be accounted for by a potential energy state diagram with the aid of an extended-Hückel MO method as shown in Figure 9. The electrophilic deuteration of α-RH in the excited or ground state may produce the excited (5)* or ground (2) σ complex, respectively. After the formation of the ground σ complex (5) from the decay of the excited one (5)* for the

photochemical reaction or the ground σ complex (2) for the thermal reaction, deprotonation or deuteration from the complexes gives the isotope-exchange product or the starting material, respectively.

(6) The kinetic isotope effects ${}^{1}k_{q}^{H}/{}^{1}k_{q}^{D}$ ($\simeq {}^{1}k_{R}^{H}/{}^{1}k_{R}^{D}$) and ${}^{1}k_{H}/{}^{1}k_{D}$ in α-RH were determined to be 1.7–2.2 and 1.7–2.0, respectively.

Nitrogen Quadrupole Coupling Measurements on ON–NO2 Using the Flygare–Balle Pulsed-Beam Spectrometer

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Abstract: High-resolution measurements of the $1_{01} \leftarrow 0_{00}$, $2_{12} \leftarrow 1_{11}$, $2_{02} \leftarrow 1_{01}$, $2_{11} \leftarrow 1_{0}$, $3_{12} \leftarrow 3_{13}$, and $4_{13} \leftarrow 4_{14}$ transitions in the ON–NO2 complex were made by using a pulsed-beam, Fourier transform microwave spectrometer. Nearly all hyperfine structure components were resolved on observed transitions except for the $2_{02} \leftarrow 1_{01}$ group. The quadrupole coupling tensors in the principal axis system were determined for both nitrogen atoms. The nitrogen quadrupole coupling components for the NO group are $eQq_{aa} = -1.7766 \pm 0.0037$ MHz and $eQq_{bb} = 0.0585 \pm 0.0021$ MHz. For the NO2 group $eQq_{aa} = -0.5260 \pm 0.0035$ MHz and $eQq_{bb} = -4.1941 \pm 0.0018$ MHz. The rotational constants obtained are $A = 12\,412 \pm 22$ MHz, $B = 4226.530 \pm 0.012$ MHz, and $C = 3152.966 \pm 0.012$ MHz. Rotational transition frequencies and estimates of spin–rotation interaction strengths are given. The observed quadrupole coupling strengths are substantially different from those observed for the free NO and NO2 molecules.

Introduction

The ON–NO2 complex is a ${}^{1}\Sigma$ diamagnetic complex formed from the two paramagnetic molecules NO and NO2. The structure of this complex was determined by Brittain et al.[1] from a detailed microwave study involving seven isotopic species. Although the structure appears to have been accurately determined, the resolution was not high enough for an accurate determination of the quadrupole coupling. The two inequivalent, spin-1 nitrogen atoms in this molecule cause rather complex hyperfine structure patterns for most of the observed rotational transitions. This study was undertaken to obtain the quadrupole coupling tensor components at both nitrogen sites in this molecule. The quadrupole coupling components may be used to obtain the electric field gradients and can be used to determine electronic structure and bonding parameters for the N–N bond. There are many examples of inorganic complexes involving the nitrosyl group, and this case may be helpful in characterizing the bonding in this group of complexes.

Experimental Section

The microwave spectra were observed by using a pulsed-beam, Fourier transform spectrometer developed by Balle, Flygare, and co-workers.[2,3] A mixture of 2% NO and 2% NO2 in argon at 1–2 atm was rapidly expanded into the region between two spherical mirrors by using a pulsed solenoid valve operating at about 1 pulse/s. A 90° microwave pulse of 2-μs duration was used to excite a "free induction decay" signal from the gas sample between the mirrors. The "free induction decay" signal was beat down to 30 MHz by using a superhet receiver and then beat against a 30-MHz signal in a balanced mixer. The resulting beat signal was digitized at 0.5 μs/point for 256 points. The digitized signals are averaged and Fourier transformed to obtain the frequency spectrum with a resolution of 3.9 kHz/point. The beam is directed perpendicular to the

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Table I. Center Frequencies for Rotational Transitions Observed in ON–NO2

transition	frequency, MHz	transition	frequency, MHz
$1_{01} \leftarrow 0_{00}$	7 379.541 (12)	$2_{11} \leftarrow 1_{10}$	15 832.551 (12)
$2_{12} \leftarrow 1_{11}$	13 685.411 (12)	$3_{12} \leftarrow 3_{13}$	6 435.669 (12)
$2_{02} \leftarrow 1_{01}$	14 660.6 (1)	$4_{13} \leftarrow 4_{14}$	10 695.832 (12)

cylinderical axis of the cavity to minimize Doppler broadening. Some Doppler broadening or splitting is observed due to the finite divergence angle of the molecular beam. The effective resolution is 12 kHz for typical measurements. The gasses were typically 95% pure or better and obtained from commercial suppliers. Signals could also be observed by mixing a 1:4 mixture of oxygen and nitric oxide in argon to form the ON–NO2.

