^{17}O Nuclear Quadrupole Coupling in Molecular and Lattice Systems by *ab initio* Calculation of Electric Field Gradients*

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We present *ab initio* Hartree-Fock calculations of electric field gradients, which are related to experimental determinations of nuclear quadrupole coupling constants. The nucleus of special interest is ^{17}O but other nuclei in the molecules, especially ^{14}N, ^{2}H and ^{33}S are included. The calculations were performed (a) as single molecules either at the SCF and MP2 correlated levels, (b) as clusters of molecules about a test site, or (c) as lattice calculations computed in the unit cell environment. The basis sets are triple zeta valence plus polarisation in (a). Because of limitations in exponent range in (c), the bases in both (b) and (c), where comparison was sought, are DZ at the SCF level.

1.0. Introduction

Our previous papers on a variety of organic and inorganic molecules contained ^{14}N, $^{10,11}B$ or ^{33}S, as well as other quadrupolar nuclei. They can be classified in three types: (a) studies of individual molecules at equilibrium [1–3]; (b) small clusters of molecules [4–6] where a test molecule was surrounded by its nearest shell of neighbours from the crystal lattice; (c) lattice calculations where the calculation was carried out in the unit cell structure of the crystal [7–11]. In the present paper, we give examples of each type, from both organic and inorganic species; the principal isotopes of interest will be ^{17}O, but also ^{2}H and ^{14}N where present in the object. In (a) comparison is with gas-phase data (usually microwave spectral results); for (b) and (c) comparison is with NQR data from the solid state, and some NMR data from solution.

It is important to note a series of papers by Gready [12–15], in which the ^{17}O tensor assignments for a variety of small organic molecules were discussed, some of which are reconsidered here. These earlier papers used DZ bases [16] at experimental structures; the present work is more extensive, including several cases of inorganic systems, but will refer to the Gready assignments in a number of cases.

2.0. Methods

2.1. Electric Field Gradients and Nuclear Quadrupole Coupling Constants

In each of Methods a, b, c, the electric field gradients (EFG, q_{ij}) are obtained from the electronic wavefunction (the 'electronic term', E) and converted to nuclear quadrupole coupling constants (NQCC, χ_{ii}) by means of the equations (1) and (2). In (1) we give only one electronic component of the tensor elements, a diagonal element $(3z^2-r^2)/r^5$); the full 3×3 symmetric tensor includes other diagonal elements by permutation of $3z^2$ with $3x^2$ and $3y^2$, as well as the off-diagonal elements $3xy/r^5$ etc. The total EFG elements contain the corresponding terms based on the positions of the nuclei (the 'nuclear term', N); thus, if the structure differs from the experimental one, the nuclear positions will build in a difference irrespective of the effect of the electronic components. It is also important to note that the sign of the EFG can often be reversed with no change in meaning, through alternative use of (1), where either the sum or difference of the electronic and nuclear terms is taken, the sign being absorbed in the method of calculation of the electronic components. Thus GAMESS-UK operates on the sum of the electronic and nuclear terms, leading to the EFG terms being reversed in sign to other work. Other programs derived from PA60 of the POLYATOM code follow this practice of taking the sum of E+N.

$$q_{zz} = \langle \Psi_0 | (3z^2-r^2)/r^5 | \Psi_0 \rangle . \quad (1)$$

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In (2) the best current value for Q_N, Q_O^{17}, Q_S^{33} and Q_H^2 are taken from Pyykko [17], and are $+2.01$, -2.558, -6.78 and $+0.2860\,\text{fm}^2$, where $1\,\text{barn} = 10^{-28}\,\text{m}^2 = 100\,\text{fm}^2$. These values are used in the present work. In order to reduce the number of tables, EFG elements have not been given directly, but can be obtained by use of the above values for Q_Z.

$$\chi_{ii} = e^2\, Q_Z\, q_{ii}/h = 234.96\, Q_Z\, q_{ii}. \qquad (2)$$

2.2. Basis Sets

The GAMESS-UK program was used for single molecule and cluster studies, as in our previous work [1–6]. We used a Huzinaga/Dunning [18–20] double zeta (DZ) or triple zeta valence with polarisation functions (TZVP) for some small system calculations. These are comparable with our previous work [4–6] and generally give reliable values for structural features and NQCC when compared with NQR data. The molecules were studied with the TZVP basis set using both SCF and MP2 methodology, so that the MP2 structures are at an electron correlated level, in which the whole set of electrons (core and valence) participate. This leads to a higher level of electron correlation than singles/doubles CI, which is usually limited to the valence shell as active space. The molecular systems studied are shown in Tab. 1, the equilibrium structures in Tab. 2, and the NQCC results and comparison with experimental data in Table 3.

