However, we can make some estimations. Based on group theory, the T_{2u} sublevel should couple with either of the a_{2g}, e_g, t_{1g}, and t_{2g} vibrational modes in order to acquire allowed dipole character. Hartley and Ware[6] assigned the Raman band of 92 cm^{-1} observed for $[Mo_6Cl_{14}]^{2-}$ to t_{2g}. This is exactly in accord with the result obtained above (eq 8) if the potential displacement for the T_{2u} sublevel is identical to that for the T_{1u} sublevel. We may thus conclude that the T_{2u} phosphorescence gains allowed character through vibronic coupling with the 90-cm^{-1} t_{2g} vibrational mode.

The vibrational species to couple with the E_u sublevel should be either t_{1g} or t_{2g}. All the four t_{2g} vibrational modes for this cluster ion were observed[6] at 92, 195, 225, and 247 cm^{-1}. Two Raman-inactive t_{1g} vibrations have not been observed; however, in view of rather heavy constituent atoms (Mo and Cl), none of the vibrational modes are regarded as high as 710 cm^{-1}. Thus, the above result (eq 7) demonstrates that the E_u sublevel is displaced along a totally symmetric mode to some extent as compared with the other two sublevels. This displacement is the main cause of the peculiar temperature dependence of the spectral shift.

Conclusions. In this paper, we were able to determine the relative radiative rate constants of the three emitting sublevels, and this result directly substantiates the previously proposed sublevel assignment. We were also able to determine the individual sublevel spectra. The agreement between the observed and simulated spectra was not complete, especially at higher temperatures, but we believe that the method presented here is a powerful method to apply for such a broad and structureless spectrum where approaches from vibrational analysis are totally impossible.

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Electric Field Gradients and Nuclear Quadrupole Coupling Constants of Isonitriles Obtained from Møller–Plesset and Quadratic Configuration Interaction Calculations

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Electric field gradients and nuclear quadrupole coupling constants of 12 nitrogen-containing molecules have been calculated using basis sets of valence DZ+P and valence TZ+P quality at *n*th-order Møller–Plesset perturbation (MP*n*, $n = 2, 3, 4$), Coupled Cluster (CC) and quadratic configuration interaction (QCI) theory. MP*n* results are problematic since calculated values oscillate with the order *n* of the perturbation calculation. Test calculations for N_2, HCN, and HNC indicate that reliable values can be obtained for a VTZ+2P basis set at the MP4, QCISD, or QCISD(T) level of theory. However, for comparison with experimental values vibrational corrections have to be known. Alternatively, a smaller basis set and a less costly method can be applied provided an effective quadrupole moment $Q^*(^{14}N)$ has been determined that covers basis set, correlation, and vibrational corrections. Using the Q^* approach, nuclear quadrupole coupling constants have been calculated for the isonitriles CH_3NC, CF_3NC, NCNC, $HC{\equiv}CNC$, FCH_2NC, F_2CHNC, CH_3CH_2NC, $H_2C{=}CHNC$, and $HC{\equiv}C\text{-}CH_2NC$. Satisfactory results are obtained at the MP3/TZ+P level of theory. This is due to the fact that at MP3 errors cancel largely and, therefore, the Q^* approach becomes very effective.

1. Introduction

In a molecule, the electric field gradient (efg) **q** at the site of a nucleus A is given by the second derivatives of the Coulomb potential V with respect to the Cartesian coordinates where V is determined by the charge distribution surrounding A. Accordingly, **q** is a tensor of rank 2 that comprises contributions both from the nuclear and the electronic charge distribution in the molecule. The elements $q_{\alpha\beta}$ ($\alpha, \beta = x, y, z$) of the efg tensor **q** at nucleus A are determined by eq 1 where Z_B is the nuclear

$$q_{\alpha\beta}(A) = \sum_{B \neq A} Z_B(3\mathbf{R}_{BA,\alpha}\mathbf{R}_{BA,\beta} - \delta_{\alpha\beta}R_{BA}{}^2)/R_{BA}{}^5 - \langle\Phi|\sum_p(3\mathbf{r}_{pA,\alpha}\mathbf{r}_{pA,\beta} - \delta_{\alpha\beta}r_{pA}{}^2)/r_{pA}{}^5|\Phi\rangle \quad (1)$$

charge of nucleus B, $\mathbf{R}_{BA}$ is a vector from nucleus A to nucleus B, $\mathbf{r}_{pA}$ is a vector from A to electron p, and δ is the Kronecker delta.

The value of the quadrupole coupling constant χ of a nucleus with spin $I \geq 1$ depends on its scalar nuclear quadrupole moment Q and the efg at the nucleus according to

$$\chi_{\alpha\beta} = eQq_{\alpha\beta}/h \quad (2)$$

where e and h have their usual meaning. With the experimental χ in MHz and the efg **q** in atomic units (au) from (1), the nuclear quadrupole moment Q in mbarn is given by eq 3.[1a]

$$Q = 4.256\chi_{\alpha\beta}/q_{\alpha\beta} \quad (3)$$

The nuclear quadrupole moment of the ^{14}N nucleus has been experimentally determined by Ensslin and co-workers[2] to be 17.4 (2) mbarn and more recently by Winter and Andrä[3] to be 19.3 (8) mbarn. Efforts have been made to determine $Q(^{14}N)$ from ab initio calculations of efg in connection with experimental values of $\chi_{\alpha\beta}$ utilizing eq 3. For example, Sundholm and co-workers[4] have carried out both numerical Hartree–Fock (HF) and CASSCF calculations on N_2 and NO^+ obtaining for $Q(^{14}N)$ 20.5 (5) mbarn. Cernusak and co-workers[5] have calculated $Q(^{14}N) = 20.5$ (1) mbarn for N_2 employing many-body perturbation

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theory up to fourth order and large basis sets. Gerber and Huber[1] have reported values of 20.0 and 19.9 mbarn for N_2 and NO^+, respectively, using basis sets of high local quality and fourth-order Møller–Plesset perturbation theory in the constrained space of single, double, and quadrupole excitations (MP4(SDQ)). Scuseria and Schaefer[6] have derived a value of 20.7 ± 0.4 mbarn from full CI calculations of the $^1P_1$(..2p3p) state of N^+ utilizing the experimental coupling constant. Hence, a $Q(^{14}N)$ value of 20.5 mbarn with an error limit of less than 5% is most likely.

