Nitrogen Nuclear Quadrupole Interactions in RDX, β-HMX and Cocaine Systems

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Using the Hartree-Fock-Roothaan procedure, the nuclear quadrupole interactions (NQI) of the ^{14}N ($I = 1$) nucleus in the energetically important molecules RDX, β-HMX and the physiologically important molecule Cocaine, are studied. The coupling constants ($e^2 q Q$) and asymmetry parameters (η) for the three ring nitrogens in RDX are found to be -5.671, -5.808 and -5.838 MHz and 0.542, 0.556 and 0.562, respectively, in good quantitative agreement with the experimental results of 5.735, 5.799 and 5.604 MHz for the magnitudes of $e^2 q Q$ and 0.6215, 0.6146 and 0.6024 for η obtained in the single crystal. For β-HMX, where two sets of $e^2 q Q$ and η are expected from symmetry considerations, our calculated values are -5.936 and -6.069 MHz for $e^2 q Q$ and 0.432 and 0.490 for η, compared to experimentally measured magnitudes of 5.791 and 6.025 MHz and η-values of 0.4977 and 0.5180, respectively, obtained in the single crystal. For Cocaine free base which contains only one ^{14}N nucleus, our calculated values of $e^2 q Q$ and η are -5.038 MHz and 0.067, in very good agreement with the experimental results of 5.0229 MHz for the magnitude of $e^2 q Q$ and 0.0395 for η. Possible reasons for the small remaining differences between theory and experiment in $e^2 q Q$ and η for all three systems and the significant differences in trends over the three nitrogens in RDX between theory and experiment are discussed. Also, the calculated quadrupole interaction parameters for the ^{14}N nuclei in the NO_2 groups outside the ring for both RDX and β-HMX are presented with the hope that they will be measured in the future to provide a more complete understanding of the electron distributions in these systems.

1. Introduction

The material RDX (1,3,5-trinitro S-triazine, $C_3H_6N_6O_6$), β-HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, $C_4H_8N_8O_8$) and Cocaine ($C_{17}N_{21}NO_4$) are of great current interest, the former two because of their energetic characteristics [1] and the latter for its physiological effects [2]. Additionally, nuclear quadrupole interaction (NQI) properties have been measured experimentally [3–5] for ^{14}N in all three molecules. The measured NQI parameters provide an opportunity to test the ability of the electronic wave-functions to provide a quantitative explanation of the field gradient tensor at the ^{14}N nuclei from first principles [6].

In RDX, the nuclear quadrupole coupling constants ($e^2 q Q$) have been obtained [3] only for the three ring ^{14}N nuclei (Fig. 1) at 298 K, no results being available yet for the NO_2 groups in the peripheral region. The measured magnitudes of $e^2 q Q$ for the ring nitrogens are 5.735, 5.799 and 5.604 MHz, the corresponding asymmetry parameters η being 0.6215, 0.6146 and 0.6024. The temperature dependences of the observed ^{14}N nuclear quadrupole frequencies have been used to make [3] an assignment for one of the $e^2 q Q$, namely 5.735 MHz, to one (N4) of the three ring nitrogens (N4, N5, N6). In β-HMX (Fig. 2), the $e^2 q Q$ and η have again been measured [4] for only the ring ^{14}N nuclei. Although there are four ^{14}N nuclei in the ring, because of reflection symmetry, there are two sets (N3, N4) and (N5, N6) of two equivalent nuclei each, termed equatorial and axial sets respectively. Consequently only two distinct $e^2 q Q$, with magnitudes 6.025 and 5.791 MHz have been found, the corresponding η being 0.5189 and 0.4977. In this system, also assignments of the measured $e^2 q Q$ and η have been made based on the observed temperature dependences of the nuclear quadrupole frequencies, the assignments being complete since there are only two sets of equivalent ring nitrogens. The $e^2 q Q$ of 6.025 MHz and η of 0.5189 are assigned to the axial nitrogens (N5, N6), whereas the $e^2 q Q$ and η of 5.791 and 0.4977 have been assigned to the equatorial nitrogens (N3, N4). Theoretical investigations of the ^{14}N nuclear quadrupole interaction parameters are thus useful not only to compare with the observed values but also to examine

