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Nitrogen Quadrupole Coupling in Cyclopentadienylnickel Nitrosyl

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Abstract: High-resolution rotational spectra of $C_5H_5{}^{58}Ni^{14}N^{16}O$ were obtained with a Flygare-Balle type pulsed-beam microwave spectrometer. Quadrupole hyperfine structure was clearly resolved for $J = 1 \rightarrow 2$, $2 \rightarrow 3$, $3 \rightarrow 4$, and $4 \rightarrow 5$ transitions involving $K = 0, 1, 2, 3$, and 4 states. A nitrogen quadrupole coupling strength of eqQ = −1.216 (11) MHz and rotational constant $B = 1259.2743$ (8) MHz were obtained by fitting the observed spectra. D_{JK} and D_J were also obtained from fitting the spectra. This appears to be the first gas-phase, microwave measurement of nitrogen quadrupole coupling in a transition-metal complex. The quadrupole coupling strength is compared with values for other molecules and complexes containing the NO group.

There has been considerable interest in π-bonded organometallic transition-metal complexes since the discovery and characterization of ferrocene. A fairly large number of the "sandwich-type", symmetrical complexes are now known.[1] This has been an area of intense study due to the possible roles of transition-metal complexes in the reactions of olefins, acetylenes, and related compounds.

The symmetric-top structure and C_{5v} symmetry of cyclopentadienylnickel nitrosyl (CpNiNO) were established by microwave spectroscopy.[2,3] The rotational constant is small (1259 MHz), and so the observed transitions had fairly high J values, and no quadrupole coupling structure was observed in earlier work.

In the present work well-resolved multiplets due to the nitrogen quadrupole coupling were observed on all of the measured rotational transitions involving $K = 0$ through $K = 4$ states.

Experimental Section

The sample of CpNiNO was obtained by reacting Cp_2Ni with nitric oxide as described by Piper, Cotton, and Wilkinson.[4] Sufficient vapor pressure was obtained at 30 °C to make 1–3% mixtures in argon for use in the pulsed-beam spectrometer.

Rotational transitions of $Cp^{58}NiNO$ were measured in the range of 5 to 13 GHz with a Flygare-Balle type[5] pulsed-beam, Fourier transform microwave spectrometer. A mixture of 1–3% CpNiNO in argon was pulsed through the nozzle to obtain the spectra. A typical spectrum is shown in Figure 1. Total pressure behind the nozzle was normally 0.4 to 1 atm. Transitions for other isotopic species were observed with use of the natural abundance sample, but no analysis will be included in this work.

Frequencies for 32 transitions are listed in Table I with assignments of rotational angular momenta J and J' and total angular momenta F and F' ($\bar{F} = \bar{I} + \bar{J}$ where I is the nitrogen nuclear spin). The #PT column indicates how many times a particular transition was observed and can be used as an approximate indication of relative intensity within each $J \rightarrow J'$ group of transitions. More data was taken on the $J \rightarrow J' = 1 \rightarrow 2$ and $2 \rightarrow 3$ transitions since the quadrupole splittings were better resolved and the effective resolution was better due to a lack of observed doppler doubling. The typical resolution was 12 KHz for $1 \rightarrow 2$ and $2 \rightarrow 3$ transitions.

