ScN ($X^1\Sigma^+$): $J = 1 \rightarrow 0$

Fourier Transform Microwave Spectroscopy
of
Metal Nitrides and Imides: Quadrupole Structure in ScN ($X^1\Sigma^+$),
YN ($X^1\Sigma^+$), and BaNH ($\tilde{X}^1\Sigma^+$)

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Abstract

Pure rotational spectra of ScN, YN and BaNH in their $^1\Sigma^+$ ground electronic states were recorded in the 15 – 55 GHz region using Fourier transform microwave/millimeter-wave spectroscopy. Hyperfine components arising from the $J = 1 \rightarrow 0$ transitions were measured for all three molecules, and for YN, in the $J = 2 \rightarrow 1$ line, as well. The ^{15}N isotopologues were also observed for the nitride species. The molecules were created in a supersonic jet by the reaction of metal vapor with ammonia using a discharge-assisted laser ablation source (DALAS). From these data, electric quadrupole and nuclear spin rotation hyperfine parameters were determined for the nitrogen nucleus in all species; metal hyperfine constants were additionally measured for ScN and YN. DFT calculations using the B3LYP functional were also performed to help aid in spectral assignments. For ScN, the scandium quadrupole coupling constant ($eQq = 33.818(19)$ MHz) was found to be considerably smaller than in the corresponding halides, suggesting a different electronic structure. The nitrogen coupling constant for ScN is consistent with a more covalent molecule, perhaps even a diradical structure as well. In BaNH, a relatively small value of the nitrogen quadrupole coupling constant of $eQq = 0.039(11)$ MHz was determined, attributable to the non-terminal position of the nitrogen atom and the Ba-N triple bond.

Keywords:

Fourier transform microwave/mm-wave spectroscopy; hyperfine structure; quadrupole coupling constants; laser ablation

1. Introduction

Understanding the nature of the metal-nitrogen bond is important for many areas of chemistry. Such bonds play a major role in semiconductors [1], as well as in catalysts [2] and biochemical nitrogen fixation processes [3]. Insight into the M-N bond can be obtained via high-resolution spectroscopy, in particular by observing nitrogen and metal hyperfine interactions. Two classes of molecules are relevant in this regard: metal nitrides (MN) and metal imides (MNH). Although a variety of nitride and imide species have been investigated in the gas-phase spectroscopically, such as TiN, VN, CrN, MoN, ScNH, YNH and LaNH [4-9], few have been studied with sufficient resolution to examine their hyperfine structure. ScN, YN, and BaNH are three such species for which no hyperfine parameters are known.

ScN was first observed in the gas phase using Fourier transform emission spectroscopy [10], in which several $\Delta v = 0$ vibrational bands of the $A^1\Sigma^+ - X^1\Sigma^+$ transition were recorded. This work was followed by two jet-cooled laser induced fluorescence spectroscopic investigations by Nakhate and Mukund [11,12]. In these studies several new excited electronic states were observed and equilibrium rotational and vibrational parameters, as well as RKR potential energy curves, were determined for the $X^1\Sigma^+$, $A^1\Sigma^+$ and $a^3\Sigma^+$ states. From these works, the ground state of ScN was firmly established as $^1\Sigma^+$. ScN has also been the subject of several computational studies, all of which predict the ground state term to be $^1\Sigma^+$ [13-16]. However, the description of the Sc – N bond in the $X^1\Sigma^+$ state differs depending on the computational method. MC-SCF calculations of Kunze and Harrison [13] predict a highly ionic $\text{Sc}\equiv\text{N}$ triple bond, whereas the multi-reference *ab initio* studies of Daoudi et al. [14,15] suggests a far less ionic, diradical species with a Sc – N double bond and two unpaired electrons, $\cdot\text{Sc}=\text{N}\cdot$.