2.3. Lattice Calculations

We present a number of results using 'CRYSTAL-92', an *ab initio* Hartree-Fock SCF programme for periodic systems; this programme computes the electronic wave-function in the reciprocal space of the unit cell system, and hence generates a wave-function which represents the bulk material, rather than just a local environment. Integration is carried out over a set of cells until the integrals between the 'origin' and the extremities fall below some preset tolerance, and hence can be ignored. More detail concerning the basic method is given in the papers by Saunders et al. [9–11] and our implementation of it in recent papers on inorganic and organic molecules [7, 8]. The data input is the crystallographic space group, unit cell parameters, the asymmetric unit, the tolerances and other convergence criteria and the basis set. The principal results with these lattice calculations are shown in the NQCC data of Table 3.

Table 1. Molecules studied with TZVP basis: total energies (a.u.)

Compound	SCF energy	MP2 (MP3) energy
σ bonded		
Water	−76.05601	−76.29096
Methanol	−115.08641	−115.48087
Di-methyl ether	−154.01916 (DZ)	−154.67093
Oxirane	−152.92000	−153.46014
σ + π bonded		
CO	−112.77694	−113.11547
CO_2	−187.70089	−188.26455
SO_2	−547.23766	−547.87605
SO_2	−547.23766	(−547.84909)
SO_3	−622.07172	−622.92247
SO_3		(−622.88827)
SCO	−510.32353	−510.86063
SCO		(−510.85480)
SSO	−869.88438	−870.48810
SSO		(−870.48057)
OPF_3	−714.18036	−715.22429
HNCO	−167.82225	−168.36769
HNCO		(−168.35824)
Formaldehyde	−113.90932	−114.27979
Benzoquinone	−379.35241	−380.66500
Furan	−228.69890	−229.52890
γ-Pyrone	−341.47278	−242.64646
Formic acid	−188.83584	−189.41933
Formic acid dimer	−377.69286	−378.86220
Methyl formate	−227.86951	−228.61621

In order to give quantitative comparisons between the lattice and cluster or single molecule calculations, we used the Huzinaga/Dunning [18, 19] DZ bases in 'CRYSTAL-92'. Low GTO exponents (a_i) for 2p in O, N and C (the values are 0.2137, 0.1654 and 0.1146, respectively, with the DZ basis) in a crystal lattice lead to nearly zero eigenvalues of the overlap matrix (S_{ij}) and hence numerical problems when it is inverted. This was overcome by projecting out the S_{ij} eigenvector whose eigenvalue is 10^{-4} or smaller. 'Direct-scf' calculations were performed in most cases; i.e. the Fock matrix was computed directly without a complete set of integrals being preformed. This extends the CPU time by many times, since the overall integral set has to be recalculated at each iteration, but avoids the formation of very large 2-electron integral files. Use of the TZVP basis was not possible for these CRYSTAL-92 studies, because of the enhanced overlap problems.

3.0. Results and Discussion

3.1. Structural Features and Comparison with Experiment

Equilibrium structures with split valence (or better) GTO basis sets generally give good agreement with