The value of $Q(^{14}N)$ can be used in conjunction with eq 3 to predict quadrupole coupling constants of larger molecules from calculated efg values. Of course, numerical HF and CASSCF calculations are not feasible for larger molecules, and, therefore, one has to sacrifice the accuracy of calculated efg values by using methods that can handle larger molecules at reasonable computational costs. However, calculated $\chi_{\alpha\beta}$ values can be improved by introducing an effective nuclear quadrupole moment Q^* that provides the best fit between calculated and experimental $\chi_{\alpha\beta}$ data. Such an approach of empirically correcting calculated $\chi_{\alpha\beta}$ for ^{14}N values has been used by Barber and co-workers,[7] Gerber and Huber,[1b] Maksic and co-workers,[8] Aray and co-workers,[9,10] Palmer and co-workers,[11-14] Miller and Ragle,[15] and Brown and Head-Gordon.[16]

It is obvious that Q^* depends on both the basis set and the method used as well as on the set of reference molecules. The latter should contain important structural features of the molecules to be investigated (target molecules). In this way, the Q^* approach has been successfully applied for N-containing molecules with $\chi_{\alpha\beta}$ values in the range 1–6 MHz. So far, there are no reports in the literature that reveal whether the Q^* approximation can also be used in the case of weakly coupling molecules with $\chi_{\alpha\beta} \leq 1$ MHz.

In this work, we report ab initio calculations on N_2 (**1**), HCN (**2**), HNC (**3**), CH_3NC (**4**), CF_3NC (**5**), NCNC (**6**), $HC{\equiv}CNC$ (**7**), FCH_2NC (**8**), F_2CHNC (**9**), CH_3CH_2NC (**10**), $H_2C{=}CHNC$ (**11**), and $HC{\equiv}CCH_2NC$ (**12**) to determine their efg and $\chi_{\alpha\beta}$ values. Molecules **1**–**3** are reference molecules that are studied to analyze basis set and correlation effects and to assess the level of theory that is needed to obtain reliable efg and χ values. Molecules **4**–**12** (together with **3**) belong to the class of isonitriles. These molecules are presently the target of microwave investigations,[17] and, therefore, reliable predictions of their nuclear coupling constants $\chi_{\alpha\beta}$ are needed to facilitate the assignment of the hyperfine structure in the microwave spectrum, especially in the presence of a second coupling nucleus such as deuterium. In addition, a comparison of experimental and theoretical coupling constants can add proof to the structure determination. The coupling constants depend on the molecular structure and, therefore, agreement between experimental and theoretical data indicates that the correct structure has been determined.

2. Computational Methods

The efg values of reference molecules **1**–**3** have been calculated using three different basis sets. These are the 6-31G(d,p), the 6-311G(d,p), and the 6-311G(2d,2p) bases[18] which are of DZ+P, TZ+P, and TZ+2P quality in the valence shell (VDZ and VTZ basis sets). Calculations have been carried out at the Hartree–Fock (HF) level and at six different post-HF levels to account for electron correlation. Methods used comprise Møller–Plesset (MP) perturbation theory at second order (MP2), third order (MP3), and fourth order (MP4).[19,20] MP2 provides a reasonable estimate of correlation effects due to double (D) excitations without considering the coupling between different D excitations. This is done at the MP3 level, which therefore is comparable with CID. At MP4, the correlation effects due to single (S), D, and quadruple (Q) excitations can be considered thus leading to MP4(SDQ). If in addition correlation effects due to triple (T) excitations are included, a full MP4 treatment denoted as MP4(SDTQ) is achieved. At the moment it is not possible to go beyond the MP4 level to obtain the coupling between SDTQ excitations (MP5) or to consider the effects of pentuple and hextuple excitations (MP6). However, we will use results of the theoretical analysis of these methods[21] to make predictions with regard to changes of the efg at these levels of theory.

Coupled cluster theory (CC) has the advantage of introducing infinite-order effects in the correlation treatment, and, therefore, its description of correlation effects is more reliable than that obtained at the MP level. We have used CC theory with D excitations (CCD)[22] and the recently developed quadratic CI (QCI) methods[23] which can be considered as simplified CC approaches. In particular, we have used QCI with S and D excitations (QCISD) as well as QCISD with a perturbative treatment of T excitations (QCISD(T)) to get infinite order correlation effects due to S, D, and T excitations.

The correlation methods used in this work are methods (apart from CCD) without a wave function. Therefore, it is appropriate to calculate a one-electron property as a response property rather than as an expectation value. In the case of the efg $\mathbf{q}$ this implies the evaluation of[24]

$$q_{\alpha\alpha} = \sum_{\mu\nu} P_{\mu\nu}^{\mathrm{Res}} \langle \mu | (3r_\alpha^2 - r^2)/r^5 | \nu \rangle \tag{4a}$$

$$q_{\alpha\beta} = \sum_{\mu\nu} P_{\mu\nu}^{\mathrm{Res}} \langle \mu | 3r_\alpha r_\beta / r^5 | \nu \rangle \tag{4b}$$

with α, β = x, y, z and the one-electron integrals are the efg integrals expressed in the space of the basis functions χ_μ. $\mathbf{P}^{\mathrm{Res}}$ is the response density matrix, which, in case of a HF wave function, is identical with the SCF density matrix $\mathbf{P}^{\mathrm{SCF}}$. For correlated wave functions, $\mathbf{P}^{\mathrm{Res}}$ contains also the correlation correction matrix $\mathbf{P}^{\mathrm{Cor}}$:

$$\mathbf{P}^{\mathrm{Res}} = \mathbf{P}^{\mathrm{SCF}} + \mathbf{P}^{\mathrm{Cor}} \tag{5}$$

We have recently described how to calculate response densities at the MPn and QCI level of theory[24-29] using the **z**-vector method.[30] We will use this procedure and the corresponding programs[31] to calculate the efg for the various methods outlined above.