The first experimental observation of YN in the gas phase was reported by Ram and Bernath [17]. They assigned the ground state as $^1\Sigma^+$ in analogy with ScN and rotationally analyzed several $\Delta v = 0$ bands in the $A^1\Sigma^+ - X^1\Sigma^+$ transition. Subsequently, Jakubek et al. [18, 19] used molecular jet techniques to study yttrium nitride and discovered several new excited states of this molecule. Rotational and vibrational constants for the $A^1\Sigma^+$, $a^3\Sigma^+$ and $X^1\Sigma^+$ states were determined from these measurements. In contrast to ScN, however, computational studies of YN are limited. The initial investigation by Shim and Gingerich [20] used CASSCF methods to examine nine electronic states of this nitride. The ground state was reported to be $^1\Sigma^+$ with a Y – N double bond. The only other theoretical work calculated potential energy curves for 14 low-lying energy states of YN using the MSCASPT2 method [21].

Only one gas-phase experimental study of BaNH exists to date. The millimeter-wave spectra of $^{138}\text{BaNH}$, $^{137}\text{BaNH}$, $^{138}\text{BaND}$ and $^{137}\text{BaND}$ were recorded by Janczyk et al. [22] using direct absorption methods and Broida-oven synthetic methods. Rotational constants were determined for each isotopologue, allowing a more sophisticated $r_m^{(1)}$ structure to be derived. DFT calculations were also performed in order to examine the preferential production of the imide (MNH) as opposed to the amide (MNH₂). The computational work suggested a Ba – N triple bond and a charge distribution analysis indicated the Ba – N bond had significant covalent character.

In order to further investigate metal-nitrogen bonding, we have recorded the Fourier transform microwave/millimeter-wave (FTMmmW) spectra of ScN, YN and BaNH in their $^1\Sigma^+$ ground electronic states in the 15- 55 GHz region, as well as Sc¹⁵N and Y¹⁵N. Pure rotational data did not previously exist for either nitride species. Hyperfine structure arising primarily from the nitrogen nucleus, and in the case of ScN, scandium, were resolved for all species. From these

measurements, electric quadrupole and nuclear spin-rotation parameters have been determined for the first time for these molecules. These constants have been used to interpret the character of the metal-nitrogen bond.

2. Experimental

Pure rotational transitions of ScN, YN and their ^{15}N isotopologues, as well as BaNH, were recorded using the Fourier transform microwave/mm-wave (FTMmmW) spectrometer of the Ziurys group. The instrument is equipped with a discharge-assisted laser ablation source or DALAS [23] for the synthesis of metal-containing molecules. Briefly, the spectrometer consists of a Fabry-Perot cavity with two spherical aluminum mirrors in a near confocal arrangement, housed in a vacuum chamber evacuated by a cryo pump [24]. Two separate sets of mirrors are employed for work in the lower (4 – 40 GHz) and higher (40-60 GHz) bands. The injection and detection of microwave radiation occurs via antennas (4 – 40 GHz) or waveguide (40 – 60 GHz) embedded in opposite mirrors [24,25]. A pulsed valve is used to introduce a supersonic jet into the cavity 40° relative to the optical axis. Spectra are created via a fast Fourier transform from time domain signals recorded over a 600 kHz frequency range. Transitions appear as Doppler doublets and transition frequencies are taken as the doublet average with an instrumental uncertainty of ± 2 kHz.

ScN, YN and BaNH were synthesized by the reaction of metal vapor with NH_3 in the presence of a DC discharge, using DALAS. A 0.2% concentration of ammonia (Matheson Gas Products, Inc.) in argon was used as the reaction gas mixture, with a gas backing pressure of 34 psi (flow ~ 40 sccm). Rods of solid scandium (American Elements) and yttrium (ESPI Metals) were employed for the ablation, using the second harmonic (532 nm) of a Nd:YAG laser (200 mJ per pulse). For barium, a thin layer of the metal (Sigma Aldrich) was glued to an aluminum rod

in a process described previously [26]. For ^{15}N isotopologues, $^{15}\text{NH}_3$ (^{15}N : 98%, Cambridge Isotope Laboratories) was used under identical conditions. The timing sequence for each experiment, conducted at a 10 Hz rate, was as follows. At the start of the sequence, the pulse valve was opened for 750 μs and the DC discharge (1250 V) applied for a duration of 1390 μs . Optimal conditions for BaNH required a discharge of 1000 V for 1500 μs . At 990 μs after the start, the ablation laser was fired, and the microwave radiation injected into the cavity about 500 μs thereafter. For ScN and YN, 1,000 shots were averaged per frequency step, but the weaker BaNH signals required 10,000 shots to achieve a comparable S/N ratio.