Results and Data Analysis

Four R-branch ($\Delta J = +1$) and two Q-branch ($\Delta J = 0$) were measured in the present work. The center frequencies of the observed transitions are listed in Table I. An attempt was made to observe the $6_{24} \leftarrow 6_{25}$ transition near 5964 MHz and the $7_{25} \leftarrow 7_{26}$ transition near 9876 MHz, but neither of these transitions was observed. The rapid expansion of the beam produces very effective rotational cooling of the gas mixture, and it is believed that these higher J transitions were not sufficiently well populated.

The simplest observed transition was the $1_{01} \leftarrow 0_{00}$ at 7379.54 MHz. Only the $J = 1$ level is split by the nitrogen quadrupole

(1) A. H. Brittain, A. P. Cox, and R. L. Kuczkowski, *Trans. Faraday Soc.*, **65**, 1963–1974 (1969).
(2) T. J. Balle and W. H. Flygare, *Rev. Sci. Instrum.*, **52**, 33–45 (1981).
(3) T. J. Balle, E. J. Campbell, M. R. Keenan, and W. H. Flygare, *J. Chem. Phys.*, **72**, 922–932 (1980); **71**, 2723–2724 (1979).
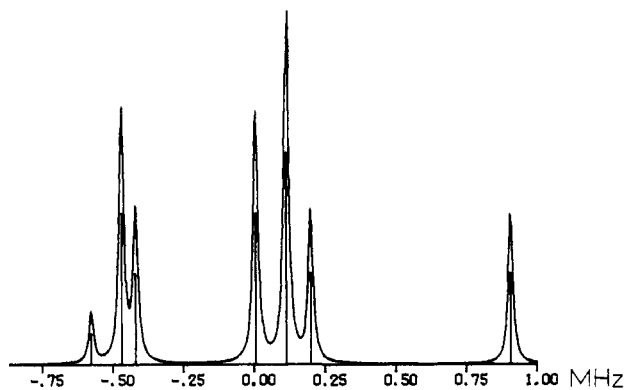
Figure 1. Calculated spectrum for the $1_{01} \leftarrow 0_{00}$ transition centered at 7379.541 MHz. The frequency scale is in MHz relative to the line center frequency of 7379.541 MHz.
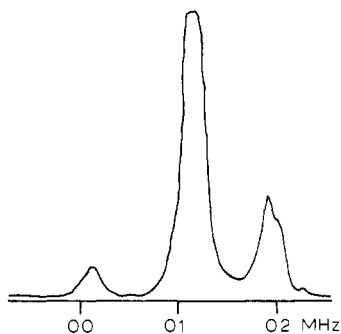

Figure 2. Experimental spectrum for the three components of the $1_{01} \leftarrow 0_{00}$ transition at 7379.549, 7379.658, and 7379.742 MHz. The frequency scale is in MHz relative to the line center frequency of 7379.541 MHz.
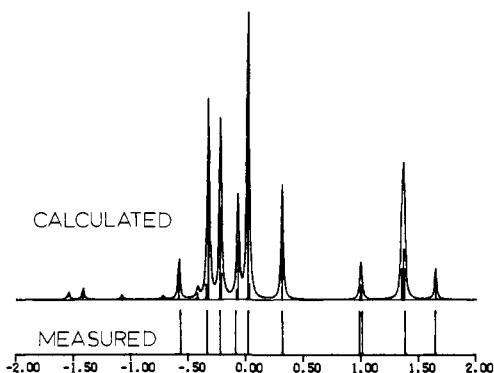

Figure 3. Calculated and experimental spectrum for the $2_{11} \leftarrow 1_{10}$ transition centered at 15832.55 MHz. Frequencies in MHz.

interactions and only the eQq_{aa} quadrupole coupling tensor component contributes to these splittings. The calculated spectrum for this transition is shown in Figure 1. Three of the components of the $1_{01} \leftarrow 0_{00}$ transition are shown in Figure 2. A more typical example of the observed hyperfine structure is illustrated in Figure 3 for the $2_{11} \leftarrow 1_{01}$ transition at 15832.55 MHz. Both the calculated and observed spectrum are shown in this figure.