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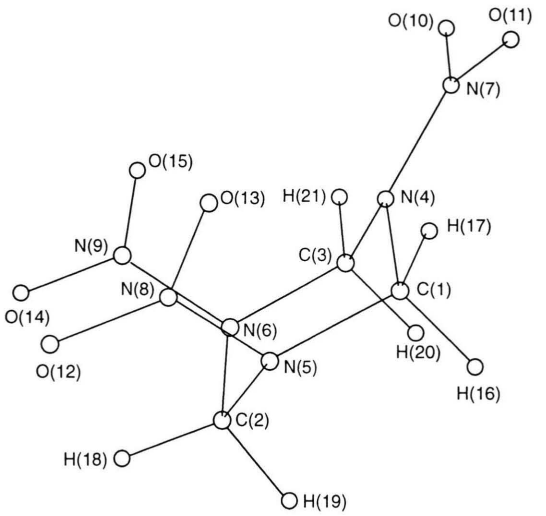

Fig. 1. Atomic arrangement in RDX (1,3,5-trinitro S-triazine, $C_3H_6N_6O_6$) based on the crystal structure data in [13].

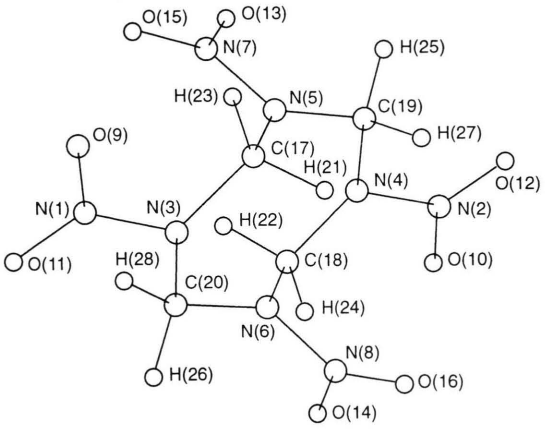

Fig. 2. Atomic arrangement in β-HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine, $C_4H_8N_8O_8$) based on the crystal structure data in [14].

if the assignments made experimentally are correct, and help in the assignment of the two other [3] e^2qQ and η in RDX. In Cocaine free base there is only one ^{14}N nucleus (Fig. 3) for which the observed [5] magnitude of e^2qQ is 5.0229 MHZ and η is 0.0395 at 295 K.

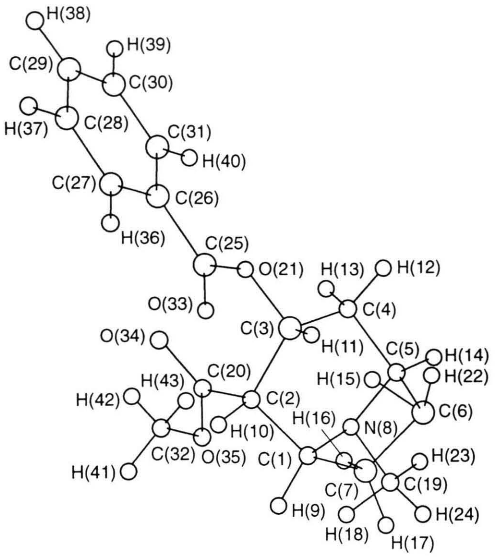

Fig. 3. Atomic arrangement in Cocaine ($C_{17}H_{21}NO_4$) based on the crystal structure data in [15] for Cocaine hydrochloride. All atomic positions except the Hydrogens 22 to 24 are based on [15]. The positions of Hydrogens 22 to 24 have been determined by energy optimization as explained in the text, because of apparent errors in [15] in the positions of these atoms.

