Electric Field Gradients and Nuclear Quadrupole Coupling Constants of Isonitriles
Obtained from Möller–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 nth-order Möller–Plesset perturbation (MPn, n = 2, 3, 4), Coupled Cluster (CC) and quadratic configuration interaction (QCI) theory. MPn results are problematic since calculated values oscillate with the order n of the perturbation calculation. Test calculations for N2, 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 to provide an effective quadrupole moment \( Q^* \) for \( ^{14}N \) which 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 \( \text{CH}_2\text{NC} \), \( \text{CF}_3\text{NC} \), \( \text{NCNC} \), \( \text{H}_2\text{NC} \), \( \text{FCH}_2\text{NC} \), \( \text{F}_2\text{CHNC} \), \( \text{CH}_3\text{CH}_2\text{NC} \), \( \text{H}_2\text{C}=\text{CHNC} \), and \( \text{HC}≡\text{CHNC} \). 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) \( g \) 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, \( g \) is a tensor of rank 2 that comprises contributions both from the nuclear and the electronic charge distribution in the molecule. The elements \( g_{\alpha\beta}(\alpha, \beta = x, y, z) \) of the efg tensor \( g \) at nucleus \( A \) are determined by the charge distribution surrounding \( A \). According to the nuclear quadrupole moment \( Q \) at the nucleus according to

\[
x_{\alpha\beta} = eQ_{\alpha\beta}/h
\]

where \( e \) and \( h \) have their usual meaning. With the experimental

\[
Q = 4.256x_{\alpha\beta}/q_{\alpha\beta}
\]
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 Möller–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 \(\text{IP}_(1p,2p3p)\) state of \(NO\)\(^+\) utilizing the experimental coupling constant. Hence, a \(Q(N^+\text{NO})\) value of 20.5 mbarn with an error limit of less than 5% is most likely.

The value of \(Q(N^+)\) can be used in conjunction with \(3\) to predict quadrupole coupling constants of large molecules from calculated efg values. Of course, numerical HF and CAS-SCF 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 \(\chi_{\text{eff}}\) values can be improved by introducing an effective nuclear quadrupole moment \(Q^*\) that provides the best fit between calculated and experimental \(\chi_{\text{eff}}\) data. Such an approach of empirically correcting calculated \(\chi_{\text{eff}}\) for \(4\)\(^{14}\)\(^{16}\)\(^{18}\)\(^{23}\) values has been used by Barber and co-workers\(^1\), Gerber and Huber\(^1\), Maksic and co-workers\(^6\), Aray and co-workers\(^6\),\(^8\),\(^10\) Palmer and co-workers\(^1\),\(^11\),\(^12\) Miller and Ragle\(^1\), and Brown and Head-Gordon\(^1\). 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 \(\chi_{\text{eff}}\) 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 \(\chi_{\text{eff}}\) \(\leq 1\) MHz.

In this work, we report ab initio calculations on \(N_2\) (1), HCN (2), HNC (3), CH\(_2\)NC (4), CF\(_2\)NC (5), CN\(_2\)NC (6), HCC=CNC (7), FCH\(_2\)NC (8), F\(_2\)CHNC (9), CH\(_3\)CH\(_2\)NC (10), H\(_2\)CC=CH\(_2\)NC (11), and HCO=CH\(_2\)NC (12) to determine their efg and \(\chi_{\text{eff}}\) 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 \(\chi_{\text{eff}}\) values. Molecules 4–12 (together with 3) belong to the class of ioninitrites. These molecules are presently the target of microwave investigations\(^1\),\(^7\),\(^17\) and, therefore, reliable predictions of their nuclear coupling constants \(\chi_{\text{eff}}\) 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\(^14\) 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 Möller–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 CIP. 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 ofpentuple and heptuple 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 (QCISD)\(^23\) methods in particular, we have used coupled-Cl with 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 \(q\) this implies the evaluation of

\[
q_{\text{res}} = \sum_{\mu \nu} P_{\mu \nu} \rho_{\text{res}}(\mu)\left(3r_{\mu}^2 - r^2 \right) r_{\nu}^2 (\nu) 
\]

and

\[
q_{\text{cor}} = \sum_{\mu \nu} P_{\mu \nu} \rho_{\text{cor}}(\mu) 3r_{\mu\nu} (\mu
\]

with \(\alpha, \beta = x, y, z\) and the one-electron integrals are the efg integrals expressed in the space of the basis functions \(\chi_{\mu}\). \(P_{\text{res}}\) is the response density matrix, which, in case of a HF wave function, is identical with the SCF density matrix \(P_{\text{SCF}}\). For correlated wave functions, \(P_{\text{cor}}\) contains also the correlation correction matrix \(P_{\text{cor}}\).

\[
P_{\text{res}} = P_{\text{SCF}} + P_{\text{cor}}
\]

We have recently described how to calculate response densities at the MPn and QC1 level of theory\(^{24–29}\) using the z-vector method.\(^30\) We will use this procedure and the corresponding program\(^21\) 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.


