



# B3LYP calculation of $^{17}\text{O}$ quadrupole coupling constants in molecules

William C. Bailey

*Department of Chemistry and Physics, Kean University, Union, NJ 07083, USA*

Received 21 April 1998; in final form 28 May 1998

## Abstract

The B3LYP/6-311 + G(3df,3p) model for the calculation of  $^{17}\text{O}$  nuclear quadrupole coupling constants (NQCC) in molecules is shown to yield results superior to calculations previously performed at the more demanding MP4 level of theory. For 10 molecules for which experimental NQCCs and accurate molecular structures are known, the root-mean-square difference between the calculated and experimental NQCCs is 0.12 MHz (2.2%). © 1998 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

The energy of interaction of the electric quadrupole moment of the nucleus of an atom with the gradient of the molecular electric field (EFG) at the site of the nucleus is measured spectroscopically by determination of the nuclear quadrupole coupling constant (NQCC).

Quantum chemistry calculation of the molecular EFG permits calculation of the NQCC, the NQCC being proportional to the EFG. Oxygen ( $^{17}\text{O}$ ) has been the subject of several such investigations at different levels of theory, including calculations by Eggenberger et al. [1] at the level of MP4 theory.

Becke's [2] three-parameter hybrid method used in conjunction with the correlation functional of Lee et al. [3,4] (designated B3LYP) has been found effective for calculation of the NQCCs for  $^{11}\text{B}$  [5] and  $^2\text{H}$  [6]. We report in this Letter the results of B3LYP calculations of the NQCCs at the site of the  $^{17}\text{O}$  nucleus in a variety of molecular environments.

## 2. Calculation

The components of the NQCC tensor  $\chi_{ij}$  are related to those of the EFG tensor  $q_{ij}$  by

$$\chi_{ij} = \left( \frac{eQ}{h} \right) q_{ij} \quad (1)$$

where  $e$  is the proton charge,  $h$  is Planck's constant, and  $Q$  is the electric quadrupole moment of the nucleus.

Experimentally, the coupling constants measurable are the diagonal elements  $\chi_{aa}$ ,  $\chi_{bb}$ , and  $\chi_{cc}$  of the NQCC tensor, where  $a$ ,  $b$ ,  $c$  are the principal axes of the inertia tensor of the molecule. For direct comparison with the experimental data, the  $q_{ij}$  calculated in this work were transformed to the  $a$ ,  $b$ ,  $c$  system of coordinates.

Following the procedure previously employed [5,6], the coefficient  $eQ/h$  in Eq. (1) is determined from least-squares linear-regression analysis of the calculated EFGs versus the experimental NQCCs.

Although not independent, all three diagonal components of the calculated EFG tensor are plotted against the corresponding components of the experimental NQCC tensor. This assures, because the tensors are traceless, that the slope of the least-squares line pass through the origin. In this way, the model is calibrated for a selected set of molecules by the best-fit value of  $eQ/h$ , which may then be used for prediction of NQCCs in other molecules.

All calculations were performed using the GAUSSIAN94 [7] package of programs. Numerical integrations were performed over a grid consisting of 75 radial shells with 302 angular points per shell ( $75 \times 302$ ) pruned to about 7000 integration points per atom (the GAUSSIAN94 default grid). For the B3LYP/6-311++G(3df,3p) model, the calculations were repeated using a much finer spherical product integration grid consisting of 96 radial shells around each atom with 32  $\theta$  points and 64  $\varphi$  points per shell, for a total of 196 608 integration points. Furthermore, with this finer grid, the tight SCF convergence option was used, whereas with the

coarser grid the GAUSSIAN94 default convergence was used. No significant differences in the EFGs were observed between the two calculations, the differences being generally less than one part per thousand. The results presented in this Letter are those obtained with the coarser integration grid and the default convergence criteria.

### 3. Results

The molecules investigated and the corresponding experimental NQCCs [8–17] are listed in Table 1. The first five in the list ( $\text{H}_2\text{O}$ , CO, OCS, HNCO, and  $\text{H}_2\text{CO}$ ) were chosen for calibration of the model. Once calibrated, the model was used for ‘prediction’ of the NQCCs for the remaining five molecules. All calculations were performed on the experimental structures [18–26].