Our aim in the present work is to try to interpret the experimental data [3–5] in the three systems, RDX, β-HMX and Cocaine and to examine how well one can quantitatively explain the observed e^2qQ and η using first-principle electronic structure investigations. Such a theoretical understanding is needed before one can attempt to study the influence of intermolecular interactions on the nuclear quadrupole parameters and the influence of motional effects in the solid state systems containing these compounds, both of which are necessary to understand the trends in e^2qQ and η over the nitrogens in each of the systems and also their observed temperature dependences [3–5] as well as spin-lattice relaxation times [7]. For our investigations, we have studied the electronic structures of the individual molecules for these systems using the Variational Hartree-Fock Roothaan procedure [6, 8] with Gaussian basis states [9] centered about the various atoms. This procedure has been successfully applied recently [6, 10] to study nuclear quadrupole interactions in several molecular and solid state systems.

Section II of this paper will briefly describe the procedure used for our investigation. In Sect. III our results and discussion will be presented. Finally, Sect. IV summarizes the main conclusions from our investigation and suggests possible future work that will be needed to further enhance the understanding of the nuclear quadrupole interactions in these systems.

2. Procedure

As mentioned in the preceding section, we have employed the Roothaan Variational approach [8] to the Hartree-Fock procedure for the calculation of electronic energy levels and wavefunctions for the RDX, β-HMX and Cocaine molecules. Since this procedure has been discussed extensively in [9, 10], we shall not describe it again. Only a few points essential for the explanation of some of the details of our present investigations will be touched upon later in this section. We have made use of the Gaussian 92 set of programs [11]. The use of Gaussian orbitals in these programs allows for speed in the computations of multicenter integrals, which is important for these rather large molecular systems. Also we have employed the Restricted Hartree-Fock approximation [12], since all these molecules are diamagnetic involving even numbers of electrons.

The atomic arrangement [13] in the RDX molecule is shown in Figure 1. This molecule, which has alternate CH_2 and $N-NO_2$ groups in a puckered ring, consists of 21 atoms and 114 electrons. It has approximate reflection symmetry about a plane passing through the atoms N(4) and C(2). The environment around the carbon atoms is essentially tetrahedral, whereas the $N-NO_2$ groups are almost planar. The atomic coordinates used in our calculations are taken from the structure obtained [13] by X-ray diffraction combined with single crystal neutron diffraction measurements to determine the hydrogen positions. The atomic arrangement [14] in β-HMX is shown in Figure 2. Here the molecule also has a ring structure with alternate CH_2 and $N-NO_2$ groups. The $N-NO_2$ groups are again essentially planar and the molecule has two-fold symmetry about the line joining N(3) and N(4) in Figure 2. The geometry used for atomic positions in β-HMX is again taken from the structure obtained [14] from combined X-ray and single crystal neutron diffraction measurements.

The atomic arrangement in the Cocaine molecule, which consists of 43 atoms, is shown in Figure 3. Unfortunately, structural data are not available for free Cocaine. We have therefore used atomic positions based on structural data available in the closely related molecule Cocaine hydrochloride. For the latter, the structure, involving the positions of all the atoms including the hydrogen atoms, has been determined from X-ray measurements [15], using three-dimensional Patterson synthesis. However, in [15] the position coordinates of three of the hydrogen atoms, H(22), H(23) and H(24) in Fig. 3 appeared to be erroneous, leading to excessively large associated CH bond lengths, namely 6.60, 7.19 and 6.86 Å, respectively, as compared to 1.09 Å, the usual [16] single bond CH distance. To obtain the correct positions of these three H-atoms, we followed the optimization procedure [11] involving minimization of the total Hartree-Fock energy of the molecular systems with respect to their positions. Since the Cocaine molecule is rather large, involving 43 atoms and 162 electrons, an optimization procedure using the entire molecule and allowing all atoms to vary in positions would be very time-consuming. We therefore used the following simplifications. The first was to truncate the molecule to a smaller size, the truncated ends being about equidistant from the nitrogen atom in the molecule, and the dangling bonds on the atoms at the boundary were terminated by hydrogen atoms as one does in the Hartree-Fock Cluster procedure [10] for simulating solid state systems. To study the convergence of our results as a function of the sizes of the truncated systems, we have utilised two sizes for it, namely 17 and 24 atoms. The next simplification was to use a minimal choice for the basis set involving STO-3G approximation [17]. With these simplifications, the optimized positions of three hydrogens H(22), H(23) and H(24) led to CH bond distances 1.112, 1.093, 1.084 Å and 1.101, 1.093, 1.084 Å for the 17 and 24 atom truncated systems, respectively, as shown in Table 1, are close to the usual single bond distance of 1.09 Å. The near equality of the two sets of CH distances suggests that the positions obtained for the three hydrogens are expected to be representative of the complete cocaine molecule. The use of the STO-3G approximation is expected to give reasonably accurate bond distances, and in particular for C_{60} fullerene it has been shown to lead to about 1 to 2 percent agreement [18] with experiment and theoretical results [19] involving much larger basis sets. One can therefore consider our calculated positions for H(22), H(23) and H(24) to be suitable ones to use in place of the corresponding published experimental values. Since these hydrogen atoms are bonded to carbon atoms that are one or more atoms away from the nitrogen atom for which we are interested in the ^{14}N quadrupole interaction, any slight errors in their calculated coordinates are not expected to significantly influence the calculated electric field gradient (efg) tensor at the ^{14}N nucleus. We have made use of the H(22),