3. Results and Analysis

Rotational constants from either optical (ScN and YN [10,17]) or millimeter-wave (BaNH [22]) spectroscopic studies were used to predict the $J = 1 \rightarrow 0$ transition for the most abundant isotopologue of each molecule. The rotational constants for the previously unobserved ^{15}N isotopologues were estimated via scaling by the reduced mass. A 10-14 MHz region, centered on each predicted transition frequency, was scanned to locate the multiple hyperfine transitions present.

Figure 1 presents FTMmmW spectra for ScN. In the top panel, the $J = 1 \rightarrow 0$ transition of Sc^{14}N is shown. There are two frequency breaks to display the data and Doppler doublets are indicated by brackets. The spectrum consists of three well-separated quadrupole hyperfine components arising from the scandium nuclear spin $I = 7/2$ and labeled by quantum number F_1 , where $\mathbf{F}_1 = \mathbf{J} + \mathbf{I}(\text{Sc})$. Within each of these components much smaller hyperfine splittings are visible due to the ^{14}N nuclear spin of $I = 1$; these features are indicated by quantum number F ($\mathbf{F} = \mathbf{F}_1 + \mathbf{I}(\text{N})$). The relative magnitude of the hyperfine interactions is consistent with the quadrupole moments of scandium ($-0.2 \times 10^{24} \text{ cm}^{-2}$) and nitrogen ($Q = +0.02 \times 10^{24} \text{ cm}^{-2}$) [27].

In the lower panel of Figure 1, the $J = 1 \rightarrow 0$ rotational transition of Sc^{15}N is shown. Two frequency breaks are again present in the figure. The three hyperfine components arising from scandium exhibit a nearly identical pattern as compared to Sc^{14}N . Nitrogen hyperfine splittings are much smaller in magnitude as compared to Sc^{14}N , however, and are most clearly visible in the $F_1 = 4.5 \rightarrow 3.5$ hyperfine component. Because the ^{15}N nucleus has $I = 1/2$, there is no quadrupole moment, and the smaller interactions in the spectra arise solely from nuclear spin-rotation coupling.

Figure 1. Spectra of the $J = 1 \rightarrow 0$ transition of Sc^{14}N (upper panel) and Sc^{15}N (lower panel) measured near 31-33 GHz using FTMmmW methods. Doppler doublets are indicated by brackets above the spectral features. The data for each isotopologue contains two frequency breaks in order to display the three scandium hyperfine components, labeled by quantum number F_1 , where $F_1 = J + I(\text{Sc})$. Additional splittings within each scandium hyperfine component arise from the N nucleus and are indicated by F , where $F = F_1 + I(\text{N})$. Each individual spectrum is 600 kHz wide and required 1000 pulse averages.

Table 1 lists the measured transition frequencies for Sc¹⁴N and Sc¹⁵N. As the table shows, eight lines for the main isotopologue were recorded, attributable to 19 individual transitions. For the ¹⁵N species, five frequencies were measured arising from 10 transitions.