Table 2. Equilibrium structures of oxygen compounds

Compound	Method	Basis	Bond lengths/Å bond angles/°
H_2O	M-wave[a]		OH 0.9584 HOH 104.45
H_2O	SCF	TZVP	OH 0.9406 HOH 107.12
H_2O	MP2	TZVP	OH 0.9574 HOH 105.01
H_2O	MP3	TZVP	OH 0.9532 HOH 105.22
H_2O	MP2	DZ	OH 0.9782 HOH 110.69
H_2O	MP3	DZ	OH 0.9747 HOH 110.80
MeOH	M-wave[a]		OH 0.9630 CO 1.4214 COH 108.0 CH 1.0937 HCH 108.5 tilt 3.2
MeOH	TZVP	SCF	OH 0.9401 CO 1.4024 COH 110.2 CH 1.0845 HCH 108.6 tilt 3.1
MeOH	TZVP	MP2	OH 0.9582 CO 1.4218 COH 107.9 CH 1.0880 HCH 108.7 tilt 3.6
CO	M-wave[a]		CO 1.1282
CO	SCF	TZVP	CO 1.1047
CO	MP2	TZVP	CO 1.1382
CO	MP3	TZVP	CO 1.1212
CO_2	TZVP	SCF	CO 1.1359
CO_2	TZVP	MP2	CO 1.1691
SCO	M-wave[a]		SC 1.561 CO 1.157
SCO	TZVP	SCF	SC 1.5715 CO 1.1235
SCO	TZVP	MP2	SC 1.5683 CO 1.1678
SCO	TZVP	MP3	SC 1.5741 CO 1.1450
HNCO	M-wave[a]	IR	HN 0.986 NC 1.209 CO 1.166 HNC 128.0 NCO (170.0)
HNCO	TZVP	MP2	HN 1.0018 NC 1.2181 CO 1.1729 HNC 126.24 NCO 171.94
HNCO	TZVP	MP3	HN 0.9995 NC 1.2112 CO 1.1580 HNC 124.22 NCO 172.92
SO_2	M-wave[a]		SO 1.431 OSO 119.3
SO_2	TZVP	SCF	SO 1.4209 OSO 117.7
SO_2	TZVP	MP2	SO 1.4847 OSO 118.1
SO_2	TZVP	MP3	SO 1.4493 OSO 117.4
SO_3	M-wave[b]		SO 1.4198 OSO 120.0
SO_3	TZVP	SCF	SO 1.4198 OSO 120.0
SO_3	TZVP	MP2	SO 1.4609 OSO 120.0
SO_3	TZVP	MP3	SO 1.4352 OSO 120.0
SSO	M-wave[c]		SS 1.882 SO 1.464 SSO 118.3
SSO	TZVP	SCF	SS 1.8779 SO 1.4331 SSO 116.9
SSO	TZVP	MP2	SS 1.9347 SO 1.5106 SSO 116.8
SSO	TZVP	MP3	SS 1.9139 SO 1.4747 SSO 115.9
F_3PO	M-wave[d]		FP 1.522 PO 1.437 FPF 101.4
F_3PO	TZVP	SCF	FP 1.5235 PO 1.4262 FPF 100.3
F_3PO	TZVP	MP2	FP 1.5575 PO 1.4571 FPF 100.1
H_2CO	M-wave[a]		HC 1.116 CO 1.2078 HCO 121.74
H_2CO	SCF	TZVP	HC 1.0923 CO 1.1797 HCO 121.98
H_2CO	MP2	TZVP	HC 1.0975 CO 1.2117 HCO 121.99
Oxirane	M-wave[a]		CO 1.436 CC 1.472 CH 1.082 COC 61.40 HCH 116.7
Oxirane	SCF	TZVP	CO 1.4013 CC 1.4538 CH 1.0759 COC 62.50 HCH 115.37
Oxirane	MP2	TZVP	CO 1.4335 CC 1.4630 CH 1.0804 COC 61.36 HCH 116.08
Furan	M-wave[a]		CO 1.362 C_2C_3 1.361 C_3C_4 1.431 CH_2 1.075 CH_3 1.077 OCC 110.7 COC 106.5 HCO 115.9 HC_3C_2 126.9
Furan	TZVP	SCF	CO 1.3424 C_2C_3 1.3375 C_3C_4 1.4405 CH_2 1.0666 CH_3 1.0683 OCC 110.7 COC 107.2 HCO 116.4 HC_3C_2 126.7
Furan	TZVP	MP2	CO 1.3611 C_2C_3 1.3642 C_3C_4 1.4268 CH_2 1.0729 CH_3 1.0742 OCC 110.5 COC 106.7 HCO 115.8 HC_3C_2 126.2
γ-pyrone	M-wave[c]		OC_4 1.2261 O_1C_2 1.3583 C_2C_3 1.3438 C_3C_4 1.4627 C_2H 1.0791 C_3H 1.0818 COC 117.3 O_1CC 123.9 $C_2C_3C_4$ 120.9 $C_3C_4C_5$ 113.1 OCH 110.9 C_2C_3H 119.1
γ-pyrone	TZVP	SCF	OC_4 1.195 O_1C_2 1.340 C_2C_3 1.325 C_3C_4 1.469 C_2H 1.070 C_3H 1.071 COC 118.4 O_1CC 124.0 $C_2C_3C_4$ 120.4 $C_3C_4C_5$ 112.9 OCH 111.5 C_2C_3H 120.4
Formic acid	M-wave[a]		HC_1 1.097 C_1O_1 1.202 C_1O_2 1.343 OH 0.972 HCO 124.1 OCO 124.6 COH 106.3
Formic acid	TZVP	SCF	HC_1 1.0839 C_1O_1 1.1763 C_1O_2 1.3215 OH 0.9471 HCO 124.7 OCO 124.9 COH 109.7
Formic acid	TZVP	MP2	HC_1 1.0971 C_1O_1 1.1970 C_1O_2 1.3540 OH 0.9628 HCO 124.1 OCO 122.5 COH 108.8
Formic acid Dimer	ED		HC_1 (1.0106) C_1O_1 1.220 C_1O_2 1.332 OH 1.058 HCO 122.5 OCO 125.5 COH 107.8
Formic acid Dimer	TZVP	SCF	HC_1 1.0831 C_1O_1 1.1905 C_1O_2 1.2993 OH 0.9596 HCO 122.7 OCO 125.6 COH 111.6
Formic acid Dimer	TZVP	MP2	HC_1 1.0888 C_1O_1 1.2195 C_1O_2 1.3178 OH 0.9882 HCO 122.5 OCO 126.2 COH 109.3
Me formate	M-wave[a]		HC_1 1.101 C_1O_1 1.200 C_1O_2 1.334 O_2C_2 1.437 C_2H 1.086 OCO 125.9 COC 114.8 HC_1O 109.3 HC_2H 110.7
Me formate	TZVP	SCF	HC_1 1.085 C_1O_1 1.179 C_1O_2 1.315 O_2C_2 1.420 C_2H 1.080 OCO 125.7 COC 117.5 HC_1O 108.9 HC_2H 110.0
Me formate	TZVP	MP2	HC_1 1.091 C_1O_1 1.206 C_1O_2 1.342 O_2C_2 1.438 C_2H 1.084 OCO 125.7 COC 114.4 HC_1O 109.0 HC_2H 110.3