Calculations for the reference molecules **1**–**3** have been carried out at experimental geometries[32-34] to guarantee comparison with other investigations already published in the literature. For the

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TABLE I: Calculated Electric Field Gradient q_{zz} (au) for N_2, HCN, and HNC at Their Experimental Equilibrium Geometries[a]

method	basis set	N_2	HCN	HNC
HF	6-31G(d,p)	−1.106	−0.967	0.196
	6-311G(d,p)	−1.307	−1.153	0.090
	6-311G(2d,2p)	−1.337	−1.173	0.059
MP2	6-31G(d,p)	−0.871	−0.741	0.215
	6-311G(d,p)	−1.067	−0.915	0.130
	6-311G(2d,2p)	−1.105	−0.942	0.089
MP3	6-31G(d,p)	−0.928	−0.810	0.228
	6-311G(d,p)	−1.138	−1.003	0.134
	6-311G(2d,2p)	−1.175	−1.033	0.091
MP4(SDQ)	6-31G(d,p)	−0.910	−0.787	0.238
	6-311G(d,p)	−1.114	−0.971	0.144
	6-311G(2d,2p)	−1.150	−0.999	0.104
MP4(SDTQ)	6-31G(d,p)	−0.885	−0.761	0.240
	6-311G(d,p)	−1.076	−0.930	0.151
	6-311G(2d,2p)	−1.109	−0.955	0.111
CCD	6-31G(d,p)	−0.915	−0.798	0.231
	6-311G(d,p)	−1.126	−0.990	0.136
	6-311G(2d,2p)	−1.162	−1.019	0.094
QCISD	6-31G(d,p)	−0.913	−0.788	0.241
	6-311G(d,p)	−1.119	−0.973	0.148
	6-311G(2d,2p)	−1.154	−1.001	0.107
QCISD(T)	6-31G(d,p)	−0.895	−0.774	0.239
	6-311G(d,p)	−1.094	−0.951	0.150
	6-311G(2d,2p)	−1.127	−0.977	0.109

[a] Experimental r_e geometries are as follows: N_2, r(NN) = 1.0977 Å;[32] HCN, r(HC) = 1.0655 Å, r(CN) = 1.1532 Å;[33] HNC, r(HN) = 0.9940 Å, r(NC) = 1.1689 Å.[34]

TABLE II: Basis Set Truncation Error $\Delta q^{\mathrm{Basis}}$, Correlation Error Δq^{cor}, and Vibrational Correlation Δq^{vib} (All in au) for N_2, HCN, and HNC

molecule	basis set	$\Delta q^{\mathrm{Basis}}$	Δq^{cor}	Δq^{vib}
N_2[a]	6-31G(d,p)	−0.230	0.210	
	6-311G(d,p)	−0.026	0.213	
	6-311G(2d,2p)	0.005	0.209	
				0.012
HCN[b]	6-31G(d,p)	−0.229	0.195	
	6-311G(d,p)	−0.043	0.203	
	6-311G(2d,2p)	−0.023	0.196	
				0.001
HNC[b]	6-31G(d,p)	−0.170	0.043	
	6-311G(d,p)	−0.064	0.060	
	6-311G(2d,2p)	−0.033	0.051	
				−0.047

[a] HF limit value and Δq^{vib} obtained at r(NN) = 1.0943 Å from ref 4, Δq^{cor} from eq 7. At this r(NN) value, q_{zz}(NN) is −1.106 (HF/6-31G(d,p)), −1.311 (HF/6-311G(d,p)), −1.341 au (HF/6-311G-(2d,2p)). [b] Estimated HF limit value and Δq^{vib} from ref 37, Δq^{cor} from eq 7.

target molecules, isonitriles **4–12**, experimental geometries are not available in all cases. Therefore, we have determined HF/6-31G(d) geometries for all target molecules. This level of theory is sufficient to provide a consistent description of molecular geometries.[29,35]

3. Results

Reference Molecules. Calculated efg's, q_{zz} (with z being the principal axis), of N_2, HCN, and HNC are given in Table I. In Table II, vibrational corrections and basis set truncation errors of theoretical efg values are listed. Utilizing calculated efg values together with vibrational corrections and experimental quadrupole coupling data, the ^{14}N nuclear quadrupole moment shown in Table III has been obtained from eq 3. In the following, calculated efg values are discussed in detail.

TABLE III: Nuclear Quadrupole Moment $Q(^{14}N)$ (in mbarn) for (a) N_2, (b) HCN, and (c) HNC As Obtained from Calculated q_{zz} Values (Table I), Vibrational Corrections Δq^{rib} (Table II), and Experimental Nuclear Quadrupole Coupling Constants χ_{zz} (N_2, −5.39;[36,38] HCN, −4.7091;[39] HNC, 0.28 MHz[45])

method	6-31G(d,p)	6-311G(d,p)	6-311G(2d,2p)
	(a) N_2		
HF	21.0	17.7	17.3
MP2	26.7	21.7	21.0
MP3	25.0	20.4	19.7
MP4(SDQ)	25.5	20.8	20.2
MP4(SDTQ)	26.3	21.6	20.9
CCD	25.4	20.6	19.9
QCISD	25.4	20.7	20.1
QCISD(T)	26.0	21.2	20.6
	(b) HCN		
HF	20.7	17.4	17.1
MP2	27.0	22.0	21.3
MP3	24.8	20.0	19.4
MP4(SDQ)	25.5	20.7	20.1
MP4(SDTQ)	26.4	21.6	21.0
CCD	25.2	20.3	19.7
QCISD	25.5	20.6	20.0
QCISD(T)	25.9	21.2	20.6
	(c) HNC		
HF	8.0	27.8	102.7
MP2	7.1	14.3	28.3
MP3	6.6	13.7	27.2
MP4(SDQ)	6.2	12.3	21.1
MP4(SDTQ)	6.2	11.4	18.7
CCD	6.5	13.4	25.3
QCISD	6.1	11.9	19.9
QCISD(T)	6.2	11.5	19.1

Molecular Nitrogen. The nuclear quadrupole coupling constant of N_2 (**1**) is not accessible by microwave (MW) spectroscopy but can be measured in the solid by nuclear quadrupole resonance (NQR) spectroscopy. The question of whether a solid-state quadrupole coupling constant can be meaningfully compared with a calculated value corresponding to the gas phase has been adequately answered by Sundholm and co-workers,[4] who found that the NQR coupling constant combined with the theoretical efg value according to (3) led to the same $Q(^{14}N)$ as in the case of NO$^+$ for which the gas-phase value of $\chi_{\alpha\beta}$ is available. The authors argue that the librational effects[36] in solid **1** are correctly accounted for by calculating vibrational corrections to **q** and that intermolecular effects on the value of **q** are small.

