Non-empirical Calculation of Quadrupole Coupling Constants in the Hydrogen Bonded System $D(OH_2)_2^+$

J. Koller and A. Ažman

Chemical Institute Boris Kidrič, University of Ljubljana,
Ljubljana, Yugoslavia

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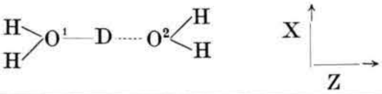
The electric field gradient at the hydrogen bonded deuteron in $D(OH_2)_2^+$ is calculated. The results do not indicate relations between the quadrupole coupling constants and the OD or OO interatomic distances.

A large number of experimental deuteron quadrupole coupling constants (DQCC) of hydrogen bonded systems has been accumulated. There have been many succesfull attempts to correlate the magnitude of the DQCC with the interatomic distances involved in the bond[1]. Particularly important is the attempt to correlate the quadrupole coupling constants with $R(OO)$ or $r(OD)$: $DQCC \sim 1/R$ or $1/r$. There seems to be still some controversion from the theoretical point of view. Olympia and Fung's[2] calculation supports the above mentioned relations, but the system studied by them (linear three atomic) is not very realistic. The purpose of this communication is to report results on the deuteron and oxygen quadrupole coupling constant in the $D(OH_2)_2^+$ ion. The calculations have been performed for two O–O distances: $R = 2.7$ Å and $R = 1.6$ Å. We have used the Pople et al.[3] STO – 3G basis set, and the electric field gradient was calculated with the Polyatom program[4]. For $R = 2.7$ Å the equilibrium distance of the proton is $r(OH) = 1.1238$ Å. The po-

Table 1. Electric field gradients q (in atomic units) at the hydrogen bonded deuteron and at the oxygens. $q_{D\vert}$, $q_{D\vert\vert}$, $q_{D\vert\vert}$ ($q_{O\vert}^{1}$; $q_{O\vert\vert}^{1}$; $q_{O\vert\vert\vert}^{1}$; $q_{O\vert}^{2}$; $q_{O\vert\vert}^{2}$; $q_{O\vert\vert\vert}^{2}$) are the principal components of q at deuteron (oxygen 1; oxygen 2). α (in degrees) is the angle between the x axis and $q_{D\vert}$. The numbers in the first and second rows are nuclear and electronic contributions to q (third rows), respectively. The geometry of $D(OH_2)_2^+$ ion: OH bond length 1 Å; H_2O bond angle 110°; angle between OH bond and the hydrogen bridge axis 115°.



				R (00) = 2.7 Å					
$r(OD) = 1.0000$									
α	$q_{D\vert}$	$q_{D\vert\vert}$	$q_{D\vert\vert\vert}$	$q_{O\vert}^{1}$	$q_{O\vert\vert}^{1}$	$q_{O\vert\vert\vert}^{1}$	$q_{O\vert}^{2}$	$q_{O\vert\vert}^{2}$	$q_{O\vert\vert\vert}^{2}$
5.5	1.4752	1.4576	−2.9329						
	−1.3124	−1.3466	2.6590						
	0.1629	0.1110	−0.2739	1.8441	−0.6613	−1.1828	2.2375	−0.0909	−2.1466
$r(OD) = 1.1238$									
α	$q_{D\vert}$	$q_{D\vert\vert}$	$q_{D\vert\vert\vert}$	$q_{O\vert}^{1}$	$q_{O\vert\vert}^{1}$	$q_{O\vert\vert\vert}^{1}$	$q_{O\vert}^{2}$	$q_{O\vert\vert}^{2}$	$q_{O\vert\vert\vert}^{2}$
22.3	0.7438	1.1735	−1.9172						
	−0.6919	−1.1701	1.8620						
	0.0519	0.0034	−0.0553	1.8016	−0.4649	−1.3368	2.0818	−0.0687	−2.0131
$r(OD) = 1.2500$									
α	$q_{D\vert}$	$q_{D\vert\vert}$	$q_{O\vert\vert\vert}$	$q_{O\vert}^{1}$	$q_{O\vert\vert}^{1}$	$q_{O\vert\vert\vert}^{1}$	$q_{O\vert}^{2}$	$q_{O\vert\vert}^{2}$	$q_{D\vert\vert\vert}^{2}$
66.6	−1.5514	1.0337	0.5177						
	1.6185	−1.0729	−0.5457						
	0.0671	−0.0391	−0.0280	1.7945	−0.2715	−1.5230	1.9244	−0.0869	−1.8375
$r(OD) = 1.3500$									
α	$q_{D\vert}$	$q_{D\vert\vert}$	$q_{D\vert\vert\vert}$	$q_{O\vert}^{1}$	$q_{O\vert\vert}^{1}$	$q_{O\vert\vert\vert}^{1}$	$q_{O\vert}^{2}$	$q_{O\vert\vert}^{2}$	$q_{O\vert\vert\vert}^{2}$
72.1	−1.7076	1.0021	0.7046						
	1.7885	−1.0498	−0.7387						
	0.0819	−0.0477	−0.0341	1.8354	−0.1540	−1.6814	1.8354	−0.1540	1.6814
				R (00) = 1.6 Å					
$r(OD) = 1.3000$									
α	$q_{D\vert}$	$q_{D\vert\vert}$	$q_{D\vert\vert\vert}$	$q_{O\vert}^{1}$	$q_{O\vert\vert}^{1}$	$q_{O\vert\vert\vert}^{1}$	$q_{O\vert}^{2}$	$q_{O\vert\vert}^{2}$	$q_{O\vert\vert\vert}^{2}$
1	11.0631	10.9579	−22.0210						
	−4.9941	−5.3981	10.3922						
	6.0689	5.5599	−11.6288	2.2573	−0.8997	−1.3576	2.2573	−0.8997	−1.3576

tential curve for the proton between the O atoms has two minima with an energy barrier between them of 2 kcal/mol. The values of electric field gradients at various $r(\mathrm{OD})$ distances are listed in Table 1. One conclusion from this type of calculation is immediate. The asymmetry influenced by the H atoms attached to the O atoms is very large and there is no correlation of the type experimentaly and theoreticaly reported. This effect is very pronounced at $R(\mathrm{OO}) = 1.6$ Å where the nuclear part of the field gradient greatly overbalances the electronic part. To correlate the DQCC's with the interatomic distances $r(\mathrm{OD})$ one has to be carefull. Such a relation exists only for systems with not to much asymmetry around the simple triatomic $\mathrm{O-D\ldots O}$ fragment. Another result of interest is the field gradient at the O atoms. The quadrupole moment of D is $Q_{\mathrm{D}} = 2.796 \cdot 10^{-27}\,\mathrm{cm}^2$ and that of O^{17} $D_{\mathrm{O}} = -26.5 \cdot 10^{-27}\,\mathrm{cm}^2$. From Table 1 it can be seen that the quadrupole coupling constant (electric field gradient multiplied by quadrupole moment) of O is more sensitive to distance changes than the DQCC. This conclusion seem's to be of interest in regard of the recently measured [5] value of the oxygen QCC in hydrogen bonded systems.

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