[a] For general reference see text; [b] V. Meyer, D. H. Sutter, and H. Dreizler, Z. Naturforsch. **46A,** 710 (1991); [c] J. N. MacDonald, S. A. MacKay, J. K. Tyler, A. P. Cox, and I. C. Ewart, J. Chem. Soc. Faraday Trans. II **77,** 79 (1981). E. Tiemann, J. Hoeft, F. J. Lovas, and D. R. Johnson, J. Chem. Phys. **60,** 5000 (1974); [d] Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys. **20,** 164 (1952).

substitution structures from microwave spectroscopy. This is particularly true with σ-bonded structures; hence we make relatively few comments here. However, in the general case where the bond lengths and angles are significantly different from experiment, the inertial axes (IA) will be differently positioned, and hence M-wave IA-NQCC results will not compare, except where symmetry constraints apply.

Several of the molecules studied here are well-known with microwave substitution structures (r_S) [21]; we compare with the equilibrium structures (r_e) (Tab. 2) using the TZVP basis at both SCF and MP2 levels. Generally the MP2 calculations reduce the difference between the SCF results and the substitution structures, but both sets are close to experiment. It is not expected that r_S will be idential with r_e. A typical case is methyl formate, where several CO bond lengths occur; the MP2 structure is clearly an improvement over the SCF one. For furan, the problem with most basis sets is getting a balance between the C_2O and

Table 3. ^{17}O (MHz) quadrupole coupling constants:[a–c] comparison with experiment

Molecule	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
H_2O (gas)	M-wave	+10.1068 (π)	−8.8964	−1.2104	0.7605
	B-maser	+10.175 (π)	−8.891	−1.283	0.750
H_2O	TZVP (SCF)	+10.9258 (π)	−10.3583	−0.5675	0.8961
	TZVP/CI	+10.7945 (π)	−10.2241	−0.5705	0.8943
	TZVP/MP2	+10.4187 (π)	−9.3899	−1.0288	0.8025
	TZVP/MP3	+10.7790 (π)	−9.7828	−0.9962	0.8151
	DZ/SCF	+11.7201 (π)	−11.6230	−0.0971	0.9830
	DZ/MP2	+10.8212 (π)	−10.1015	−0.7197	0.8670
	DZ/MP3	+11.2047 (π)	−10.5129	−0.6919	0.8765
	DZ[d]	+12.313	−10.8702	−1.4425	0.7657
	39-STO	+10.92	−9.71	−1.21	0.779
H_2O (IceIh)	NQR	(+)6.525	(−)6.280	(−)0.245	0.925
H_2O (IceII)	NQR	(+)6.983	(−)6.512	(−)0.471	0.865
H_2O (IceII) (a)	DZ	+9.385	−5.237	−4.148	0.116
H_2O (IceII) (b)	DZ	+8.960	−6.989	−1.971	0.560
MeOH	M-wave	∼ +11 (π)	−7.86 (aa)		
MeOH	TZVP/SCF	+12.142 (π)	−11.299	−0.843	0.861
MeOH	TZVP/MP2	+11.249 (π)	−10.401	−0.848	0.849
MeOH	TZVP/MP2	+11.249 (π)	−7.854 (aa)	−3.414 (bb)	0.324
α-MeOH	NQR	−8.730	8.490	0.240	0.945
β-MeOH	NQR	−8.445	7.706	0.739	0.825
glycol	NQR	8.895	8.762	0.133	0.970
PhOH	NQR	8.476	7.594	0.882	0.792
ME_2O	TZVP/SCF	−13.970 (T)	+13.430 (π)	+0.540 (R)	0.923
ME_2O	TZVP/MP2	−11.867 (T)	+11.781 (π)	+0.087 (R)	0.985
Oxirane	M-wave	+12.6 (π)	−7.4	−5.2	0.175
Oxirane	DZ[e]	+14.74	−8.84	−5.90	0.199
Oxirane	DZ	+16.002 (π)	−10.027 (R)	−5.976 (T)	0.253
Oxirane	TZVP/SCF	+13.937 (π)	−7.514 (R)	−6.424 (T)	0.078
Oxirane	TZVP/MP2	+13.102 (π)	−7.818 (R)	−5.285 (T)	0.193
furan	NMR	11.0			
furan	DZ/CI	−10.413 (T)	+6.732 (π)	+4.042 (R)	0.224
furan	TZVP/SCF	−9.100 (T)	+4.981 (π)	+4.119 (R)	0.095
furan	TZVP/MP2	−7.671 (T)	+3.921 (π)	+3.763 (R)	0.019
xanthene	NQR	9.868	7.908	1.960	0.6027
tetrahydrofuran	NMR	13			
CO	M-wave	4.337	−2.1685	−2.1685	0.0
	TZVP/SCF	+4.6613	−2.3306	−2.3306	0.0
	TZVP/MP2	+4.3443	−2.1721	−2.1721	0.0
	TZVP/MP3	+4.4402	−2.2201	−2.2201	0.0
	TZVP/MP4	+4.07	−2.035	−2.035	0.0
CO_2	TZVP/SCF	+3.8456	−1.9228	−1.9228	0.0
CO_2	TZVP/MP2	+4.1280	−2.0640	−2.0640	0.0