Table 1. Results for hydrogen positions obtained through energy optimization in Cocaine.

Clustersize [a]	Nuclei [b]	X	Y	Z	L(CH) [c]
17	H(22)	5.966	−2.604	8.383	1.112
	H(23)	7.705	−4.193	5.830	1.093
	H(24)	7.939	−2.811	4.727	1.084
24	H(22)	5.972	−2.632	8.395	1.101
	H(23)	7.705	−4.193	5.830	1.093
	H(24)	7.939	−2.812	4.727	1.084

[a] Refers to the number of atoms used in the truncated molecule employed in the energy optimization calculation.
[b] H(n) refers to the position of the hydrogen labelled by n in Figure 3. These hydrogens are the ones whose positions appeared to be erroneous in [15] for the molecular structure and have been redetermined here by energy minimization of the cocaine molecule. X, Y and Z refer to the co-ordinate system used in [15].
[c] Refers to the lengths of the CH bonds between the hydrogen atoms and their nearest carbons neighbors.

H(23) and H(24) co-ordinates obtained from the 24 atom cluster listed in Table 1 in our work.

Turning next to the procedure for calculating the ^{14}N nuclear quadrupole interaction parameters, this requires the calculation of the efg tensor, the components of which are given by [20]

$$V_{jk} = \sum_{\mathrm{N}} \zeta_{\mathrm{N}} \frac{(3\,R_{j\mathrm{N}} R_{k\mathrm{N}} - R_{\mathrm{N}}^2 \delta_{jk})}{R_{\mathrm{N}}^5} - 2 \sum_{\mu} \left\langle \psi_\mu \left| \frac{3\,r_j r_k - r^2 \delta_{jk}}{r^5} \right| \psi_\mu \right\rangle . \qquad (1)$$

The first term on the right of (1) represents the contributions from the nuclear charges ζ_{N} in the molecule, $\boldsymbol{R}_{\mathrm{N}}$ the position vector of the nucleus N with respect to the nucleus at which the efg is being studied, with R_{N} the magnitude, and $R_{j\mathrm{N}}$ and $R_{k\mathrm{N}}$ the components of $\boldsymbol{R}_{\mathrm{N}}$, $j, k = 1, 2, 3$ referring to the X, Y, and Z components in the chosen cartesian axes system. The second term on the right represents the electronic contribution from the occupied states, the summation over μ referring to each of the doubly occupied states with spatial wave-function ψ_μ. In this term, r refers to the magnitude of the position vector $\boldsymbol{r}$ of the electron with respect to the nucleus under study and r_j and r_k its components. The contributions V_{jk} are in atomic units ($e\,a_0^{-3}$), where e is the magnitude of the electronic charge and a_0 the Bohr radius. The principal components $V_{j'k'}$ of the efg tensor and the principal axes (X', Y', Z') are obtained by diagonalization of the tensor in the (X, Y, Z) system with components V_{jk}. The parameter q in the quadrupole coupling constant $e^2 q Q$ (Q being the nuclear quadrupole moment) is given by the maximum component $V_{z'z'}$ and the asymmetry parameter $\eta = \frac{V_{x'x'} - V_{y'y'}}{V_{z'z'}}$, where the convention for choosing the X', Y' and Z' axes is the usual one [20] of $|V_{x'x'}| < |V_{y'y'}| < |V_{z'z'}|$. It should be noted that, since all the electrons, including the core electrons on the atoms, are chosen as molecular orbitals including the influence of electron-electron interactions and the charges on the nuclei on these orbitals, Sternheimer antishielding effects on the efg tensor are directly included and there is no need to incorporate them through Sternheimer antishielding parameters [21].