The experimental value of q can be considered as being approximated by the HF value of the efg obtained with a finite basis set plus appropriate correction terms for deficiencies of the basis set (basis set truncation error, $\Delta q^{\mathrm{Basis}}$), the correlation error (Δq^{Cor}), and vibrational effects (Δq^{Vib}). In addition, one has to consider the fact that at the HF/basis level the r_e geometry of the molecule differs both from the true r_e geometry as well as from the r_0 or r_s geometry determined by MW spectroscopy. Accordingly, a correction Δq^{Geom} has to be applied:

$$q^{\mathrm{exp}} = q^{\mathrm{HF}} + \Delta q^{\mathrm{Basis}} + \Delta q^{\mathrm{Cor}} + \Delta q^{\mathrm{Geom}} + \Delta q^{\mathrm{Vib}} \qquad (6)$$

However, by using experimental geometries or theoretical geometries close to experimental ones, Δq^{Geom} can be neglected or considered to be absorbed into the basis set truncation correction $\Delta q^{\mathrm{Basis}}$.

In Table II, corrections $\Delta q^{\mathrm{Basis}}$, Δq^{Cor}, and Δq^{Vib} are given for **1–3**. In the case of **1** $\Delta q^{\mathrm{Basis}}$ has been determined from the numerical HF value of q_{zz} = −1.3366 au (at R(NN) = 1.0943 Å) given by Sundholm and co-workers.[4] Values of Δq^{Cor} are approximated by

$$\Delta q^{\mathrm{Cor}} = q^{\mathrm{QCISD(T)}} - q^{\mathrm{HF}} \qquad (7)$$

since QCISD(T) is the most advanced correlation method used in this work. Vibrational corrections have been taken from refs 4 and 37.

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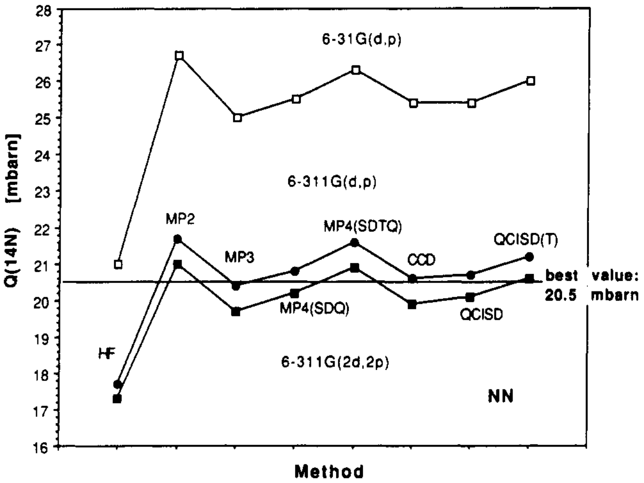

Figure 1. Dependence of the calculated $Q(^{14}N)$ nuclear quadrupole moment of N_2 (**1**) on method and basis set.

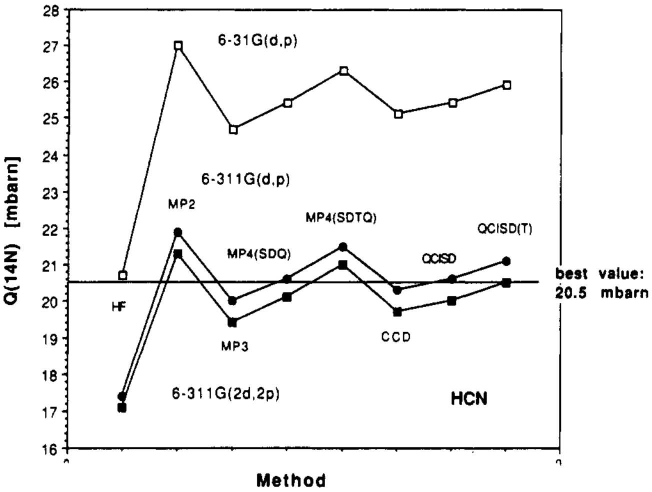

Figure 2. Dependence of the calculated $Q(^{14}N)$ nuclear quadrupole moment of HCN (**2**) on method and basis set.

The data in Table II reveal that the basis set error is substantial (ca. 20%) for the 6-31G(d,p) basis but becomes smaller than 3 and 1%, respectively, for the two VTZ basis sets. As in the case of molecular multipole moments[24,29], this shows that an accurate determination of one-electron properties requires basis sets of at least TZ+2P quality.

The correlation correction of $q_{zz}(N_2)$ is close to 20% and almost independent of the basis set used. Since it has the opposite sign than the basis set correction, a fortuitous cancellation of errors is observed for the HF/6-31G(d,p) result (see Table I). Compared to the correlation error, the vibrational correction is negligible leading to an increase of $q_{zz}(N_2)$ of less than 1%. We conclude that of all the corrections considered in eq 4, the correlation correction is the most important one in the case of **1** provided a sufficiently large basis set is used.