\(^{(17)}\) Krüger, B.; Kreischer, H., unpublished results.

TABLE I: Calculated Electric Field Gradient $q_{zz}$ (au) for $^{14}$N$_2$, HCN, and HNC at Their Experimental Equilibrium Geometries$^a$

<table>
<thead>
<tr>
<th>method</th>
<th>basis set</th>
<th>$N_2$</th>
<th>HCN</th>
<th>HNC</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>6-31G(d,p)</td>
<td>-1.106</td>
<td>-0.967</td>
<td>0.196</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-1.307</td>
<td>-1.153</td>
<td>0.090</td>
</tr>
<tr>
<td>MP2</td>
<td>6-31G(d,p)</td>
<td>-0.871</td>
<td>-0.741</td>
<td>0.215</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-1.067</td>
<td>-0.915</td>
<td>0.130</td>
</tr>
<tr>
<td>MP3</td>
<td>6-31G(d,p)</td>
<td>-0.928</td>
<td>-0.810</td>
<td>0.228</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-1.138</td>
<td>-1.003</td>
<td>0.134</td>
</tr>
<tr>
<td>MP4(SDQ)</td>
<td>6-31G(d,p)</td>
<td>-0.910</td>
<td>-0.787</td>
<td>0.238</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-1.114</td>
<td>-0.971</td>
<td>0.144</td>
</tr>
<tr>
<td>MP4(SDTQ)</td>
<td>6-31G(d,p)</td>
<td>-0.885</td>
<td>-0.761</td>
<td>0.240</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-1.076</td>
<td>-0.930</td>
<td>0.151</td>
</tr>
<tr>
<td>CCD</td>
<td>6-31G(d,p)</td>
<td>-0.915</td>
<td>-0.798</td>
<td>0.231</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-1.126</td>
<td>-0.990</td>
<td>0.136</td>
</tr>
<tr>
<td>QCISD</td>
<td>6-31G(d,p)</td>
<td>-0.913</td>
<td>-0.788</td>
<td>0.241</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-1.119</td>
<td>-0.973</td>
<td>0.148</td>
</tr>
<tr>
<td>QCISD(T)</td>
<td>6-31G(d,p)</td>
<td>-0.895</td>
<td>-0.774</td>
<td>0.239</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-1.094</td>
<td>-0.951</td>
<td>0.150</td>
</tr>
</tbody>
</table>

$^a$Experimental $r_e$ geometries are as follows: $N_2$, $r(14NN) = 1.0977$ Å; HCN, $r(1HN) = 1.0655$ Å, $r(CN) = 1.1532$ Å; HNC, $r(HN) = 0.9940$ Å, $r(NH) = 1.1689$ Å.

TABLE II: Basis Set Truncation Error $\Delta q_{zz}^{\text{basis}}$, Correlation Error $\Delta q_{zz}^{\text{corr}}$, and Vibrational Correlation $\Delta q_{zz}^{\text{vib}}$ (All in au) for $N_2$, HCN, and HNC

<table>
<thead>
<tr>
<th>molecule</th>
<th>basis set</th>
<th>$\Delta q_{zz}^{\text{basis}}$</th>
<th>$\Delta q_{zz}^{\text{corr}}$</th>
<th>$\Delta q_{zz}^{\text{vib}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>6-31G(d,p)</td>
<td>-0.230</td>
<td>0.210</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>0.005</td>
<td>0.209</td>
<td>0.012</td>
</tr>
<tr>
<td>HCN</td>
<td>6-31G(d,p)</td>
<td>-0.229</td>
<td>0.195</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-0.043</td>
<td>0.203</td>
<td>0.001</td>
</tr>
<tr>
<td>HNC</td>
<td>6-31G(d,p)</td>
<td>-0.070</td>
<td>0.043</td>
<td>-0.047</td>
</tr>
<tr>
<td></td>
<td>6-31G(2d,2p)</td>
<td>-0.064</td>
<td>0.060</td>
<td>-0.047</td>
</tr>
</tbody>
</table>

$^b$HF limit value and $\Delta q_{zz}^{\text{vib}}$ obtained at $r(14NN) = 1.0943$ Å from ref 4, $\Delta q_{zz}^{\text{corr}}$ from eq 7. At this $r(14NN)$ value, $q_{zz}(14NN) = -1.106$ (HF/6-31G(d,p)), -1.311 (HF/6-31G(2d,2p)), -1.341 au (HF/6-31G(2d,2p)). $^c$Estimated HF limit value and $\Delta q_{zz}^{\text{vib}}$ from ref 37, $\Delta q_{zz}^{\text{corr}}$ from eq 7.