The nature of the electronic wave-functions is expected to influence the efg tensor more sensitively than the energy and interatomic distances because the latter properties involve averaging over larger regions of the molecule while the former gets major contribution from the region near the nucleus under study. For this reason, and to study the convergence of the results with respect to the sizes of the fragments used, as in the case of energy optimization to determine positions of some of the hydrogens in Cocaine as discussed earlier, we have studied the efg tensor in Cocaine with STO-3G and the more flexible basis set D95 [22], and for RDX and β-HMX using D95 and D95u, the latter involving uncontracting [9, 10] of the p-basis functions of the D95 basis set for nitrogen, carbon and oxygen. To give an idea of the sizes of basis sets and primitive Gaussians involved for our calculations on Cocaine, for the full molecule with 43 atoms and 162 electrons, the STO-3G approximation involved 131 basis functions and 393 primitive Gaussians, D95 involved 262 basis functions and 612 primitives. In addition, we have also studied the convergence of the efg tensor for ^{14}N with respect to the sizes of fragments used for the hydrogen position determination discussed earlier. The efg tensors for the 17 and 24 atom fragments and the whole Cocaine molecule with 43 atoms were both studied using STO-3G basis sets. The results for these different sizes, as discussed in the next section, varied by only about 1 percent. A similar convergence was observed between 24 and 43 atom (entire molecule) clusters using D95 basis set.

For RDX and β-HMX, the full molecules were used for the efg calculation employing D95 and D95u. For RDX with 21 atoms and 114 electrons, the D95 choice involved 162 basis functions and 384 Gaussian primitives while D95u involves 207 basis function and the same number of Gaussian primitives. For β-HMX with 28 atoms and 152 electrons, the corresponding numbers are 216 and 276 basis functions for D95 and D95u, respectively, and the same number, 512, of Gaussian primitives in both cases.

Table 2. Nuclear quadrupole coupling constants and asymmetry parameters for RDX and β-HMX systems.

Systems	Basis set	Nuclei	e^2qQ [a]		η	
			Theory	Exp. [b]	Theory	Exp. [b]
RDX	D95 [c]	4	−5.639	5.735	0.574	0.6215
		5	−5.806	5.799	0.579	0.6146
		6	−5.838	5.604	0.582	0.6024
		7	1.287		0.976	
		8	1.217		0.643	
		9	1.216		0.623	
	D95u [d]	4	−5.671	5.735	0.542	0.6215
		5	−5.808	5.799	0.556	0.6146
		6	−5.838	5.604	0.562	0.6024
		7	1.425		0.693	
		8	1.359		0.554	
		9	1.359		0.554	
β-HMX	D95 [c]	1,2	1.352		0.785	
		7,8	1.265		0.679	
		3,4	−5.929	5.791	0.458	0.4977
		5,6	−5.999	6.025	0.516	0.5189
	D95u [d]	1,2	1.442		0.553	
		7,8	1.369		0.571	
		3,4	−5.936	5.791	0.432	0.4977
		5,6	−6.069	6.025	0.490	0.5189

[a] The coupling constants e^2qQ are expressed in MHz.

[b] The experimental results are taken from [3] for RDX and [4] for β-HMX. The blanck spaces indicate that no experimental data are currently available for the ^{14}N nuclei in the NO_2 groups.

[c] D95 basis sets are taken from [22].

[d] D95u refers to uncontracted basis sets for C, N and O based on the D95 set.