Table 1. Measured Rotational Transitions for ScN ($X^1\Sigma^+$)^a

J'	F ₁ '	F'	→	J''	F ₁ ''	F''	ν_{obs}	$\nu_{\text{obs}} - \nu_{\text{calc}}$
Sc ¹⁴ N								
1	2.5	2.5		0	3.5	2.5	33139.179	0.002
1	2.5	2.5		0	3.5	3.5	33139.179	0.002
1	2.5	3.5		0	3.5	2.5	33139.179	<0.001
1	2.5	3.5		0	3.5	3.5	33139.179	<0.001
1	2.5	3.5		0	3.5	4.5	33139.179	<0.001
1	2.5	1.5		0	3.5	2.5	33139.195	-0.001
1	4.5	4.5		0	3.5	3.5	33141.540	-0.001
1	4.5	4.5		0	3.5	4.5	33141.540	-0.001
1	4.5	3.5		0	3.5	2.5	33141.562	-0.001
1	4.5	3.5		0	3.5	3.5	33141.562	-0.001
1	4.5	3.5		0	3.5	4.5	33141.562	-0.001
1	4.5	5.5		0	3.5	4.5	33141.574	0.001
1	3.5	2.5		0	3.5	2.5	33147.813	0.002
1	3.5	2.5		0	3.5	3.5	33147.813	0.002
1	3.5	4.5		0	3.5	3.5	33147.822	-0.003
1	3.5	4.5		0	3.5	4.5	33147.822	-0.003
1	3.5	3.5		0	3.5	2.5	33147.856	0.001
1	3.5	3.5		0	3.5	3.5	33147.856	0.001
1	3.5	3.5		0	3.5	4.5	33147.856	0.001
Sc ¹⁵ N								
1	2.5	2		0	3.5	3	31463.522	0.002
1	2.5	3		0	3.5	3	31463.526	-0.002
1	2.5	3		0	3.5	4	31463.526	-0.002
1	4.5	5		0	3.5	4	31465.873	-0.001
1	4.5	4		0	3.5	3	31465.885	0.001
1	4.5	4		0	3.5	4	31465.885	0.001
1	3.5	4		0	3.5	3	31472.162	0.001
1	3.5	4		0	3.5	4	31472.162	0.001
1	3.5	3		0	3.5	3	31472.162	-0.001
1	3.5	3		0	3.5	4	31472.162	-0.001

^a In MHz.

In Figure 2, the $J = 1 \rightarrow 0$ transitions of Y¹⁴N and Y¹⁵N are shown in the upper and lower panels, respectively. Brackets mark the Doppler doublets. Yttrium has a nuclear spin of 1/2, and thus no quadrupole moment. In the Y¹⁴N spectrum, the main hyperfine interaction therefore

arises from the quadrupole moment of the nitrogen nucleus, indicated by F_1 . The splitting in this case is roughly 400 kHz in magnitude – comparable to that found in ScN for the nitrogen nucleus. The small additional splittings (< 20 kHz) arise from nuclear spin-rotation coupling of the yttrium nucleus, labeled by F . In the $Y^{15}N$ spectrum, the very compact hyperfine structure arises exclusively from spin-rotation interactions of both nuclei.

Figure 2. Spectra of the $J = 1 \rightarrow 0$ transition of $Y^{14}N$ (upper panel) and $Y^{15}N$ (lower panel) measured near 24 - 26 GHz using FTMmmW methods. Doppler doublets are indicated by brackets above the spectral features. For $Y^{14}N$, nitrogen quadrupole interactions dominate the spectrum, labeled by F_1 , where $\mathbf{F}_1 = \mathbf{J} + \mathbf{I}(N)$, while smaller splittings are due to yttrium nuclear spin-rotation coupling, indicated with F , where $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}(Y)$. For $Y^{15}N$, the hyperfine components are barely discernable and arise exclusively from nuclear-spin rotation coupling. Both spectra are a composite of 1000 pulse averages.

Table 2 presents all lines measured for YN. For both isotopologues, the $J = 2 \rightarrow 1$ transition was also recorded. For the main isotopic species, 6 lines were measured, corresponding to 11 transitions; for $Y^{15}N$, 5 individual features were recorded for 9 transitions.