This is also reflected by the values of $Q(^{14}N)$ (see Table IIIa) obtained from the theoretical $q_{zz}(N_2)$ values after correcting for vibrational effects and an experimental nuclear quadrupole coupling constant χ_{zz} of −5.39 (5) MHz.[36,38] They are too high by 5–6 mbarn for the 6-31G(d,p) results but cluster between 20 and 21 mbarn for the two larger basis sets when correlation corrections are included into the calculation. Figure 1, which gives a graphical display of calculated $Q(^{14}N)$ values versus method and basis set used, reveals additional interesting aspects.

(1) Correlation corrections are indeed almost independent of the basis set used. Depending on the method applied, they range from 3 to 5 mbarn.

(2) At the MP*n* level, calculated values oscillate depending upon the order *n* of perturbation theory applied. If *n* is even (MP2, MP4), the *Q* value becomes too large; if *n* is odd (MP1 = HF, MP3), the *Q* value is too small. This has to do with the fact that correlation effects are very often overestimated (underestimated) at even (odd) orders of perturbation theory.[21] It is likely that these oscillations continue at MP5 and MP6.[21]

(3) The CCD and QCI results that cover infinite-order effects approach a limiting value that seems to be already reached at the QCISD(T) level: 26.0 for 6-31G(d,p); 21.2 for 6-311G(d,p); and 20.6 mbarn for 6-311G(2d,2p) (see Table III). We conclude that QCISD(T)/6-311G(2d,2p) leads to the most reliable value of $Q(^{14}N)$. Comparison with previously published values of $Q(^{14}N)$[4-6,37] confirms this observation.

Similar observations (independent of correlation effects from basis set, oscillatory behavior of Δq^{Cor} at MP*n*, and superiority of QCI/TZ+2P results) have been made before when calculating other response properties.[24,29]

Hydrogen Cyanide (2). Most observation made for **1** are also valid for **2**. Even though there is no HF limit value of q_{zz} for **2**, an estimate of the basis set truncation error can be made by comparing the relevant data in Table I with the HF/(11s,7p,2d,1f/6s,2p,1d) [6s,4p,2d,1f/4s,2p,1d] value $q_{zz}(\mathbf{2})$ = −1.196 au obtained by Cummins and co-workers.[37] Obviously, Δq^{Basis} is equal or larger than in the case of **1**, but this is not surprising because of the larger anisotropy of the density distribution in **2** that requires a larger and more flexible basis set for an accurate description. Nevertheless, the two augmented VTZ basis sets can be considered to provide reasonable accuracy while the VDZ+P basis is clearly too small.

Vibrational corrections Δq^{vib} for **2** are negligibly small (<1%), while correlation corrections Δq^{Cor} are similar to those obtained for **1** (ca. 20%). In Table IIIb and in Figure 2 calculated $Q(^{14}N)$ values (corrected for vibrational effects and obtained from χ_{aa} = −4.7091 (13) MHz[39]) are given which clearly stress the necessity of correlation corrections. Magnitude and trends of correlation effects are consistent with those observed for **1**.

Hydrogen Isonitrile (3). **3** was first observed with matrix isolation techniques.[40,41] The microwave spectrum of **3** was assigned by Snyder and Buhl[42] to an emission line from galactic sources and later confirmed by laboratory data.[43] The nuclear quadrupole coupling constant χ_{az} = −0.4 MHz is also of astrophysical origin.[44] It was later redetermined by Frerking and co-workers[45] to be 0.28 (3) MHz from the emission line of $HN^{13}C$.

The efg at ^{14}N in **3** is about an order of magnitude smaller than in **2** as reflected by the corresponding data in Table I. However, calculated changes due to an increase of the basis are as large as $q_{zz}(\mathbf{3})$ itself, which suggests a strong basis set dependence of theoretical efg values in the case of **3**. This is confirmed when comparing the data of Table I with the HF/(11s,7p,2d,1f/6s,2p,1d) [6s,4p,2d,1f/4s,2p,1d] value of $q_{zz}(\mathbf{3})$ = 0.0264 au obtained by Cummins and co-workers.[37] Obviously, smaller basis sets lead to q_{zz} values which are too positive by a factor of 2–7. Correlation corrections Δq^{Cor} are smaller than those obtained for

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TABLE IV: Calculated Electric Field Gradients $q_{\alpha\beta}$ (au) Along the Principal Axes of Inertia

molecule	method	q_{aa}	q_{bb}	q_{cc}	q_{ab}
CH_3NC, **4**	HF	0.071	−0.036	−0.036	0
	MP2	0.150	−0.075	−0.075	0
	MP3	0.142	−0.071	−0.071	0
CF_3NC, **5**	HF	0.244	−0.122	−0.122	0
	MP2	0.221	−0.111	−0.111	0
	MP3	0.241	−0.121	−0.121	0
NC*N*C, **6**[a]	HF	0.334	−0.167	−0.167	0
	MP2	0.308	−0.154	−0.154	0
	MP3	0.321	−0.161	−0.161	0
HC≡CNC, **7**	HF	0.235	−0.118	−0.118	0
	MP2	0.240	−0.120	−0.120	0
	MP3	0.240	−0.120	−0.120	0
FCH_2NC, **8**	HF	0.063	−0.052	−0.011	−0.079
	MP2	0.101	−0.031	−0.070	−0.082
	MP3	0.101	−0.048	−0.053	−0.092
F_2CHNC, **9**[b]	HF	0.134	−0.098	−0.035	0.073
	MP2	0.137	−0.079	−0.058	0.077
	MP3	0.150	−0.096	−0.054	0.081
CH_3CH_2NC, **10**	HF	0.023	−0.005	−0.017	−0.027
	MP2	0.088	−0.027	−0.061	−0.064
	MP3	0.079	−0.025	−0.054	−0.062
CH_2=CHNC, **11**	HF	0.048	−0.053	0.004	0.060
	MP2	0.092	−0.064	−0.028	0.077
	MP3	0.086	−0.065	−0.021	0.075
HC≡CCH_2NC, **12**	HF	0.054	−0.005	−0.049	−0.095
	MP2	0.089	0.004	−0.093	−0.129
	MP3	0.082	0.002	−0.083	−0.130

[a] Nucleus in question in italics. [b] The off-diagonal element is q_{ac}.