3. Results and Discussion

In this Section, we present our results for the ^{14}N NQI parameters, the nuclear quadrupole coupling constants e^2qQ and asymmetry parameters η for RDX and β-HMX and Cocaine. The procedure discussed in the preceding section for obtaining Hartree-Fock wave-functions and NQI parameters is used for obtaining these results. The calculation of the quadrupole coupling constant e^2qQ requires a knowledge for the nuclear quadrupole moment of the ^{14}N nucleus. For this purpose, we have made use of the value 0.015 barns from an accurate many-body calculation [23] of the efg in the ground state of nitrogen atom to derive $Q(^{14}N)$ from the measured e^2qQ in the atom. The results we have obtained for the three molecular systems presented in this work are discussed in terms of their agreement with experiment and their trends with respect to each other. Possible sources of improvement and additional effects that need to be investigated in the future are also discussed.

We shall consider first the results for RDX and β-HMX molecules. These molecules bear close resemblance to each other in that they are both known for their energetic properties and also they have multiple nitrogen sites (Figs. 1 and 2), one set associated with the ring system and the other with NO_2 groups attached to the rings. Our theoretical results and the experimental results [3, 4] for both molecules are listed in Table 2. The theoretical results, listed in Table 2, were obtained through the use of D95 and D95u basis sets. As explained in Sect. II, dealing with the procedure used, the former is a rather extensive basis set and the latter is one that uncontracts the *p*-orbitals in D95 to further increase the flexibility of the basis set employed. This is done to test the convergence of the theoretical results, the *p*-orbitals [20] with $l = 1$ being the orbitals which have anisotropy at the nuclear site in contrast to *s*-orbitals with $l = 0$, and which also have the largest density at the nucleus as compared to other $l > 0$ orbitals, and therefore make the largest contribution to the efg at the ^{14}N nucleus. From Table 2 it is clear that there is very good convergence with respect to the size of the basis set for the theoretical results. The experimental results [3, 4] for the two molecules, available so far only for the ring nitrogens, are listed in the last column of Table 2.

The results for RDX and β-HMX in Table 2 show that the values of the calculated e^2qQ and asymmetry parameters η using the D95u basis set are in rather close agreement with the experimental values [3, 4] for the ring nitrogen (^{14}N) nuclei, the agreement being somewhat closer for the e^2qQ. The experimental quadrupole resonance measurements of course do not provide the signs of the e^2qQ, but the observed magnitudes are in good agreement with theory. The similarity of the experimental values of e^2qQ and η for RDX and β-HMX in Table 2 indicates that the departures of the electron distributions around the ^{14}N nuclei from both spherical symmetry and axial symmetry are quite close in both molecules, and this is also reflected very well by the theoretical results for e^2qQ

and η. In trying to obtain a more detailed check on the nature of the electron distributions around the ring ^{14}N nuclei, it is helpful to compare the trends in the $e^2 q Q$ and η over the three ring nitrogens in RDX, and between the equatorial and axial nitrogen pairs in β-HMX. For β-HMX, where the two observed sets of quadrupole coupling constants and asymmetry parameters have both been appropriately assigned to the equatorial and axial ^{14}N pairs from their observed temperature dependences, theory provides a good explanation of the experimentally observed trend.