Table 2. Measured Rotational Transitions for YN ($X^1\Sigma^+$)^a

J'	F_1'	F'	$\rightarrow$	J''	F_1''	F''	ν_{obs}	$\nu_{\text{obs}} - \nu_{\text{calc}}$
$Y^{14}N$								
1	1	1.5		0	1	0.5	25582.706	< 0.001
1	1	1.5		0	1	1.5	25582.706	< 0.001
1	1	0.5		0	1	0.5	25582.711	< 0.001
1	1	0.5		0	1	1.5	25582.711	< 0.001
1	2	2.5		0	1	1.5	25582.812	< 0.001
1	2	1.5		0	1	0.5	25582.822	< 0.001
1	2	1.5		0	1	1.5	25582.822	< 0.001
1	0	0.5		0	1	0.5	25582.930	< 0.001
1	0	0.5		0	1	1.5	25582.930	< 0.001
2	3	3.5		1	2	2.5	51165.080	0.004
2	3	2.5		1	2	1.5	51165.080	-0.004
$Y^{15}N$								
1	1.5	2		0	0.5	1	24117.590	0.001
1	1.5	1		0	0.5	0	24117.597	-0.001
1	1.5	1		0	0.5	1	24117.597	-0.001
1	0.5	1		0	0.5	0	24117.607	-0.001
1	0.5	1		0	0.5	1	24117.607	-0.001
1	0.5	0		0	0.5	1	24117.616	0.001
2	2.5	2		1	1.5	1	48234.746	-0.002
2	2.5	3		1	1.5	2	48234.746	0.006
2	1.5	2		1	0.5	1	48234.746	-0.004

^a In MHz.

In Figure 3, the FTMmmW spectrum of the $J = 1 \rightarrow 0$ transition of BaNH is displayed. It consists of three discernable quadrupole hyperfine components, arising from the nitrogen nucleus. Doppler doublets are indicated by brackets. The measured transition frequencies from these data are listed in Table 3.

Figure 3. The FTMmmW spectrum of the $J = 1 \rightarrow 0$ transition of BaNH near 16 GHz, composed of three ^{14}N quadrupole hyperfine components. Doppler doublets are indicated by brackets. This spectrum was created from 10,000 pulse averages.

Table 3. Measured Rotational Transitions for BaNH ($\tilde{X}^1\Sigma^+$)^a

J'	F'	$\rightarrow$	J''	F''	ν_{obs}	$\nu_{\text{obs}} - \nu_{\text{calc}}$
1	0		0	1	15969.012	<0.001
1	2		0	1	15969.030	<0.001
1	1		0	1	15969.041	<0.001

^a In MHz.

Because of the complex spectra and presence of blended features, DFT calculations were also conducted to provide estimates of the hyperfine parameters and aid in the analysis. These calculations were carried out using Gaussian09 [28]. The B3LYP functional [29] and several basis sets, including aug-cc-pVTZ (Sc and N), LANL2DZ (Sc, Y) and SDD (Sc, Y, Ba, N, H), were chosen because of their utility for transition metal containing molecules; see [30-32]. Table 4 lists the derived quadrupole coupling (eQq) and nuclear spin rotation (C_I) parameters for each species.

Table 4. DFT B3LYP Calculations of Hyperfine Parameters^a

Molecule	Basis Set	eQq (M)	C_I (M)	eQq (N)	C_I (N)
Sc ¹⁴ N	aug-cc-pVTZ	41.540	0.05037	-0.4385	0.01096
	aug-cc-pVTZ/LANL2DZ ^b	14.671	0.05559	-0.5363	0.01099
	SDD	13.508	0.05856	-0.1540	0.009174
Sc ¹⁵ N	aug-cc-pVTZ	41.540	0.04781		-0.01459
	aug-cc-pVTZ/LANL2DZ ^b	14.671	0.05277		-0.01464
	SDD	13.508	0.05559		-0.01222
Y ¹⁴ N	aug-cc-pVTZ/LANL2DZ ^b		-0.001785	-1.076	0.008638
	SDD		-0.001749	-0.9251	0.007333
Y ¹⁵ N	aug-cc-pVTZ/LANL2DZ ^b		-0.001682		-0.011142
	SDD		-0.001649		-0.009695
BaNH	SDD			1.38	0.001840