Table 3. (cont.)

Molecule	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
H_2CO	M-wave	+12.37 (T)	−10.48 (π)	−1.89 (R)	0.694
	DZ/SCF[d]	+15.701 (T)	−11.513 (π)	−4.188 (R)	0.467
	DZ/CI	+15.702 (T)	−11.477 (π)	−4.225 (R)	0.462
	TZVP/SCF	+13.234 (T)	−11.578 (π)	−1.656 (R)	0.750
	TZVP/CI	+13.040 (T)	−11.320 (π)	−1.720 (R)	0.736
	TZVP/MP2	+12.234 (T)	−10.135 (π)	−2.099 (R)	0.657
$C_6H_4O_2$	NQR	11.511	8.380	3.143	0.454
$C_6H_4O_2$	TZVP	+12.908 (T)	−10.490 (π)	−2.490 (R)	0.616
γ-Pyrone	TZVP/SCF (O4)	+11.552 (T)	−7.599 (π)	−3.952	0.316
	TZVP/SCF (O1)	−10.258 (T)	+6.488 (π)	+3.771 (R)	0.265
γ-Pyrone	TZVP/MP2 (O4)	+10.588 (T)	−6.337 (π)	−4.252	0.197
	TZVP/MP2 (O1)	−8.534 (T)	+4.979 (π)	+3.555 (R)	0.167
Formic A.	NQR[g]	6.687	3.344	3.344	0.000
Formic A.	NQR[g]	7.829	4.349	3.480	0.111
Formic A.	DZ/SCF (O_1)	+12.782 (T)	−6.753 (π)	−6.029 (R)	0.000
Formic A.	DZ/SCF (O_2)	−11.360 (T)	+8.393 (π)	+2.966 (R)	0.478
Formic A.	TZVP/SCF (O_1)	+10.069 (T)	−6.899 (π)	−3.170 (R)	0.370
Formic A.	TZVP/SCF (O_2)	−9.737 (T)	+7.274 (π)	+2.463 (R)	0.494
Formic A.	TZVP/CI (O_1)	+9.943 (T)	−6.719 (π)	−3.224 (R)	0.352
Formic A.	TZVP/CI (O_2)	−9.719 (T)	+7.318 (π)	+2.401 (R)	0.506
Formic A.	TZVP/MP2 (O_1)	+8.927 (T)	−5.757 (π)	−3.170 (R)	0.290
Formic A.	TZVP/MP2 (O_2)	−8.357 (T)	+6.500 (π)	+1.858 (R)	0.555
Formic A.	Lattice/DZ (O1)	+10.293	−6.901 (π)	−3.392	0.341
Formic A.	Lattice/DZ (O2)	−9.834	+6.773 (π)	+3.060	0.376
$(HCO_2H)_2$	NQR (O_1)	7.818	4.183	3.635	0.070
$(HCO_2H)_2$	TZVP/SCF (O_1)	−9.603 (T)	+5.271 (π)	+4.332	0.098
$(HCO_2H)_2$	TZVP/CI (O_1)	−9.561 (T)	+5.305 (π)	+4.256	0.110
$(HCO_2H)_2$	TZVP/MP2 (O_1)	−8.460 (T)	+4.260 (π)	+4.200	0.107
$(HCO_2H)_2$	NQR (O_2)	−6.900	+3.716	+3.369	0.077
$(HCO_2H)_2$	TZVP/SCF (O_2)	+8.901 (T)	−5.672 (π)	−3.229	0.274
$(HCO_2H)_2$	TZVP/CI (O_2)	+8.832 (T)	−5.596 (π)	−3.236	0.267
$(HCO_2H)_2$	TZVP/MP2 (O_2)	+7.298 (T)	−4.542 (π)	−2.755	0.245
Maleic A.	NQR (O1)	7.485	4.790	2.695	0.280
Maleic A.	NQR (O2)	8.593	4.748	3.845	0.105
Maleic A.	NQR (O3)	7.000	3.640	3.360	0.040
Maleic A.	NQR (O4)	7.223	3.756	3.472	0.040
Maleic A.	DZ/Lattice (O1)	+10.284	−7.415	−2.869	0.499
Maleic A.	DZ/Lattice (O2)	+12.229	−7.320	−4.909	0.197
Maleic A.	DZ/Lattice (O3)	−9.529	+5.998	+3.531	0.259
Maleic A.	DZ/Lattice (O4)	−10.121	+6.478	+3.642	0.280
Oxalic A.	NQR (O1)	8.455	4.228	4.228	0.000
Oxalic A.	NQR (O2)	7.545	4.376	3.169	0.160
Oxalic A.	DZ/Lattice (O1)	+10.284	−7.415	−2.869	0.499
Oxalic A.	DZ/Lattice (O2)	+12.229	−7.320	−4.909	0.197