6-31G and 6-311G Pople-type bases augmented by various combinations of diffuse functions and polarization sets were investigated in conjunction

Table 1  
Nuclear quadrupole coupling constants,  $\chi_{ij}$  and  $eQq_1$  (MHz)

Mol.	<i>ij</i>	B3LYP <sup>a</sup>	MP4 <sup>b</sup>	Expt.	Reference	
					NQCC	Struc.
$\text{H}_2\text{O}^c$	<i>aa</i>	−8.948	−9.03	−8.891(21)	[8]	[18]
	<i>bb</i>	−1.166	−1.05	−1.283(87)		
	<i>cc</i>	10.114	10.08	10.175(67)		
$\text{CO}^c$	<i>aa</i>	4.266	4.07	4.337(56)	[9]	[19]
$\text{OCS}^c$	<i>aa</i>	−1.353	−1.55	−1.333(22)	[10]	[20]
$\text{HNCOC}^c$	<i>aa</i>	−3.279	−3.85	−3.276(24)	[11]	[21]
	<i>bb</i>	−0.112	−0.00	−0.176(13)		
	<i>cc</i>	3.391	3.85	3.452(27)		
	<i>ab</i>	0.373	0.37			
$\text{H}_2\text{CO}^c$	<i>aa</i>	−1.946	−2.14	−1.900(118)	[12]	[22]
	<i>bb</i>	12.404	12.18	12.35(52)		
	<i>cc</i>	−10.458	−10.05	−10.45(48)		
$\text{C}_2\text{H}_4\text{O}$	<i>aa</i>	−5.310	−5.36	−5.2(1)	[13]	[23]
	<i>bb</i>	−7.652	−7.42	−7.4(1)		
	<i>cc</i>	12.962	12.78	12.6(1)		
OH	$eQq_1$	−1.869		−1.92	[14]	[24]
NO	$eQq_1$	−1.334		−1.30(4)	[15]	[25]
$\text{O}_2$	$eQq_1$	−8.207		−8.29(5)	[16]	[26]
SO	$eQq_1$	−3.540		−3.627(61)	[17]	[24]
rms		0.121	0.270			

<sup>a</sup>B3LYP/6-311++G(3df,3p),  $eQ/h = -5.834(15)$  MHz/au.

<sup>b</sup>Ref. [1].

<sup>c</sup>Molecules and NQCCs used for calibration.

with the B3LYP method. From among these, the least residual standard deviation and the maximum correlation coefficient, namely 0.0565 MHz and 0.99996, respectively, were obtained with the B3LYP/6-311++G(3df,3p) model. The least-squares value of  $eQ/h$  for this model is  $-5.834(15)$  MHz/au (which, incidentally, corresponds to an electric quadrupole moment for the  $^{17}\text{O}$  nucleus of  $-2.483(6)$  fm $^2$ ). Fig. 1 is a plot of the EFGs calculated with this model versus the experimental NQCCs. In Fig. 1, the solid circles are the points used for calibration, while the open circles are the predicted NQCCs. The values of the calculated and predicted NQCCs for this model are given in Table 1, along with the MP4 values of Eggenberger et al. and, as mentioned above, the experimental values.

Eggenberger et al. used for calibration of their MP4 model, the same five molecules as here plus  $\text{C}_2\text{H}_4\text{O}$  — and only the largest component of the diagonal coupling constants for each, whereas we include all diagonal components. We had, at first, included  $\text{C}_2\text{H}_4\text{O}$  in our calibration but found that it alone was responsible for almost half the residual standard deviation. With  $\text{C}_2\text{H}_4\text{O}$ , the standard deviation

is 0.1059 MHz and without  $\text{C}_2\text{H}_4\text{O}$  is 0.0565 MHz. A truer, more accurate calibration is obtained without  $\text{C}_2\text{H}_4\text{O}$ .

For these six molecules (the five used for calibration plus  $\text{C}_2\text{H}_4\text{O}$ ), the B3LYP/6-311++G(3df,3p) model with  $eQ/h = -5.834(15)$  MHz/au gives a root mean square (rms) difference between the calculated and experimental NQCCs of 0.132 MHz, which is 2.2% of the average absolute experimental NQCC. For the MP4 calculations, the rms value for the same six molecules is 0.270 MHz. Thus, the rms difference is reduced by half. For all 10 molecules, the B3LYP model gives a rms difference of 0.121 MHz, also 2.2%.

Although it is not the purpose of this study to calculate the electric quadrupole moment of the nucleus, it is encouraging that the  $Q(^{17}\text{O})$  of  $-2.483$  fm $^2$  found here lies close to the recommended value of  $-2.558$  fm $^2$  [27]. Eggenberger et al., using  $Q$  as a best-fit parameter for calibration of their MP4 calculations, find a value of  $-2.403$  fm $^2$ .

#### 4. Conclusion

$^{17}\text{O}$  NQCCs calculated from B3LYP/6-311++G(3df,3p) EFGs agree with the experimental NQCCs for the 10 molecules listed in Table 1 with a rms difference of 0.121 MHz, which is 2.2% of the average absolute experimental NQCC. This result is superior to that reported by Eggenberger et al. for their more demanding MP4 calculations.