^a In MHz.^b aug-cc-pVTZ (N), LANL2DZ (M).Table 5. Spectroscopic Parameters for ScN, YN and BaNH ($X^1\Sigma^+$)^a

	Sc ¹⁴ N		Sc ¹⁵ N		Y ¹⁴ N		Y ¹⁵ N		BaNH	
	This work	Optical ^b	This work		This work	Optical ^c	This work		This work ^d	mm-wave ^e
B	16571.5278(10)	16571.42(69)	15733.6921(14)		12791.4396(32)	12791.237(51)	12058.8364(27)		7984.5273(18)	7984.5488(29)
D		0.03150 (12)			0.0217(13)	0.021262(60)	0.0186(13)		0.005711(11)	0.0057642(19)
H									-5.4(1.9) x 10 ⁻⁸	
L									1.98(94) x 10 ⁻¹¹	
eQq (M)	33.818(19)		33.811(30)							
C_I (M)	0.05553(63)		0.05275(77)		-7.6(5.7) x 10 ⁻³		-6.9(3.8) x 10 ⁻³			
eQq (N)	-0.127(19)				-0.307(10)				0.039(11)	
C_I (N)	7.3(3.0) x 10 ⁻³		-8.5 (6.1) x 10 ⁻³		8.1 (2.3) x 10 ⁻³		-10.4 (3.1) x 10 ⁻³			
rms	0.001		0.001		< 0.001		0.001		0.026	0.029

^a Uncertainties are 3 σ .^b Ref. [10]^c Ref. [17]^d Combined fit with mm-wave data from Ref. [22]^e Ref. [22]

The data for ScN, YN and BaNH were fit to the following effective Hamiltonian [33], which consists of rotational, quadrupole and nuclear spin-rotation terms:

$$\hat{H}_{eff} = \hat{H}_{rot} + \hat{H}_{quad} + \hat{H}_{nsr} \quad (1).$$

A least squares fit was performed for each individual isotopologue using Pickett's SPFIT program [34]. Signs of the fitted hyperfine parameters were chosen to agree with the DFT results in Table 4. Pure rotational transitions measured in this work were weighted with an uncertainty of ± 2 kHz. In the case of BaNH, a combined fit of the newly measured $J = 1 \rightarrow 0$ transition and previously measured millimeter-wave lines (weighted uncertainty of ± 50 kHz) was performed. Additional centrifugal distortion constants (H and L) were necessary in this combined fit. Because only one transition of ScN and Sc¹⁵N was measured, the centrifugal distortion constant was set to zero in these analyses.

Table 5 lists the spectroscopic constants determined from the analysis for the isotopologues of ScN, YN and BaNH, along with previously-derived rotational constants. Of greatest significance are the molecular hyperfine parameters for Sc, Y and N, which have been measured for the first time in the three molecules. The experimental hyperfine constants are within an order of magnitude of the computational values (see Table 4); differences would most likely be minimized by using larger basis sets. Although the ¹⁵N nuclear spin rotation constants for Sc¹⁵N and Y¹⁵N have relatively large uncertainties, this parameter was required to reproduce the small splittings observed in the spectra. Also, the nuclear spin-rotation parameters for ScN and YN scale as the product of the nuclear g factor (g_I) and the rotational constant for a given pair of isotopologues [35], lending further credence to the analysis. For BaNH, the relative intensities of the hyperfine components are consistent with a positive value of eQq (N) [33].