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 quadrupole moment shown in Table III has been obtained from eq 3. In the following, calculated efg values are discussed in detail.

Molecular Nitrogen. The nuclear quadrupole coupling constant of $N_2$ (I) is not accessible by microwave (MW) spectroscopy but can be measured in the solid by nuclear quadrupole resonance

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 $\nu_{\text{e}}(N_2)$ 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 $\nu_{\text{e}}(N_2)$ of less than 1%. We conclude that all of 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 $Q^I(N^I)$ (see Table IIIA) obtained from the theoretical $q_{zz}(N^I)$ values after correcting for vibrational effects and an experimental nuclear quadrupole coupling constant $\chi_{zz}$ of -5.39 (5) MHz.36,38 They are too high by 5-6 mbar for the 6-31G(d,p) results but cluster between 20 and 21 mbar for the two larger basis sets when correlation corrections are included into the calculation. Figure 1, which gives a graphical display of calculated $Q^I(N^I)$ 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 mbar.

(2) At the MPn 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 underestimated (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 QC results that cover infinite-order effects approach a limiting value that seems to be already reached at the QCSD(T) level: 26.0 for 6-31G(d,p); 21.2 for 6-311G(d,p); and 20.6 mbar for 6-31G(2d,2p) (see Table IIII). We conclude that QCSD(T)/6-311G(2d,2p) leads to the most reliable value of $Q^I(N^I)$. Comparison with previously published values of $Q^I(N^I)$44-47 confirms this observation.

Similar observations (independent of correlation effects from basis set, oscillatory behavior of $\Delta_{\text{corr}}$ at MPn, and superiority of QC1/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 $q_{zz}(2) = -1.196$ au obtained by Cummins and co-workers.37 Obviously, $\Delta_{\text{corr}}$ 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 $\Delta_{\text{vib}}$ for 2 are negligibly small (<1%), while correlation corrections $\Delta_{\text{cor}}$ are similar to those obtained for 1 (ca. 20%). In Table IIIII and in Figure 2 calculated $Q^I(N^I)$ values (corrected for vibrational effects and obtained from $x_{zz} = -4.7091$ (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 Isotopichile (3).** 3 was first observed with matrix isolation techniques.40,41 The microwave spectrum of 3 was assigned by Snyder and Buhl42 to an emission line from galactic sources and later confirmed by laboratory data.43 The nuclear quadrupole coupling constant $\chi_{zz} = -0.4$ MHz is also of astrophysical origin.44 It was later redetermined by Freking and co-workers45 to be 0.28 (3) MHz from the emission line of HN13C.

The efg at $14^I$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 $q_{zz}(3)$ 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 $q_{zz}(3) = 0.0264$ 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 $\Delta_{\text{cor}}$ are smaller than those obtained for...
value of rather than conclude that a possible compromise between accuracy on one vibrational corrections do not seem to be negligible in the case of Table IIIc demonstrate the dependence of $Q(14N)$ on method and correlation corrections have to be evaluated at either the MP4 (SDQ)/6-31G(2d,2p) level of theory for molecules with known or negligible. Even better values are obtained at the CC or QCI level of theory. However, it has to be noted that these authors obtained $Q^*$ of 18.9 (3) mbarn for sp$_3$-hybridized and 18.2 (5) mbarn for sp$_2$-hybridized N from near-HF calculations, and a $Q^*$ of 18.9 (3) mbarn for sp$_2$-hybridized N from MP4(SDQ) calculations. 1c However, it has to be noted that these authors obtained $Q^*$ for
three reasons: 
values and described in this work.
assignments of rotational hyperfine structure as given above. Work is in progress to use calculated 
account of a particular property in an economic way. Obviously, this is the case for the calculated MP3/6-31G(d,p) 
oscillations make it very difficult to directly obtain accurate 
properties from MP theory. In this case, however, they 
can be used to find an adequate method to obtain a reasonable 
analytical 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 $\chi_{aB}$ 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 $O(K_{exp}M^2)$ and $O(K_{exp}M^2 + M')$ ($K_{exp}$ is the number of iterations to get QCI or CC amplitudes; $M$ is the number of basis functions) operations and, therefore, can only be applied for rather small molecules.

discussed for Nz and HCN. Similar oscillations have been found for many other one-electron properties calculated at MPn.24,29

Utilizing the $Q^*$ values obtained in this work, $\chi_{aB}$ constants for isonitriles 4–12 have been calculated with the aid of eq 3. They are listed in Table V together with experimental $\chi_{aB}$ constants. In Figure 4, calculated $\chi_{aB}$ values are plotted against experimental $\chi_{aB}$. 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 $Q^*$ in dependence of the order of MP theory applied as already discussed for Nz 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) $\chi_{aB}$ constants (Table V, Figure 4).