Results and Analysis

Table I. Measured and Calculated Transition Frequencies for $Cp^{58}Ni\ NO^a$

	J	F	J'	F'	K	PT	measured freq	calcd freq	dev
1	1	2	2	2	0	12	5036.734 (8)	5036.730	0.004
2	1	1	2	2	1	13	5036.780 (4)	5036.780	0.000
3	1	0	2	1	0	13	5036.780 (4)	5036.791	−0.011
4	1	1	2	1	1	13	5037.086 (7)	5037.084	0.002
5	1	1	2	2	0	13	5037.086 (7)	5037.095	−0.009
6	1	2	2	3	0	25	5037.120 (4)	5037.121	−0.001
7	1	2	2	3	1	27	5037.158 (5)	5037.158	0.000
8	1	0	2	1	1	16	5037.537 (7)	5037.540	−0.003
9	1	1	2	1	0	11	5037.702 (4)	5037.703	−0.001
10	2	3	3	3	0	3	7555.240 (3)	7555.246	−0.006
11	2	2	3	3	2	18	7555.272 (4)	7555.268	0.004
12	2	3	3	3	1	8	7555.349 (5)	7555.350	−0.001
13	2	2	3	3	1	17	7555.547 (3)	7555.545	0.002
14	2	1	3	2	0	7	7555.584 (4)	7555.577	0.007
15	2	3	3	4	0	22	7555.655 (3)	7555.652	0.003
16	2	3	3	4	1	22	7555.655 (3)	7555.654	0.001
17	2	3	3	4	2	22	7555.655 (3)	7555.659	−0.004
18	2	1	3	2	2	9	7555.879 (2)	7555.877	0.002
19	3	3	4	4	3	2	10073.715 (2)	10073.706	0.009
20	3	4	4	4	0	3	10073.762 (3)	10073.769	−0.007
21	3	3	4	4	2	7	10073.972 (6)	10073.966	0.006
22	3	4	4	5	3	4	10074.075 (1)	10074.068	0.007
23	3	3	4	4	1	7	10074.125 (2)	10074.122	0.003
24	3	4	4	5	2	7	10074.125 (2)	10074.132	−0.007
25	3	2	4	3	0	2	10074.142 (2)	10074.148	−0.006
26	3	2	4	3	1	3	10074.152 (2)	10074.155	−0.003
27	3	4	4	5	1	5	10074.176 (2)	10074.170	0.006
28	3	3	4	4	0	5	10074.176 (2)	10074.174	0.002
29	3	2	4	3	2	5	10074.176 (3)	10074.174	0.002
30	3	4	4	5	0	7	10074.182 (2)	10074.183	−0.001
31	3	4	4	4	3	5	10074.214 (4)	10074.213	0.001
32	4	4	5	5	3	3	12592.324 (2)	12592.323	0.001
33	4	5	5	6	4	8	12592.348 (8)	12592.356	−0.008
34	4	4	5	5	2	3	12592.545 (4)	12592.534	0.011
35	4	3	5	4	3	3	12592.545 (4)	12592.556	−0.011
36	4	3	5	4	2	8	12592.639 (4)	12592.630	0.009
37	4	3	5	4	1	4	12592.674 (1)	12592.674	0.000
38	4	5	5	6	1	7	12592.684 (4)	12592.687	−0.003
39	4	3	5	4	0	7	12592.684 (4)	12592.689	−0.005
40	4	5	5	6	0	5	12592.712 (4)	12592.709	0.003

[a] Frequencies in MHz. $B = 1259.2743$ (7) MHz, eqQ = −1.216 (11) MHz. Standard deviation for the fit = 0.0054 MHz. PT = number of measurements for that frequency.

The observed transitions could be fit to a prolate symmetric top Hamiltonian with centrifugal distortion parameters D_{JK} and D_j and quadrupole coupling strength $eq_{aa}Q$ along the a-axis direction. The corresponding transition frequencies are given by

$$\nu(J,F,K \rightarrow J+1,F',K) = 2(J+1)(B - D_{JK}K^2) - 4D_J(J+1)^3 + eq_{aa}Q\left[\left(\frac{3K^2}{(J+1)(J+2)} - 1\right)Y(I,J+1,F') - \left(\frac{3K^2}{J(J+1)} - 1\right)Y(I,J,F)\right]$$

All observed transitions for $Cp^{58}NiNO$ were fit to the above formula by using a linear least-squares fit. The adjustable pa-

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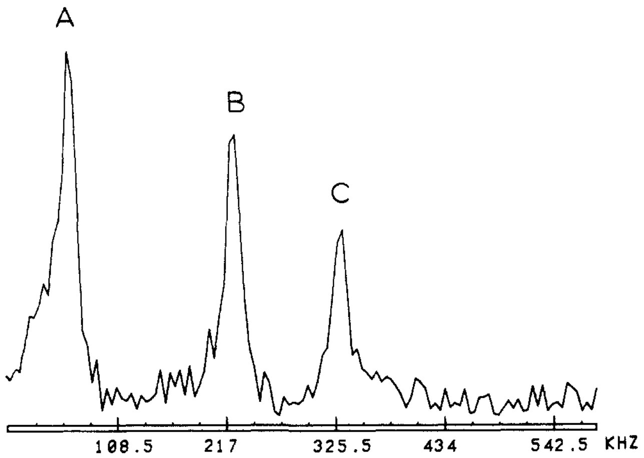

Figure 1. Fourier transform spectrum of $J = 1 \rightarrow 2$ transition for Cp^{58}NiNO. The frequency (in kHz) is relative to the microwave oscillator frequency of 5 037 483.4 kHz. The signal-to-noise ratio is approximately 10/1 for 248 gas pulses. The A peak corresponds to the $F = 0 \rightarrow 1$, $K = 1$ transition at 5 037 541.7 kHz. The B peak corresponds to the $F = 1 \rightarrow 1$, $K = 0$ transition at 5 037 706.7 kHz. The C peak corresponds to the $F = 2 \rightarrow 3$, $K = 1$ transition at 5 037 153.3 kHz.