4. Discussion

Table 6 lists the quadrupole coupling constants for diatomic, closed-shell scandium containing molecules. As noted by Gerry and coworkers, a simple quantitative interpretation of eQq in terms of the Townes-Dailey model is difficult for transition metals [35]. However, a qualitative comparison can be made. As shown in the table, ScN has the smallest quadrupole coupling constant in comparison to the halides. For ScN, $eQq(Sc) = 33.818$ MHz, while the value for ScF is 74.09 MHz [35]. The different value of $eQq(Sc)$ for the nitride as compared to the halides indicates a change in the electronic distribution about the scandium nucleus. In ScF, the σ HOMO is thought to be composed of primarily Sc 4s atomic orbital character with an orbital population of 1.72 [35]. In contrast, a scandium 4s atomic orbital population of 0.689 in ScN is calculated by Daoudi et al. [14]. These theoretical orbital populations are consistent with the differing values of $eQq(Sc)$.

Table 6. Scandium Quadrupole Coupling Constants (in MHz)

Molecule	eQq^a
ScF	74.086(15) ^b
ScCl	68.207(9) ^b
ScBr	65.256(9) ^c
ScN	33.818(19) ^d

^a 3σ uncertainties.

^b Ref. [35].

^c Ref. [36].

^d This work.

The Townes-Dailey analysis for hybrid orbitals can be employed to provide a more quantitative interpretation of $eQq(N)$ values for the nitrides [33,37,38]. This model asserts that only valence p electrons of a given atom need to be considered for contributions to eQq . As discussed in Ref. [38], the core and valence s electrons have spherically-symmetric distributions, and therefore do not contribute to the electric field gradient. Moreover, 3d electrons produce a field gradient smaller than the 2p electrons by a factor of 47, and therefore can also be neglected.

As a consequence, $eQq(N)$ can be related directly to the atomic nitrogen 2p quadrupole coupling parameter $eQq_{21}(\chi_0)$ and the atomic orbital populations in the molecule via the expression [33,37,38]:

$$eQq(N) = eQq_{21} \left(n_{\text{hybrid}} - \frac{1}{2} n_{p_x} - \frac{1}{2} n_{p_y} \right) \quad (2).$$

Using $eQq_{21} = -11.2$ MHz [38] and the orbital populations for ScN of Kunze and Harrison [10], namely $n_{\text{hybrid}} = 3.01$, $n_{p_x} = n_{p_y} = 1.27$, $eQq(N)$ was calculated to be -2.63 MHz for scandium nitride. If the populations of Daoudi et al. [11] are employed instead ($n_{\text{hybrid}} = 2.63$, $n_{p_x} = n_{p_y} = 1.29$), the $eQq(N) = -0.280$ MHz for ScN. The value obtained using the calculations of Daoudi et al. is in better agreement with the experimental $eQq(N) = -0.127$ MHz. This result lends further support to the covalent, diradical bonding description of ScN suggested by Daoudi et al. [14], as opposed to the more ionic, triple bond scheme from ref. [10].

In the case of YN, nitrogen atomic orbital populations available from Shim and Gingerich [20] can be used to estimate $eQq(N)$. This computational study suggests YN has a double-bond comprised of two π bonds. Using their values of $n_{\text{hybrid}} = 2.89$, $n_{p_x} = n_{p_y} = 1.31$, $eQq(N)$ in this case is calculated to be -1.512 MHz, nearly an order of magnitude larger than the experimental value of -0.307 MHz. This discrepancy may indicate a lower bond order in YN.

The value of $eQq(N) = 0.039$ MHz for BaNH is rather low relative to the other two nitrides. Unfortunately, $eQq(N)$ values for other MNH species are not available for comparison. However, triply-bonded terminal nitrogen atoms typically possess higher quadrupole constants than those that are not [37], for example, CH_3NC ($eQq(N) = 0.4885(1)$ MHz) vs. CH_3CN ($eQq(N) = -4.22410(98)$ MHz) [39, 40]. The previous millimeter-wave/DFT study of BaNH indicated the presence of a triple bond between the barium and nitrogen atoms,

with nitrogen being the middle atom. The smaller value of eQq (N) determined for BaNH is consistent with this description.

Acknowledgements

This research was supported by NSF Grant CHE 10-57924. JPY, MKLB and PMS would like to thank Canisius College for providing travel funds and the Ziurys group for the use of their spectrometer and their hospitality.

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