For RDX, as mentioned earlier, only the NQI parameters corresponding to ^{14}N at site N4 in the ring have been assigned using temperature dependence data. The parameters corresponding to N5 and N6 were not assignable because the temperature dependences for the corresponding NQR frequencies are close to each other. The assignments as presented for the experimental results in Table 2 are thus arbitrary for N5 and N6. If the assignments for this were opposite to that noted in Table 2, there would be agreement in the direction of the trends in $e^2 q Q$ and η from theory and experiment as far as N5 and N6 are concerned. However, the differences between $e^2 q Q$ and η for these two nuclei are significantly smaller from theory as compared to experiment. Between N4 and N5 and N4 and N6, there are significant differences in the trends between theory and experiment. Thus, if the experimental assignments between N5 and N6 are reversed as compared to those noted in Table 2, there would be an increase in both $e^2 q Q$ and η in theory in going from N4 to N5 while the experimental results show a decrease. In going from N4 to N6, theory shows an increase for both $e^2 q Q$ and η, while experimentally $e^2 q Q$ indicates an increase and η shows a decrease. In looking for sources to explain these differences in trend for RDX, the two possibilities that suggest themselves are the influence [3] of intermolecular interactions on the electron distributions in the vicinity of the ring ^{14}N nuclei and the influence of many-body effects [24]. The latter would be more difficult to carry out quantitatively because of the relatively large sizes of these molecules. The former effect would be less difficult to study but still rather time-consuming. One type of intermolecular interactions would be that involving the effects of the charges on the atoms which can be obtained using the Mulliken approximation [25] and our calculated Hartree-Fock wave-functions. The second type of effect is that arising from the possible weak but significant covalent bonding between the atoms on neighbouring molecules that have relatively small separations from each other. The former is a more long range effect similar to that studied in ionic crystals [10]. Its effect on the total electronic energy of an RDX molecule has been studied before [26] by approximating the influence of the interaction between effective charges on the atoms in other molecules by point dipoles and quadrupoles located on them and found to be significant. It would be interesting to see if the influence of the effective charges on the atoms in the surrounding molecules on the electronic wave-functions of a molecule and the associated change in its electron distributions are significant enough to influence the field-gradient parameters q and η. The effects of the covalent bonding with neighboring molecules, which one could expect to be significant from the crystal structure data [13] for RDX because some of the atoms of neighboring molecules appear to be close enough to each other, would also be worthwhile to study in the future for their influence on the electron distributions and hence on q and η. It would be interesting to see if these interactions significantly influence the trends between N4, N5 and N6 without changing the overall good agreement seen between theory and experiment in Table 2 in the sizes of q and η found from our calculations on an isolated RDX molecule.

Similar intermolecular interaction effects would be useful to study in β-HMX molecule to see if they lead to an improvement in the agreement between theory and experiment in the quantitative trends in q and η between axial and equatorial ^{14}N nuclei without influencing the good overall agreements in the magnitudes of q and η. Lastly, the small values of the results for ^{14}N coupling constants for the NO_2 groups in both RDX and β-HMX in Table 2 suggest a significantly smaller departure from spherical symmetry around these nuclei as compared to the ring nitrogens. The calculated asymmetry parameters η, however, indicate comparable departures from axial symmetry as for the ring ^{14}N nuclei. It would be helpful to have experimental data for the ^{14}N nuclei belonging to the NO_2 groups in both RDX and β-HMX to not only examine if there is agreement with the predicted $e^2 q Q$ and η in the individual systems but also with the predicted feature of near equality between $e^2 q Q$ and η for the two molecules.

Our results for the ^{14}N nuclear quadrupole interaction parameters $e^2 q Q$ and η in Cocaine are presented in Table 3. The results in the first two rows of the

Table 3. Nuclear quadrupole coupling constants and asymmetry parameters for free cocaine system.

Cluster[a]	Basis set	Nuclei	$e^2 q Q$[c] Theory	Exp.[d]	η Theory	Exp.[d]
17	STO-3G[b]	N	−5.736		0.024	
24			−5.682		0.033	
43			−5.673	5.0229	0.030	0.0395
24	D95[b]		−4.990		0.045	
43			−5.038		0.067	

[a] Refers to the different cluster sizes with nitrogen as origin, with 43 atoms referring to a complete cocaine molecule.
[b] STO-3G basis sets are taken from [17] and D95 basis sets are taken from [22].
[c] The coupling constants $e^2 q Q$ are expressed in MHz.
[d] Experimental results are taken from [5].