The calculated standard deviation for MP3/6-311G(d,p) values of $\chi_{aB}$ constants is 0.052 MHz (see Table V). This accuracy is sufficient to make useful predictions in those cases, for which $\chi_{aB}$ is not known. For example, $\chi_{aB}$ 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 $\chi_{aB}$ for this molecule. At the HF/6-31G(d) geometry ($r(\text{N}==\text{C}) = 1.160$, $r(\text{C}==\text{N}) = 1.322$, $r(\text{C}==\text{C}) = 1.747$, $r(\text{C}==\text{F}) = 1.267$ 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 $\chi_{aB}$ = 0.264, 0.268, and 0.270 au, respectively, using the $Q^*$ values given above. Work is in progress to use calculated $\chi_{aB}$ 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 $\chi_{aB}$ constants for isonitriles is problematic because of three reasons:

- Calculated $\chi_{aB}$ values have been obtained from $Q^*$ (Table IV) and $Q^*$ values and correspond to the principal axes of inertia. References for experimental $\chi$ values are given in the last column.

- Utilizing the $Q^*$ values obtained in this work, $\chi_{aB}$ constants for isonitriles 4–12 have been calculated with the aid of eq 3. They are listed in Table V together with experimental $\chi_{aB}$ constants. In Figure 4, calculated $\chi_{aB}$ values are plotted against experimental $\chi_{aB}$. 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 $Q^*$ in dependence of the order of MP theory applied as already discussed for Nz 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) $\chi_{aB}$ constants (Table V, Figure 4).

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4. Conclusions

In this work, we have shown that a direct calculation of efg values and $\chi_{aB}$ constants for isonitriles is problematic because of three reasons:
In this situation, the Θ* approach can be applied as a useful alternative to a direct calculation of χ_{ab} constants. We have shown that the Θ* approach can be used in those cases in which nuclear quadrupole coupling constants are rather small (χ_{ab} < 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 Θ*(14N) = 16.9 (5) MHz determined at MP3/6-311G(d,p) leads to reasonable χ_{ab} 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 nitrite 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 Narayanswamy1 demonstrated that nitrite ions were produced when nitrates were irradiated with UV light and dissolved. In the following years, several research groups2-3 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 NO2− could not be explained satisfactorily by recombination of NO2− and O atoms since a large portion of the O atoms would react to form O2 which would not oxidize with NO2− under the conditions employed.6 The photochemical bleaching of the yellow color posed similar problems.

The nitrite ion absorbs at 345 nm giving solid nitrates a faint yellow color but the absorbity is too small to account for the intensity of color of irradiated nitrates. Pringsheim1 suggested that the color centers were due to electrons trapped on a small fraction of the NO2− ions producing (NO2−) which had enhanced oscillator strength compared to NO2−. The color centers can be photobleached with near-UV light but photobleaching 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 studies4-10 but these studies have not proven Pringsheim’s explanation of the color. The ozonide ion, which has been identified11 as a radiolysis product in KClO4, is strongly colored. Our ESR studies indicated that a trace level of ozonide (~2 ppm) is present in irradiated KNO3 but neither O2− nor other radical species could be the source of the color centers because KNO3 colored by 254-nm radiation, and stored at room temperature to let short-lived radicals decay, gives only the signal characteristic of O2− 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 196412 that peroxonitrite was a photolysis product from UV irradiation of NO3−(aq), Yurmazova et al.13 showed that peroxonitrite is formed in solution when UV-irradiated KNO3 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 NO2− levels during photobleaching which would not be expected if photobleaching is caused by either ONOO− isomerization to NO3− or decomposition to NO2− and 1/O2.

Miklin et al.14 attempted to resolve the inconsistency with an alternative model in which they proposed that both peroxonitrate, O2NO2−, and peroxonitrite are formed during photolysis. They suggested that O fragments are released from O2NO2− during photobleaching and oxidize NO2− to NO3−.

Investigators of nitrate photolysis in the 25 years since peroxonitrite formation was discovered have assumed (as did Papée and Petriconi12) that the decay of peroxonitrite is by isomerization to nitrate and does not involve decomposition to nitrite,13-15 We have found16 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 developed18 and is

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