SCO	M-wave	−1.32	0.66	0.66	0.0
SCO	TZVP/SCF	−0.5558	+0.2779	+0.2779	0.0
SCO	TZVP/MP2	−1.6924	+0.8462	+0.8462	0.0
HNCO	M-wave (IA)	+3.452 (cc)	−3.276 (aa)	−0.176 (bb)	0.898
	TZVP/MP2	+3.2971 (cc)	−3.5761 (R)	+0.2790 (T)	0.844
	TZVP/MP2	+3.2971 (cc)	−2.5159 (cc)	+0.7812 (bb)	0.844
SSO	TZVP/SCF	+10.4261 (T)	−5.8073 (R)	−4.6188 (π)	0.114
SSO	TZVP/MP2	+9.1408 (T)	−4.9351 (R)	−4.2047 (π)	0.080
SSO	TZVP/MP3	+10.4318 (T)	−6.5112	−3.9207 (π)	0.248
SO_2	M-wave[h]	6.6±0.6			
SO_2	TZVP/SCF	−8.864	+5.385 (π)	+3.479	0.215
SO_2	TZVP/CI	−8.741	+5.132 (π)	+3.609	0.174
SO_2	TZVP/MP2	−7.531	+4.376 (π)	+3.155	0.162
SO_2	TZVP/MP3	−8.902	+4.764 (π)	+4.138	0.070
SO_3	TZVP/SCF	−8.982 (T)	+8.228 (R)	+0.755	0.832
SO_3	TZVP/MP2	+8.415 (R)	−8.142 (T)	−0.274	0.935
SO_3	TZVP/MP3	−9.026 (T)	+8.894 (R)	+0.132	0.971
$HCONH_2$	TZVP/SCF	−10.121 (T)	+5.955 (R)	+4.167 (π)	0.177
$HCONH_2$	TZVP/MP2	−9.167 (T)	+5.055 (R)	+4.113 (π)	0.103

[a] The calculated EFG (a.u.) can be directly obtained from (1); the overall ratio of χ/q here is −6.0102, namely e^2Q/h.

[b] In these planar molecules, the c-axis is always defined to be the local out-of-plane direction, with corresponding χ_{cc}; T is tangential to the OC (or OX generally) bond, while R is radial, i.e. close to a direction along the OX bond. Both T and R lie in the molecular plane.

[c] Most references are given in the Discussion and Results.

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C_2C_3 bond lengths. This is achieved by both SCF and MP2 calculations at the TZVP level, but not so with many smaller bases. In the case of CO and the cumulative bonded molecules, CO_2, HNCO and OCS etc, the MP2 corrections have a significant effect upon the geometric parameters, and an improvement in agreement with spectroscopic values. In some cases like SO_2 and OPF_3, the MP2 correlation makes the structure less like the experimental values; MP3 correlation returns the bonds to values close to both the SCF and substitution structures. Curiously, the sulphur trioxide molecule shows the same phenomenon, namely the SCF and MP3 structures are markedly closer to experiment than the MP2 one. This is not uniformly true of SO double-bonded molecules, since OCS is well determined by all the calculations; possibly the bent features of SO_2 and SO_3 have some special significance. For the other molecules, these MP2 level of correlation refinements have more significant effects on the NQCC below.

3.2. Spectroscopic Assignments Together with Theoretical Results

In the following Sections we discuss selected groups of compounds with the experimental information and results together, in order to try to correlate with bonding characteristics. Comparison with the NQR data and lattice calculations follows where possible, so that some comparison of vapour and condensed phase results can be made. It is important to remember that the lattice calculations cannot be performed under current coding in CRYSTAL-92 with TZVP bases owing to the diffuse nature of the exponents, whereas the DZ bases give a direct comparison of the two phases. A number of the molecules are planar with C_{2v} or C_s symmetry; following our earlier procedures with cyclic molecules, where the local EFG principal axes are usually close to the radial (R) and tangential directions (T) in the ring structure, it is convenient to retain the same R/T nomenclature, but here the values relate to the two local in-plane axes, close to the XO bond (R) or perpendicular to it (T), with the third perpendicular component out-of-plane (π).