1 and **2**, but they are comparable in magnitude or even larger than the best values calculated for q_{zz} (see Table II), which suggests their increased importance. Again, a fortuitous cancellation of $\Delta\mathbf{q}^{\mathrm{Cor}}$ and $\Delta\mathbf{q}^{\mathrm{Basis}}$ is possible because of their opposite sign.

Contrary to **1** and **2**, vibrational corrections (50% of QCISD(T)/6-311G(2d,2p) value; see Tables I and II) are now as important as basis set or correlation corrections. Accordingly, $\Delta\mathbf{q}^{\mathrm{vib}}$ has to be known in order to obtain reliable efg or $Q(^{14}N)$ values in the case of **3**. This is reflected by the data in Table IIIc, which have been obtained using $\Delta\mathbf{q}^{\mathrm{vib}}(\mathbf{3})$ of Table II and $\chi_{aa} = 0.28$ MHz.[45] Calculated efg values of **3** clearly support the more recent value of χ_{aa}[45] rather than $\chi_{aa} = -0.4$ MHz.[44] The data given in Table IIIc demonstrate the dependence of $Q(^{14}N)$ on method and basis set covering a range from 6 to 103 mbarn. In order to obtain reasonable $Q(^{14}N)$ values the VTZ+2P basis set is needed and correlation corrections have to be evaluated at either the MP4 or QCI level of theory.

Target Molecules. From the investigation of molecules **1**–**3** we conclude that a possible compromise between accuracy on one hand and computational effort on the other hand is achieved at the MP4(SDQ)/6-311G(2d,2p) level of theory for molecules with two or three heavy atoms provided vibrational corrections are either known or negligible. Even better values are obtained at the CC and QCI level of theory. However, these calculations, which imply analytical gradient evaluations,[24,29] are not feasible for five- and six-heavy-atom systems such as **5**, **9**, or **12** at the moment. Also, vibrational corrections do not seem to be negligible in the case of the isonitriles, but their calculation is normally beyond the scope of routine investigations of molecular properties. Hence, a direct calculation of highly accurate efg values for molecules such as **4**–**12** is presently not possible.

Therefore, we have used the Q^* approximation which offers the possibility to cut back on basis set and method when calculating efg values. For this purpose, we have optimized geometries of **4**–**12** at the HF/6-31G(d) level of theory (see Figure 3), which have been employed to obtain efg values of **4**–**12** at HF/6-311G(d,p), MP2/6-311G(d,p), and MP3/6-311G(d,p) (see Table IV). In Table V, known quadrupole coupling constants $\chi_{\alpha\beta}$ are listed. Correlating $\chi_{\alpha\beta}$ values with HF, MP2, and MP3 values of the corresponding efg's lead to $Q^*(\mathrm{HF}) = 17.9$ (8), $Q^*(\mathrm{MP2}) = 17.2$ (8), and $Q^*(\mathrm{MP3}) = 16.9$ (5) mbarn (see Table V).

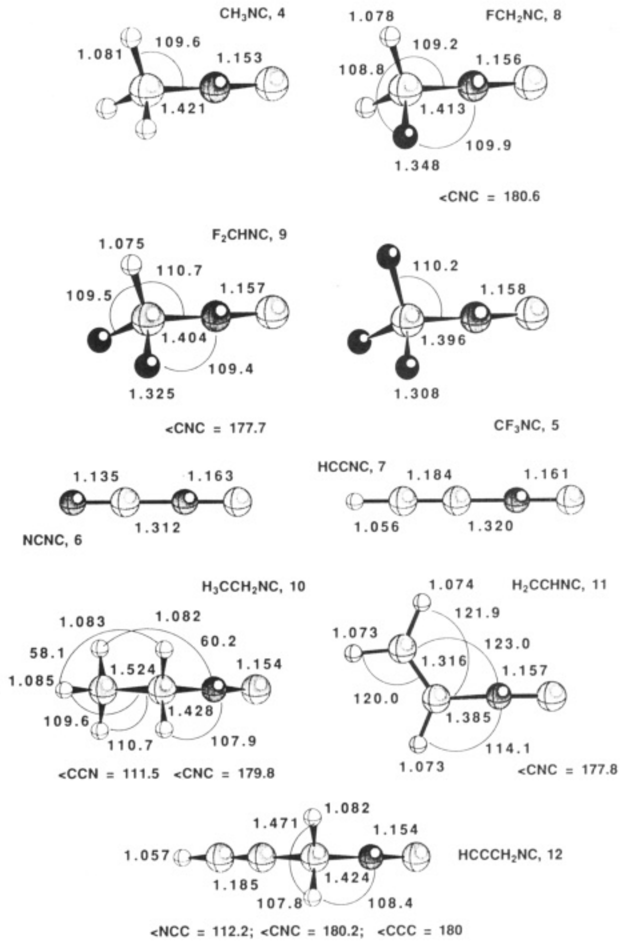

Figure 3. HF/6-31G(d,p) geometries of isonitriles **4**–**12**. Note that a CNC angle different from 180° indicates that the NC group bends away from the substituent F (**8**, **9**), CH_3 (**10**), CH_2 (**11**), or C≡CH (**12**).