Table 3 are for truncated fragments with 17 and 24 atoms, while the third row presents the results using the whole Cocaine molecule involving 43 atoms. In all three cases, the STO-3G basis set was employed. In the fourth and fifth rows we have listed the results for 24 and 43 atom clusters but using the more extended D95 basis set discussed earlier for RDX and β-HMX. In view of the much larger time that would be needed for the Cocaine molecule which has more atoms, we have not attempted to use the more flexible D95u basis set. However, our results for RDX and β-HMX indicate that one would not expect very significant differences between the results for the two basis sets. The results in the first three rows in Table 3 demonstrate the convergence with respect to the size of the cluster used for the molecule, including the full molecule. A similar convergence is seen from the fourth and fifth rows in Table 3. This feature suggests that in general in working with large molecules, the results with truncated fragments used for economy of computing effort should be quite reliable provided reasonable sizes are chosen for those fragments. However, the results from the first three rows are somewhat different from those for the fourth and fifth rows. This is not unexpected because the efg tensor depends sensitively on the anisotropy of the electron density at the ^{14}N nucleus, which can be influenced significantly by the difference in the natures of the molecular orbitals using limited sizes of different basis sets, one like D95 expected to be more complete than the STO-3G choice. It is also observed from Table 3 that the asymmetry parameter η changes more significantly in going from the STO-3G to D95 basis sets and also in going from 24 to 43 atoms system, as compared to $e^2 q Q$. This trend can be understood from the fact that, in contrast to the case of q which refers to the single principal component V_{zz}, η involves the difference between the principal V_{xx} and V_{yy} components and is therefore expected to be even more sensitive to the nature of the molecular orbitals and hence the choice of basis set. In any case, all the theoretical results in Table 3 indicate that η is rather small. The theoretical results for $e^2 q Q$ from the fifth row in Table 3 are found to be in excellent agreement with experimental results [5] noted in Table 3, and η is also found to be very small from both theory and experiment, although the difference is more pronounced percentage-wise than for $e^2 q Q$.

In exploring possible reasons for the percentage-wise difference in the theoretical and experimental values of η for Cocaine, one possibility is the fact that we have used the positions of the atoms which are based on the structure of Cocaine hydrochloride from X-ray measurements [15]. It is possible that the atomic positions in the free Cocaine molecule may be somewhat different from that in the hydrochloride. The influence of the atoms in the immediate environment of nitrogen should be particularly significant in this respect. The other possible source of error could be the fact that the hydrogen positions in Cocaine hydrochloride are determined from X-ray measurements [15] combined with Patterson analysis, in contrast to the more accurate experimental results [13, 14] from neutron diffraction in the case of RDX and β-HMX.

4. Conclusion

Our results for the nuclear quadrupole interaction parameters for nitrogen nuclei in RDX, β-HMX and Cocaine demonstrate that one gets good overall agreement between theory and experiment for the quadrupole coupling constants and asymmetry parameters in these systems using the first-principle Hartree-Fock procedure. The good comparison between experimental results and theory using single molecules has allowed us to focus on the causes for the small but significant remaining differences between theory and experiment, including trends of variations over different nitrogen nuclei in the same molecule and between different molecules. Among the possible causes pointed out for these remaining differences are the intermolecular interactions between the molecules, both short range effects involving bonding between nearest neighbor molecules, and the somewhat longer range interactions involving the influence of effective charges on the atoms in neighboring molecules on the electron distributions within a molecule containing the nucleus whose quadrupole interaction is being studied. These effects should be studied in the future, and while they are expected to be rather time consuming to work on, an understanding of the importance of these effects should provide valuable insights into the sensitivity of electron distributions to the influence of intermolecular interactions, insights which should be very helpful in the future study of more complicated phenomena such as the temperature dependences [3, 4] of the nuclear quadrupole interaction parameters and relaxation rates [7]. Such studies would require a quantitative analysis of vibrational effects associated with the atom containing the nucleus and its neighbors under the influence of intramolecular and intermolecular potentials. Lastly, the good agreement between experiment and theory using the Hartree-Fock procedure for all the three systems studied, suggests that many-body effects [24] are probably not significant in these complex molecular systems. However, it would be worthwhile in the future to test this conclusion by many-body calculations in one or more of these systems or smaller systems related to the present ones. On the experimental side, it would also be helpful in testing the calculated electron distributions over the entire molecules of RDX and β-HMX if the ^{14}N coupling constants in the NO_2 groups could be measured to compare with our theoretical predictions.

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