3.2.1. Oxygen with Two σ-Bonds

3.2.2. Water

The NQCC at both ^{2}H [22, 23] and ^{17}O [22–24] NQCC for water vapour and ice (in both its normal (ice-I, hexagonal) [25, 26] and high pressure forms (ice-II)) [27] have been obtained. A comparison with TZVP optimised structural data is shown in Table 3. The ^{17}O χ_{zz} lies along the c-axis (out-of-plane axis), with χ_{xx} along the C_{2v} symmetry (b-axis). Theoretical studies with large basis sets obtain good agreement with experiment (Table 2) [16, 28]. Although the ^{2}H asymmetry is good for all calculations (Table 4), only the MP2 calculation and a very large Slater type orbital one [28] seem to reduce the value of the χ_R-bonded term to close to the experimental value. The direction of χ_{zz} is 17.5° from the OH bond axis, such that the projection of the axes behind the O atom has an angle of 72.2° to be compared with an HOH angle of 107.1°. The out-of-plane χ_π value is slightly larger than the other in-plane χ_T value.

Condensation of steam to ice leads to a quite dramatic reduction in χ_{zz} (Table 1). Single crystal neutron diffraction studies of Ice-I [29] show a disordered structure with half-atoms assigned to two sites in addition to a regular site. Ice-II has a more ordered structure (R3-CR) [30] with hexagonal columns of O atoms and one H between each pair, but the diffraction data were refined in the lower space group R-3. There are two molecules in the asymmetric unit [30]. The NQR data show 4 ^{1}H sites, but only one ^{17}O site was found (Table 3).

The present study of the lattice could not include ice-I because of the necessity to use half-hydrogen atoms; the ice-II study with the DZ basis gave 2 sites with very differing η for ^{17}O, but similar values for χ_{zz} (Table 3). The ^{2}H EFG gave different values for η at all sites, but basically in pairs 0.182 and 0.144 for the two molecules of the asymmetric unit. This is as observed by Edmonds et al. [27], but we cannot be certain that the sites correspond in the two studies.

3.2.3. Alcohols, Phenols and Ethers

^{17}O Microwave studies [31–33] of methanol have only determined the value of (χ_{aa} -7.86) MHz, with an estimated value χ_{cc} $+11$ MHz based upon water and formaldehyde studies [31]. So far the other independent parameter $\chi_{bb}-\chi_{cc}$ has not been extracted from the data [32], and this term is the most important one, in view of the high asymmetry parameters found from ^{17}O NQR studies of alcohols, ethers and phenols (Table 3).

Thus ^{17}O NQR studies in these compounds are limited to methanol [34], ethane-1,2-diol [35], phenol [36], and hydroquinones [37]; xanthene (dibenzopyran) appears to be the only example for ethers [38]. The most obvious feature is the high asymmetry parameter at ^{17}O in these compounds. This makes correlations with structure difficult if the directions cannot be correlated with certainty. ^{17}O NQCC have been obtained from microwave spectroscopy for oxirane [38]. A DZ basis set calculation on oxirane [39] was in agreement with the MW data concerning directions, but about 12% high for χ_{zz} (χ_π).

Based upon water and oxirane, which is not a typical ether, these MW data for methanol suggest that χ_{zz} is positive and lies in the out-of-plane c-axis (χ_π), with the smallest value χ_{xx} lying along the in-plane χ_R axis. This is reminiscent of the case with H_2S, Me_2S and C_2H_4S as discussed previously [3]. However, the NQR data for both α- and β-forms of methanol show fine structure [34], and this has led to analysis of the absolute signs for χ_{zz} being negative in each case. The proposition was that χ_{yy} lies perpendicular to the local C-O-H plane, but that χ_{zz} and χ_{xx} interchange directions, with χ_{xx} lying close to the HO bond axis and internal bisector of the C-O-H angle in the α- and β-forms of methanol, respectively [34]. If all these conclusions are correct, then the directions of the tensors switch for methanol between the gas phase and each of the solid states.

The present study on methanol used both DZ and TZVP bases to determine the equilibrium structure at the SCF and MP2 levels (Tab. 2 shows the TZVP MP2 data only); the structural features especially at the MP2 level are close to those from M-wave spectroscopy [33]. The high asymmetry is found, but the principal value for the EFG lies in the out-of-plane direction, in agreement with earlier microwave considerations [31, 38]. The inertial axis values found in the present work are in good agreement with experiment. A direct determination of the solid state EFG in methanol was impossible owing to the disordered structure in α- and β-isomers [40, 41].

The equilibrium structure for dimethyl ether at both the SCF and MP2 level with a TZVP basis gave the in-plane EFG tangential to the COC angle as the principal value. This implies a switch in axes relative to MeOH and water and, bearing in mind the high asymmetry in all three molecules, is quite probable. The oxirane calculations under the same basis set and methodologies gave the order $\chi_\pi > \chi_R > \chi_T$ in magnitudes, with χ_π positive and a much lower value for η than in methanol. These results are all compatible with earlier calculations and the microwave studies. Thus is seems that the observation that χ_{zz} is the same in sign for water and oxirane may well be coincidental; the much lower value in η is an indicator that a switch of axes may have occurred. It is clear that the value for χ_R is much larger in oxirane than the other molecules. This presumably reflects the ring strain.