Table II. Values of the Molecular Parameters Obtained by Fitting the Observed Transitions for Cp^{58}NiNO

parameter	value
B	1259.2743 (8) MHz
D_{JK}	2.70 (6) KHz
D_J	0.08 (2) KHz
eq$_{aa}$Q	−1.216 (11) MHz

rameters were the rotational constant B (or B_0), D_{JK} and D_J, and eq$_{aa}$Q. The total angular momentum values F are obtained by coupling the rotational angular momentum J with the nitrogen nuclear spin $I = 1$, to obtain $F = J + 1$, J, and $J - 1$. The function $Y(I,J,F)$ is Casimir's function and is given by

$$Y(I,J,F) = 0.25[(2I + 1)(2I + 3)(I + 1)/ I(2I - 1)]^{1/2}[J(J + 1)(2J + 1)/(2J - 1)(2J + 3)]^{1/2}\begin{Bmatrix} F & I & J \\ 2 & J & I \end{Bmatrix}$$

The results of the fit are given in Table I. We note that experimental standard deviations of the individual measured lines (Data Column) and the deviations of the "best fit" results from the data are both in the range of 1–9 kHz. We therefore would not obtain significant values for further parameters such as quadrupole distortion or spin–rotation interaction strengths. The fitted values of the adjustable parameters are given in Table II. The present rotational constant and centrifugal distortion constants are in good agreement with the earlier values.[3] We checked the second-order quadrupole terms (off-diagonal in rotational states) and found that they would contribute a few tenths of a kHz or less, so they were omitted from the analysis.

Discussion

The observed nitrogen quadrupole coupling strength eqQ = -1.216 (11) MHz is smaller than those observed for most other nitrogen-containing compounds. It is also smaller than the free NO radical value of eqQ = -1.86 MHz.[6] In obtaining the above value for NO from ref 6, we have not included the term off-diagonal in total electronic angular momentum states discussed by Lin and Mizushima,[7] since this would not be appropriate for comparison with values in the $^1\Sigma$ molecules. We note that the NO binding to Ni in the complex significantly reduces the nitrogen quadrupole coupling strength. An extreme case of this effect is the reduction of the central nitrogen quadrupole coupling strength[8] in NNO to eqQ = -0.27 MHz. The ^{14}N quadrupole coupling in the free N_2 molecule is eqQ = -2.52 MHz.[9] With use of the Townes-Dailey model,[9] the quadrupole coupling constant in terms of the occupation numbers n_x, n_y, and n_z for atomic p$_x$, p$_y$, and p$_z$ orbitals is

$$\mathrm{eq}_{zz}\mathrm{Q} = 5.0(n_x + n_y - 2n_z)\ \mathrm{MHz}$$

If we put one electron in each of the p$_x$ and p$_y$ orbitals and 1.25 electrons in the p$_z$ orbital for each atom, we obtain eqQ = -2.5 MHz. These occupation numbers ($n_x = 1.0$, $n_y = 1.0$, $n_z = 1.25$) are in good agreement with a semiempirical calculation[10] for N_2. For the free NO molecule, the addition of one more electron to the molecule presumably increases the n_x and n_y occupation numbers due to increased occupation of the π-orbitals. This causes the reduction of the NO quadrupole coupling strength to eqQ = -1.86 MHz. For the CpNiNO complex, there is a further reduction to eqQ = −1.216 (11) MHz. Since this is a strongly bound complex, we expect larger orbital occupation numbers for p$_x$, p$_y$, and p$_z$ orbitals on the nitrogen. To account for the eqQ reduction, we therefore appear to have larger increases in the p$_x$ and p$_y$ orbital occupation than in the nitrogen p$_z$. This implies greater π-type bonding (associated with p$_x$, p$_y$) to the metal atom than σ-type bonding (associated with p$_z$).

For the linear and symmetric molecules such as CpNiNO discussed above with the NO group on the symmetry axis, the π_x and π_y or nitrogen p$_x$ and p$_y$ orbitals are equivalent, so the two quadrupole coupling components along these two axes are also the same. In this case, the bonding is fairly simple and the quadrupole coupling can be characterized by a single number. In molecules that have nonlinear X–NO groups, with X being a metal or other atom, the situation is qualitatively and quantitatively quite different.

For CH_3NO, eq$_{aa}$Q = 0.5 MHz, eq$_{bb}$Q = -6.02 MHz, and eq$_{cc}$Q = 5.52 MHz,[11] and for $(NO)_2$ eq$_{aa}$Q = -4.066 MHz, eq$_{bb}$Q = -2.242 MHz, and eq$_{cc}$Q = 6.307 MHz.[12] In both of these cases there is a large positive value perpendicular to the plane of the molecule (c-axis component). The in-plane, b-component is large and negative. For these cases, the energies and orbital occupation of the orbitals that correspond to the π_x and π_y orbitals for a linear system are much different. If we apply the Townes-Daily type relations to these systems, it would appear that the orbital occupation of the nitrogen p-orbital perpendicular to the plane of the X–NO system is smaller than the occupation of the in-plane p-orbitals. We see that nitrogen quadrupole coupling in the NO group is quite sensitive to the bonding and the X–NO angle. Nitrogen is probably the case where the Townes-Dailey relation[9] between quadrupole coupling strength and unbalanced occupation of the p-orbitals works best.

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