Calculated $Q^*(^{14}N)$ values compare well with Q^* data given in the literature. Gerber and Huber[1b] have derived a Q^* of 16.2 (6) mbarn for sp-hybridized and 18.2 (5) mbarn for sp^3-hybridized N from near-HF calculations, and a Q^* of 18.9 (3) mbarn for sp- and sp^3-hybridized N from MP4(SDQ) calculations.[1c] However, it has to be noted that these authors obtained Q^* for

TABLE V: Theoretical and Experimental Quadrupole Coupling Constants χ_{aa} (MHz)[a]

	χ(calc)				
molecule	HF	MP2	MP3	χ(obs)	ref
CH_3NC, **4**	0.300 (13)	0.608 (28)	0.567 (17)	0.4894 (4)	46
CF_3NC, **5**	1.027 (46)	0.894 (42)	0.963 (28)	1.060 (30)	47
NC*N*C, **6**	1.402 (63)	1.245 (58)	1.283 (38)	1.3204 (20)	48
HC≡CNC, **7**	0.988 (44)	0.971 (45)	0.959 (28)	0.9464 (19)	52
FCH_2NC, **8**	0.265 (12)	0.407 (19)	0.403 (12)		
	−0.220 (10)	−0.125 (6)	−0.190 (6)		
	−0.046 (2)	−0.282 (13)	−0.213 (6)		
F_2CHNC, **9**	0.563 (25)	0.553 (26)	0.599 (18)	0.5990 (10)	17
	−0.413 (18)	−0.319 (15)	−0.382 (11)	−0.4065 (14)	
	−0.151 (7)	−0.234 (11)	−0.217 (7)	−0.1926 (14)	
CH_3CH_2NC, **10**	0.095 (4)	0.355 (16)	0.313 (9)	0.2532 (59)	49
	−0.022 (1)	−0.108 (5)	−0.100 (3)	−0.106 (11)	
	−0.069 (3)	−0.246 (11)	−0.214 (7)	−0.148 (11)	
CH_2=CHNC, **11**	0.203 (9)	0.372 (17)	0.344 (10)	0.258 (5)	50
	−0.222 (10)	−0.258 (12)	−0.260 (8)	−0.258 (6)	
	0.019 (1)	−0.114 (4)	−0.085 (3)	0.000 (6)	
HC≡CCH_2NC, **12**	0.226 (10)	0.360 (17)	0.326 (10)	0.2903 (78)	51
	−0.020 (1)	0.016 (1)	0.006 (1)	0.0106 (80)	
	−0.206 (10)	−0.375 (17)	−0.333 (10)	−0.3009 (80)	
Q^*, mbarn	17.9 (8)	17.2 (8)	16.9 (5)		
mean dev, kHz	66.7	71.2	40.7		
max dev, kHz	189	166	97		
min dev, kHz	6.5	0	0		
std dev, kHz	81.8	85.1	51.9		

[a] χ_{aa} values are given in the following order: χ_{aa}, χ_{bb}, χ_{cc} (first, second, third entry). Uncertainties from standard deviation of Q^* in parentheses. Calculated χ_{aa} values have been obtained from q_{aa} (Table IV) and Q^* values and correspond to the principal axes of inertia. References for experimental χ values are given in the last column.

test molecules exhibiting much larger $\chi_{\alpha\beta}$ values, thus reducing relative errors of the efg calculation. Brown and Head-Gordon[16] have published similar Q^* values on the basis of HF calculations with extensive calibration to various types of N-containing molecules.

Utilizing the Q^* values obtained in this work, $\chi_{\alpha\beta}$ constants for isonitriles **4**–**12** have been calculated with the aid of eq 3. They are listed in Table V together with experimental $\chi_{\alpha\beta}$ constants. In Figure 4, calculated $\chi_{\alpha\beta}$ are plotted against experimental $\chi_{\alpha\beta}$. Both Table V and Figure 4 reveal that HF and MP2 values frame the experimental values, while MP3 results are between HF and MP2 results and, accordingly, come closer to experimental constants. This is in line with the oscillation of calculated efg's and $Q(^{14}N)$ in dependence of the order of MP theory applied as already discussed for N_2 and HCN. Similar oscillations have been found for many other one-electron properties calculated at MPn.[24,29] Oscillations make it very difficult to directly obtain accurate response properties from MP theory. In this case, however, they can be used to find an adequate method to obtain a reasonable account of a particular property in an economic way. Obviously, this is the case for the calculated MP3/6-311G(d,p) $\chi_{\alpha\beta}$ constants (Table V, Figure 4).

The calculated standard deviation for MP3/6-311G(d,p) values of $\chi_{\alpha\beta}$ constants is 0.052 MHz (see Table V). This accuracy is sufficient to make useful predictions in those cases, for which $\chi_{\alpha\beta}$ is not known. For example, $\chi_{\alpha\beta}$ of fluoromethylisonitrile (**8**) can be used when assigning the microwave spectra of this molecule. Similarly, recent interest in FC≡CNC by both synthetic chemists and microwave spectroscopists suggests to predict χ_{aa} for this molecule. At the HF/6-31G(d) geometry (r(N≡C) = 1.160, r(C—N) = 1.322, r(C≡C) = 1.174, r(C—F) = 1.267 Å), we obtain 1.111 (50) (HF/6-311G(d,p)), 1.081 (31) (MP2/6-311G(d,p)), and 1.056 (22) MHz (MP3/6-311G(d,p)) from q_{aa} = 0.264, 0.268, and 0.270 au, respectively, using the Q^* values given above. Work is in progress[17] to use calculated $\chi_{\alpha\beta}$ values of isonitriles for assignments of rotational hyperfine structure as described in this work.

4. Conclusions

In this work, we have shown that a direct calculation of efg values and $\chi_{\alpha\beta}$ constants for isonitriles is problematic because of three reasons:

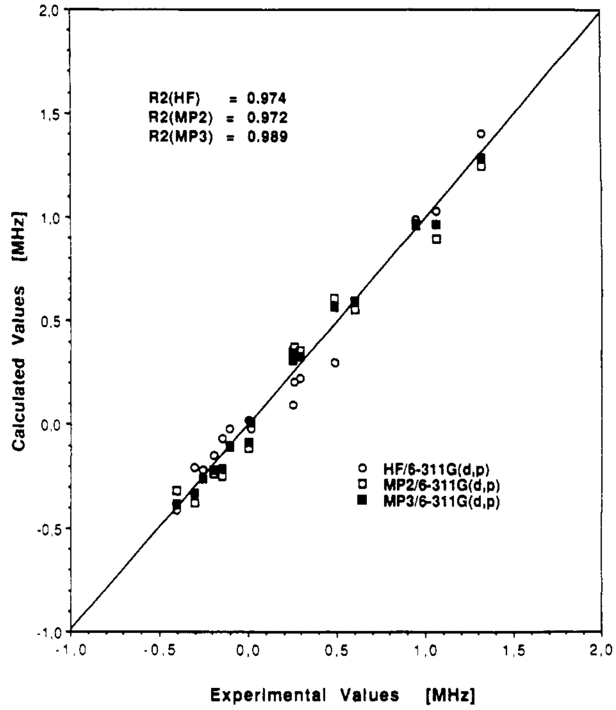

Figure 4. Comparison of calculated and experimental nuclear quadrupole coupling constants $\chi_{\alpha\beta}$ along the principal axes of inertia. The correlation coefficient R^2 is given for the three methods applied. The solid line gives the best fit for the MP3 values.