Furan and tetrahydrofuran have been studied by ^{17}O NMR yielding estimates of χ_{zz} of 11 and 13 MHz, respectively [42]. The present calculations on furan all point to the equivalence of χ_{zz} with the tangential T-axis (Tab. 3), with the equivalence of χ_{yy} with χ_π. The same situation was found for thiophene [3], which has a much larger asymmetry parameter.

3.3.1. Oxygen with π-Bonds

3.3.2. Carbon Monoxide

The ^{17}O NQCC have been evaluated from astronomical sources, and the fully resolved microwave spectral value is χ_{zz} 4337 ± 56 kHz [43, 44], in excellent agreement with the MP2 and MP4 [45] value (Table 3). We have been unable to obtain an experimental value for the corresponding experimental tensor in CO_2, but the present work suggests that very similar values (Tab. 3) will be obtained to those for CO.

3.3.3. HNCO and SCO

These molecules have an immediate relationship to CO and CO_2; so that both isocyanic acid (HNCO), and carbon oxysulphide (OCS) are simple examples for cumulative bonded structures. The ^{17}O and ^{14}N NQCC for HNCO have been observed by FT-microwave spectroscopy [46], but only in the inertial axis (IA) system of the molecule. The present results in the M-wave frame are in reasonable agreement with experiment. The linear SCO molecule [47] has a very low axial value of -1.32 MHz; the SCF and MP2 values are also low; neither is in particularly good agreement with experiment, but improved by the MP3 calculations.

3.3.4. SO_2, SO_3 and F_3PO

Except for phosphoryl fluoride, there are insufficient data for firm conclusions with these molecules. With F_3PO, the agreement with the SCF calculation is better than with the MP2 one. The dipole moment is somewhat smaller than might be expected (1.735 D in benzene); hence the PO bond is only polarised towards O by about 0.4 e, and much smaller than the P^+-O^- representation would imply. It is difficult to obtain a good balance of charge in systems such as this, and this effects the EFG strongly. The SO_2 single result from NMR measurements does not fit well with the present study, but it seems likely that the PA χ_{zz} value is positive. We cannot be certain of the sign of χ_{zz} for SO_3 in view of the high η.

3.3.5. Formaldehyde

The ^{17}O quadrupole coupling shows distinct asymmetry, as expected from the $\sigma + \pi$ bonding; the microwave data [48] show the largest χ_{zz} lying in-plane, but perpendicular to the CO bond (χ_T) (Table 3). The high asymmetry ($\eta = 0.694$), is largely a result of a very small χ_{aa} (C_2 axis, χ_R) component and a high negative π_π component. Thus the distribution is quite different from that of CO or HNCO. All of the present calculations reproduce these trends.

3.3.6. Benzoquinone and γ-Pyrone

A number of quinones have been studied by NQR [37]. As with the formaldehyde molecule above, there are high asymmetry parameters. In the present work we optimised the structure of both title compounds and found the EFG tensor elements to follow those of formaldehyde; thus at the CO groups of both molecules the value of χ_{zz} is positive and directed in the plane in the tangential (T) direction to the CO bond; χ_π is negative in both cases. γ-Pyrone has the property of both an ether and a carbonyl compound, and via a resonance situation has potentially a 6π-ring system together with an O^- external to the ring. Most evidence points to the ring being more closely related to the classical non-ionic structure [49]. The present data show some considerable differences from either of the CH_2O and Me_2O molecules, but considerable similarity to furan at the ring oxygen (O_1). There are insufficient data to cover the aromatic character argument more fully.

3.4.1. Carboxylic Acids and Derivatives

This is the group of compounds most fully discussed by Gready [12–15], and we therefore only note our own results and principal conclusions from Table 3. The NQR spectra of a number of carboxylic acids have been obtained [50, 51]. Both the NQR spectra and crystal structures show a variety of sites for several molecules; there is insufficient accuracy in the lattice calculations to confirm assignments. As an example we chose di-deutero-formic acid which crystallises in orthorhombic form $Pna2_1$ and has been studied by neutron diffraction at 4.5° [52].

3.4.2. Carbonyl of Carboxylic Acids and Derivatives

These follow the conclusions of Gready that the χ_{zz} is positive and nearly tangential to the carbonyl group CO bond axis. The asymmetry parameter is quite strongly affected by the basis set; larger bases and MP2 both selectively lower the magnitude of χ_R, leaving χ_π nearly unchanged, with an overall lowering of η.

3.4.3. Hydroxyl of Carboxylic Acids and Derivatives

The position is similar to the alcohols and water above, and discussed in detail by Gready.

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