The hyperfine structure is due to the nitrogen quadrupole coupling arising from the two inequivalent nitrogen atoms. The spin–rotation interactions were included in the analysis, but the interaction strength is only slightly larger than experimental errors. The calculated dipolar spin–spin coupling strength is approximately 0.1 kHz, so this interaction was neglected. The nitrogen spin angular momenta I_1 and I_2 are coupled to the rotational angular momentum J. The coupling scheme is $\vec{F}_1 = \vec{I}_1 + J$, $\vec{F} = \vec{I}_2 + \vec{F}_1$, where F represents the total angular momentum. Since the nitrogen quadrupole coupling strengths are the same order of magnitude, terms off-diagonal in the intermediate quantum number F_1 must be calculated and the Hamiltonian matrix diagonalized. The Hamiltonian can be expressed as $\mathcal{H} = \mathcal{H}_{q1} +$

$\mathcal{H}_{q2} + \mathcal{H}_{sr1} + \mathcal{H}_{sr2}$ where the required matrix elements are given by eq 1–4, where q_J is the electric field gradient for a given

$$\langle |\mathcal{H}_{q_1}| \rangle = (-1)^{J+I_1+F_1} eq_J Q(N_1) g(J) f(I_1) \begin{Bmatrix} F_1 & I_1 & J' \\ 2 & J & I_1 \end{Bmatrix} \quad (1)$$

$$\langle |\mathcal{H}_{q_2}| \rangle = (-1)^{J+I_1+I_2+I+2F_1+F} eq_J Q(N_2) g(J) f(I_2) \{(2F_1 + 1)(2F_1' +$$
$$1)\}^{1/2} \begin{Bmatrix} J' & F_1' & I_1 \\ F_1 & J & 2 \end{Bmatrix} \begin{Bmatrix} F & I_2 & F_1' \\ 2 & F_1 & I_2 \end{Bmatrix} \quad (2)$$

$$\langle |\mathcal{H}_{sr_1}| \rangle = (-1)^{J+I_1+F_1} C_J(N_1) h(J) h(I_1) \begin{Bmatrix} F_1 & I_1 & J \\ 1 & J & I_1 \end{Bmatrix} \quad (3)$$

$$\langle |\mathcal{H}_{sr_2}| \rangle = (-1)^{1+J+F_1+F_1'+I_1+I_2+F} C_J(N_2) h(I_2) h(J) [(2F_1 +$$
$$1)(2F_1' + 1)]^{1/2} \begin{Bmatrix} F & F_1' & I_2 \\ 1 & I_2 & F_1 \end{Bmatrix} \begin{Bmatrix} J & F_1' & I_1 \\ F_1 & J & I \end{Bmatrix} \quad (4)$$

rotational state (J) and is defined as given in eq 7 and α represents

$$q_J = 2\sum q_{\alpha\alpha} \langle J_\alpha^2 \rangle / J(J + 1) \quad (5)$$

the principal inertial axes in the molecule (eq 6 and 7). e is the

$$f(L) = \frac{1}{4} \left[\frac{(2L + 1)(L + 1)(2L + 3)}{L(2L - 1)} \right]^{1/2} \quad (6)$$

$$g(J) = \left[\frac{J(2J + 1)(J + 1)}{(2J - 1)(2J + 3)} \right]^{1/2} \quad (7)$$

electronic charge, and Q is the nuclear quadrupole moment. $C_J(N_1)$ is the spin–rotation interaction strength for a given rotational state (J) and is defined as

$$C_J(i) = \sum_g \langle J_\alpha^2 \rangle C_{\alpha\alpha} / J(J + 1)$$

$C_{\alpha\alpha}$ are the diagonal elements of the spin–rotation tensor in the inertial axis system:

$$h(L) = \{L(L + 1)(2L + 1)\}^{1/2}$$

Energies were calculated by diagonalization of the resulting Hamiltonian matrix.