#### References

- [1] R. Eggenberger, S. Gerber, H. Huber, D. Searles, M. Welker, *J. Mol. Spectrosc.* 151 (1992) 474.
- [2] A. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [3] C. Lee, W. Yang, R.G. Parr, *Phys. Rev.* 37 (1988) 785.
- [4] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* 157 (1989) 200.
- [5] W. Bailey, *J. Mol. Spectrosc.* 185 (1997) 403.
- [6] W. Bailey, *J. Mol. Spectrosc.* (1998) in press.
- [7] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J.

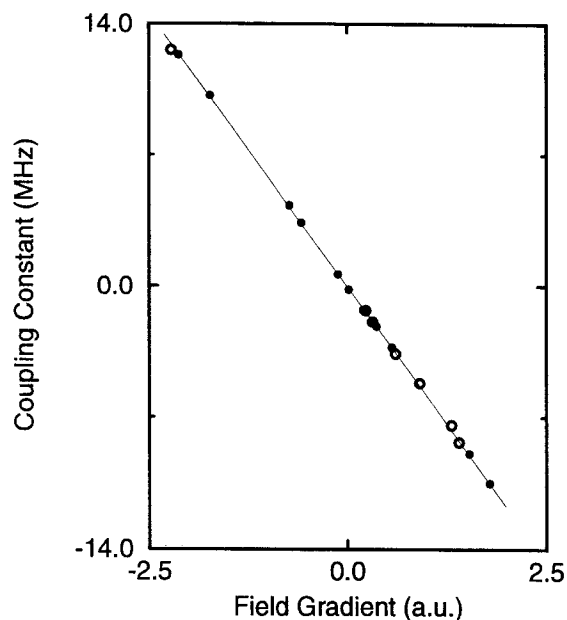


Fig. 1. Calculated electric field gradients (EFG) versus experimental nuclear quadrupole coupling constants (NQCC). Solid circles are the points used for calibration of the model.

- DeFrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN94, Revision B.1, Gaussian, Pittsburgh, PA, 1995.
- [8] J. Verhoeven, A. Dymanus, H. Bluysen, *J. Chem. Phys.* 50 (1969) 3330.
- [9] M.A. Frerking, W.D. Langer, *J. Chem. Phys.* 74 (1981) 6990.
- [10] I. Merke, H. Dreizler, *Z. Naturforsch.* 42a (1987) 1043.
- [11] M.C.L. Gerry, S.J. Howard, N. Heineking, H. Dreizler, *Z. Naturforsch.* 44a (1989) 1187.
- [12] R. Cornet, B.M. Landsberg, G. Winnewisser, *J. Mol. Spectrosc.* 82 (1980) 253.
- [13] R.A. Creswell, R.H. Schwendeman, *Chem. Phys. Lett.* 27 (1974) 521.
- [14] K.R. Leopold, K.M. Evenson, E.R. Comben, J.M. Brown, *J. Mol. Spectrosc.* 122 (1987) 440.
- [15] A.H. Saleck, M. Liedtke, A. Dolgner, G. Winnewisser, *Z. Naturforsch.* 49a (1994) 1111.
- [16] G. Cazzoli, C. Degli Esposti, *Chem. Phys. Lett.* 113 (1985) 501.
- [17] Th. Klaus, A.H. Saleck, S.P. Belov, G. Winnewisser, Y. Hirahara, H. Hayashi, E. Kagi, K. Kawaguchi, *J. Mol. Spectrosc.* 180 (1996) 197.
- [18] W.S. Benedict, N. Gailar, E.K. Plyler, *J. Chem. Phys.* 24 (1956) 1139–1156.
- [19] K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. 4* (Von Nostrand–Reinhold, New York, 1979).
- [20] Y. Morino, C. Matsumura, *Bull. Chem. Soc. Jpn* 40 (1967) 1095.
- [21] K. Yamada, *J. Mol. Spectrosc.* 79 (1980) 323.
- [22] K. Yamada, T. Nakagawa, K. Kuchitsu, Y. Morino, *J. Mol. Spectrosc.* 38 (1971) 70.
- [23] C. Hirose, *Bull. Chem. Soc. Jpn* 47 (1974) 1311.
- [24] F.J. Lovas, E. Tiemann, *J. Phys. Chem. Ref. Data* 3 (1974) 609.
- [25] A.H. Saleck, K.M.T. Yamada, G. Winnewisser, *Mol. Phys.* 72 (1991) 1135.
- [26] G. Cazzoli, C. Degli Esposti, P.G. Favero, G. Severi, *Nuovo Cimento* 62B (1981) 243.
- [27] P. Pykkö, *Z. Naturforsch.* 47a (1992) 189.