(1) Calculations require a large basis set of TZ+2P quality or better.

(2) MPn results of efg and $\chi_{\alpha\beta}$ constants oscillate with the order n of the perturbation theory. It is likely that these oscillations continue at MP5 and MP6.

(3) Accurate values can be expected when using QCISD or QCISD(T) (CCSD or CCSD(T)), but these methods require $O(K_{\mathrm{iter}}M^6)$ and $O(K_{\mathrm{iter}}M^6 + M^7)$ (K_{iter} is the number of interations to get QCI or CC amplitudes; M is the number of basis functions) operations and, therefore, can only be applied for rather small molecules.

In this situation, the Q^* approach can be applied as a useful alternative to a direct calculation of $\chi_{\alpha\beta}$ constants. We have shown that the Q^* approach can be used in those cases in which nuclear quadrupole coupling constants are rather small ($\chi_{\alpha\beta} < 1$ MHz). However, both HF/ and MP2/ small basis set calculations are not sufficient in those cases. One has to use at least MP3 in connection with a TZ+P basis set to get reasonable values, which has to do with the fact that for MP3 there is a fortuitous cancellation of basis set and correlation errors. Investigation of 10 isonitriles with $Q^*(^{14}N) = 16.9$ (5) MHz determined at MP3/6-311G(d,p) leads to reasonable $\chi_{\alpha\beta}$ values, which can be used to correctly assign the microwave spectra of hitherto uninvestigated molecules.

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Color Centers in UV-Irradiated Nitrates

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We show that the peroxonitrite anion, $ONOO^-$, is a primary product when solid nitrates are irradiated with 254-nm UV and is the source of the yellow color. Many previous investigators have attempted to interpret photolysis processes in crystalline nitrates as primarily involving nitrite anions and oxygen gas, not realizing that the nitrite and oxygen can be formed by decomposition of peroxonitrite when the solid is dissolved for analysis. A small amount of nitrite is formed in nitrate crystals directly from the nitrate ions but much of it is generated by photolysis of the peroxonitrite anion.

Introduction

There have been many investigations of the photolysis and radiolysis of inorganic nitrates in the 55 years since Narayanswamy[1] demonstrated that nitrite ions were produced when nitrates were irradiated with UV light and dissolved. In the following years, several research groups[2-5] studied the kinetics of photolysis and radiolysis in a wide variety of salts using nitrite analysis as an analytical tool to monitor the reactions and attempted to build a general theoretical model which encompassed thermal effects, photobleaching effects, and crystal structure effects. They were not altogether successful and noted inexplicable inconsistencies. For example, the yellow color of irradiated nitrates can be bleached by heating but the attendant loss of NO_2^- could not be explained satisfactorily by recombination of NO_2^- and O atoms since a large portion of the O atoms would react to form O_2 which would not oxidize with NO_2^- under the conditions employed.[6] The photochemical bleaching of the yellow color posed similiar problems.

The nitrite ion absorbs at 345 nm giving solid nitrites a faint yellow color but the absorptivity is too small to account for the intensity of color of irradiated nitrates. Pringsheim[7] suggested that the color centers were due to electrons trapped on a small fraction of the NO_2^- ions producing $(NO_2^-)^-$ which had enhanced oscillator strength compared to NO_2^-. The color centers can be photobleached with near-UV light but photoconductivity could not be detected during the photobleaching process as would be expected. The formation of at least three radical species during irradiation has been demonstrated by ESR studies[8-10] but these studies have not proven Pringsheim's explanation of the color. The ozonide ion, which has been identified[11] as a radiolysis product in $KClO_3$, is strongly colored. Our ESR studies indicated that a trace level of ozonide (~2 ppm) is present in irradiated KNO_3 but neither O_3^- nor other radical species could be the source of the color centers because KNO_3 colored by 254-nm radiation, and stored at room temperature to let short-lived radicals decay, gives only the signal characteristic of O_3^- and the ESR signal is not significantly reduced when the color is removed by photobleaching at 300 nm.

Building upon Papée and Petriconi's discovery in 1964[12] that peroxonitrite was a photolysis product from UV irradiation of NO_3^-(aq), Yurmazova et al.[13] showed that peroxonitrite is formed in solution when UV-irradiated KNO_3 is dissolved. This indicated that $ONOO^-$ might be present in the solid and responsible for the color. However, they noted (as others had observed) a decrease in measured NO_2^- levels during photobleaching which would not be expected if photobleaching is caused by either $ONOO^-$ isomerization to NO_3^- or decomposition to NO_2^- and $^1/_2O_2$.

Miklin et al.[14] attempted to resolve the inconsistency with an alternative model in which they proposed that both peroxonitrate, O_2NOO^-, and peroxonitrite are formed during photolysis. They suggested that O fragments are released from O_2NOO^- during photobleaching and oxidize NO_2^- to NO_3^-.

Investigators of nitrate photolysis in the 25 years since peroxonitrite formation was discovered have assumed (as did Papée and Petriconi[12]) that the decay of peroxonitrite is by isomerization to nitrate and does not involve decomposition to nitrite.[13-15] We have found[16] that peroxonitrite decays quantitatively by isomerization only upon rapid dissolution of the salts in acidic solution. In neutral or alkaline solutions some of the peroxonitrite decomposes to nitrite. Quantitative conversion of peroxonitrite to nitrite can be achieved by rapid dissolution in base with a copper ion catalyst. A method for concurrent analysis of nitrite and peroxonitrite based on these principles has been developed[16] and is

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