The center frequencies for the rotational transitions and the coupling strengths $eQq_{aa}(N_1)$, $eQq_{aa}(N_2)$, $C_{aa}(N_1)$, and $C_{aa}(N_2)$ were treated as adjustable parameters in a nonlinear least-squares fitting program to fit the observed transition frequencies. The $1_{01} \leftarrow 0_{00}$ transitions were fit separately first since the assignments were obvious for this case, and this yielded preliminary values for $eQq_{aa}(N_1)$ and $eQq_{aa}(N_2)$. Spectra were then calculated for other transitions by using a range of values of $eQq_{bb}(N_1)$ and $eQq_{bb}(N_2)$. Once the calculated hyperfine structure patterns matched the observed patterns, assignments of quantum numbers to transitions could be made and a fit to all transitions was carried out. The measured frequencies and calculated frequencies obtained from this fit are shown in Table II. The states are labeled by the quantum numbers I, J, K, F, where $\vec{I} = \vec{I}_1 + \vec{I}_2$ is the total spin angular momentum, J is the rotational angular momentum, K is the projection of the rotational angular momentum on the a principal axis, and F is the total angular momentum. The values of the quadrupole coupling tensor components obtained from the least-squares fit are given in Table III. In addition, the a components of the spin–rotation tensor were determined to be $C_{aa}(N_1) - \bar{C}(N_1) = 0.0014 \pm 0.0008$ MHz and $C_{aa}(N_2) - \bar{C}(N_2) = 0.0020 \pm 0.0009$ MHz, where $\bar{C}$ is one-third of the trace of the spin–rotation tensor. Other spin–rotation tensor components were smaller than experimental errors. The rotational constants obtained from the fit to the center frequencies (Table I) are $A =$

Table II. Measured and Calculated Transition Frequencies for ON–NO₂ Given in MHz. Calculated Frequencies Are Best Least-Squares Fit Values with the Standard Deviation for the Fit = 0.0035 MHz

I	J	K	F	I'	J'	K'	F'	measd	calcd	ΔF
1	0	0	1	1	1	0	0	7378.965	7378.9655	-0.0005
2	0	0	2	2	1	0	2	7379.074	7379.0738	0.0002
0	0	0	0	0	1	0	1	7379.121	7379.1231	-0.0021
1	0	0	1	1	1	0	2	7379.549	7379.5480	0.0010
2	0	0	2	2	1	0	3	7379.658	7379.6563	0.0017
1	0	0	1	1	1	0	1	7379.742	7379.7422	-0.0002
2	0	0	2	2	1	0	1	7380.449	7380.4490	0.0000
1	1	1	0	1	2	1	1	15831.999	15831.9977	0.0013
1	1	1	2	1	2	1	3	15832.213	15832.2160	-0.0030
2	1	1	2	2	2	1	3	15832.344	15832.3374	0.0066
0	1	1	1	2	2	1	2	15832.473	15832.4730	0.0000
2	1	1	3	2	2	1	4	15832.577	15832.5778	-0.0008
1	1	1	1	1	2	1	2	15832.873	15832.8721	0.0009
1	1	1	2	2	2	1	3	15833.577	15833.5788	-0.0018
2	1	1	1	0	2	1	2	15833.947	15833.9448	0.0022
1	1	1	1	1	2	1	1	15834.212	15834.2176	-0.0056
1	1	-1	2	2	2	-1	2	13683.747	13683.7428	-0.0058
1	1	-1	1	2	2	-1	2	13683.761	13683.7632	-0.0022
2	1	-1	3	2	2	-1	3	13684.052	13684.0581	-0.0061
1	1	-1	1	1	2	-1	1	13684.174	13684.1765	-0.0025
2	1	-1	1	0	2	-1	2	13684.565	13684.5620	0.0030
0	1	-1	1	2	2	-1	2	13685.025	13685.0189	0.0061
1	1	-1	2	1	2	-1	3	13685.187	13685.1866	0.0004
2	1	-1	2	2	2	-1	3	13685.320	13685.3120	0.0080
2	1	-1	3	2	2	-1	4	13685.666	13685.6637	0.0023
1	1	-1	1	1	2	-1	2	13685.872	13687.8700	0.0020
0	1	-1	1	1	2	-1	2	13687.130	13687.1257	0.0043
2	1	-1	2	2	2	-1	1	13687.488	13687.4921	-0.0041
2	1	-1	2	0	2	-1	2	13687.704	13687.7063	-0.0023
0	1	-1	1	2	2	-1	0	13688.073	13688.0762	-0.0032
0	3	-1	3	1	3	1	3	6433.771	6433.7738	-0.0028
2	3	-1	2	2	3	1	2	6434.155	6434.1570	-0.0020
1	3	-1	3	0	3	1	3	6434.634	6434.6342	-0.0002
2	3	-1	5	2	3	1	5	6434.790	6434.7899	0.0001
1	3	-1	4	1	3	1	4	6435.277	6435.2766	0.0004
2	3	-1	2	2	3	1	3	6435.921	6435.9173	0.0037
2	3	-1	3	2	3	1	2	6436.484	6436.4863	-0.0023
2	3	-1	4	2	3	1	5	6436.540	6436.5352	0.0048
2	3	-1	3	1	3	1	4	6436.931	6436.9251	0.0059
2	3	-1	3	0	3	1	3	6437.136	6437.1331	0.0029
1	3	-1	2	2	3	1	3	6437.529	6437.5296	-0.0006
1	3	-1	2	1	3	1	2	6437.704	6437.7079	-0.0039
2	3	-1	4	2	3	1	4	6437.818	6437.8186	-0.0006
2	3	-1	3	2	3	1	4	6438.245	6438.2467	-0.0017
2	3	-1	3	2	3	1	4	6438.380	6438.3766	0.0034
2	3	-1	3	1	3	1	2	6438.418	6438.4249	-0.0069
2	4	-1	2	2	4	1	3	10693.658	10693.6546	0.0034
2	4	-1	2	2	4	1	2	10693.965	10693.9638	0.0012
0	4	-1	4	1	4	1	4	10694.115	10694.1180	-0.0030
2	4	-1	3	2	4	1	3	10694.574	10694.5765	-0.0025
1	4	-1	4	0	4	1	4	10694.752	10694.7534	-0.0014
2	4	-1	6	2	4	1	6	10694.883	10694.8808	0.0022
1	4	-1	5	1	4	1	5	10695.391	10695.3928	-0.0018
1	4	-1	3	1	4	1	3	10697.831	10697.8339	-0.0029
2	4	-1	5	2	4	1	5	10697.938	10697.9345	0.0035
2	4	-1	4	2	4	1	4	10698.421	10698.4197	0.0013

12412 ± 22 MHz, $B = 4226.530 \pm 0.012$ MHz, and $C = 3152.966 \pm 0.012$ MHz.

Five transitions were observed below the listed frequencies for the $3_{12} \leftarrow 3_{13}$ transitions. These could not be assigned to frequencies calculated with the present set of rotational and coupling constants. They could be due to (a) a different rotational tran-

Table III. Nitrogen Quadrupole Coupling Tensor Components Obtained from the Least-Squares Fit

parameter	value, MHz
$eQq_{aa}(N_1)$, (NO_2)	-0.5260 ± 0.0035
$eQq_{bb}(N_1)$, (NO_2)	-4.1941 ± 0.0018
$eQq_{aa}(N_2)$, (NO)	-1.7766 ± 0.0037
$eQq_{bb}(N_2)$, (NO)	0.0585 ± 0.0021

sition, (b) a low-lying excited vibrational state, or (c) another molecule or polymer present in the beam. The observed frequencies are 6431.414, 6431.807, 6432.492, 6432.884, and 6433.170 MHz.

Discussion of Results

The rotational constants obtained in the present work are in reasonably good agreement with previously measured values of $A = 12453.7$ MHz, $B = 4226.48$ MHz, and $C = 3153.03$ MHz. We believe that the present values for B and C are more accurate due to the higher resolution measurements, but the previous value for A may be better because more transitions were measured that are more sensitive to the value of A. The present values for the NO nitrogen quadrupole coupling tensor are quite different from the previous values of $\chi_{aa} = -2.34$ MHz and $\chi_{bb} = 1.12$ MHz, and this is believed to be due to the lack of sufficient resolution in the previous work. We believe that a more careful treatment of the propagation of errors in the work of Brittain et al.[1] will give larger errors on the quadrupole coupling tensor elements than were reported.

We can compare the observed quadrupole coupling tensor elements with those for the free molecules NO_2 and NO. For NO_2, Carrington[4] gives $eQq_{aa}(NO_2) = 0.45$ MHz and $eQq_{bb}(NO_2) = -1.71$ MHz, but these must be rotated to the principal axis system for ON–NO₂. After rotation we find $eQq_{aa}'(NO_2) = -1.28$, and $eQq_{bb}' = 0.03$, which are quite different from the ON–NO₂ values determined in the present work. For the NO group we can make a comparison with the results of the NO dimer.[5] They obtain $eQq_{aa} = -4.065$ MHz and $eQq_{bb} = -2.240$ MHz. These are also substantially different from values obtained for ON–NO₂. The NO group in NO dimer is at a different angle relative to the b axis than in ON–NO₂, but the rotation angle is small and its effect on the quadrupole tensor will be much smaller than the differences between the observed results. Although ON–NO₂ is not a strongly bound molecule, the bonding appears to have a substantial effect on the electric field gradients at the nitrogen sites. This would be an interesting case for a careful molecular orbital calculation.

(4) A. Carrington, "Microwave Spectroscopy of Free Radicals", Academic Press, London, 1974, p 250.
(5) C. M. Western, P. R. R. Langridge-Smith, B. J. Howard, and S. E. Novick, *Mol. Phys.*, **44**, 145–160 (1981).