

Deuteron Quadrupole Coupling in D₂O

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Citation: *The Journal of Chemical Physics* **44**, 422 (1966); doi: 10.1063/1.1726491

View online: <https://doi.org/10.1063/1.1726491>

View Table of Contents: <http://aip.scitation.org/toc/jcp/44/1>

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In some experiments krypton has been used as a photosensitizer. Product yields for the direct and the sensitized decomposition of ethane are shown in Table II. Apart from differences in the direct photolyses⁸ it may be taken from the Tables I and II that added krypton and xenon as sensitizers exert different effects as well.

Also, relative product yields reported here differ from those obtained in radiolysis where, e.g., ethylene and acetylene do not appear in the final product. In radiolysis, charge transfer from rare-gas ions to hydrocarbon molecules was postulated to occur.⁹ Ions, however, are practically excluded in the photosensitized decomposition of our systems. Reaction seems to occur in these cases predominantly as a consequence of quenching of excited rare-gas atoms by hydrocarbon molecules.

* Detailed information will be given in a forthcoming publication.

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Deuteron Quadrupole Coupling in D₂O

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(Received 27 August 1965)

QUADRUPOLE splitting of the deuteron magnetic resonance was recently measured in single crystals of D₂O.¹ The coupling constants in the solid were found to be about 30% less than those for the free molecule. The decrease was ascribed to electronic structural changes due to hydrogen-bond formation.

The purpose of this work was to compute those coupling constants with the wavefunctions obtained in a previous paper,² to see if they could account for those structural changes.

The first step was to calculate the field gradient at the deuteron in the free molecule, with the same approximations to be used later in the solid. The most important of these² was the tetrahedral hybridization of the oxygen 2s and 2p orbitals. The following charge distributions were considered: (a) a point charge +6 in the oxygen nucleus, which includes the inner-shell electrons, (b) a pair of electrons in a molecular orbital

TABLE I. Contributions to field-gradient components in the free molecule (a.u.).

	q_{zz}	q_{yy}	q_{xy}
O ₁ nucleus	+2.0227	-1.0114	0
OD electrons	-0.6500	+0.3250	0
Other electrons	-0.7856	+0.4180	+0.0625
Totals	+0.5871	-0.2684	+0.0625

along the OD bond under consideration, (c) one electron in the tetrahedral hybrid along the other OD bond (the influence of the other deuteron and corresponding electron is neglected), (d) two pairs of electrons in the remaining tetrahedral hybrids. The experimental distance OD = d = 0.96 Å was used.

The field-gradient tensor was computed in a coordinate system with the z axis along the considered OD bond and the x axis normal to the plane of the molecule. In such a system only three independent nonvanishing components must be calculated: q_{zz} , q_{yy} , and q_{xy} . The matrix elements were evaluated by the methods given in the appendix to Ref. 3. Table I shows the obtained results.

Diagonalization of this tensor leaves the x axis invariant and rotates the y and z axes by 4°, while the experimental value⁴ for this rotation is 1°7'±47'. In the principal-axes coordinate system $q_{zz}' = 0.592$ a.u. and the asymmetry parameter $\eta = 0.08$. A coupling constant (eqQ/h) of 385 kc/sec is obtained if one uses for Q the calculated⁵ 2.82×10^{-27} cm². The experimental value⁴ of this coupling constant is 312 kc/sec and an upper value of 0.12 is quoted for η . We believe the results to be in satisfactory agreement with experiment, and to encourage a similar calculation in the solid, where tetrahedral hybridization is certainly a better approximation.

However, it is worth noting that Bersohn⁶ obtained a coupling constant almost twice the experimental value in a similar calculation. This discrepancy could be due to numerical errors found both in his paper and in the Ellison and Shull wavefunctions used there. It is also possible that a refinement in our calculation may not improve the final results.

If we now consider a pair of hydrogen-bonded molecules, O₁-D···O₂, the charge distribution will consist of two positive point charges, nine electrons in tetra-

TABLE II. Contributions to the coupling constant in the hydrogen bonded case in kilocycles per second. O₁O₂ = 2.76 Å.

d (Å)	0.75	0.96	1.01	1.17
O ₁ nucleus	+2773	+1315	+1137	+723
O ₂ nucleus and electrons	-1263	-971	-902	-692
Totals	+1510	+344	+235	+31

hedral hybrids and the four electrons involved in the bond in two molecular orbitals.² The same coordinate system of the previous case was used, with oxygen O₂ on the *z* axis at a distance of 2.76 Å from O₁. There are three possible positions for the deuterons of the second molecule, that must be averaged in the crystal, and therefore will not contribute to the asymmetry. This is consistent with the experimental finding of $\eta=0.1$ in the solid, approximately the same value as in the vapor. For this reason we only thought of interest to compute q_{zz} in the hydrogen-bonded case. However, this nonzero value of η excludes frequent deuteron tunneling and confirms our previous conclusion² that the potential barrier for deuteron transfer is very asymmetric.

A few three-center integrals had to be computed in this case, and they were approximated by Mulliken's method.

The obtained value of q_{zz} for $d=0.96$ Å was only 10% lower than that given in Table I, the difference being due to the neighbor molecule and to electron delocalization. Therefore, for fixed d , q_{zz} does not depend strongly on the O₁O₂ distance. It is, however, very sensitive to changes in d , as is shown in Table II. The coupling constant is divided there in two main contributions: one due to nucleus O₁ that is proportional to d^{-3} , and another due to the electrons and the other oxygen nucleus that is linearly dependent on d . Interpolation in Table II gives the experimental¹ coupling constant of 215 kc/sec for $d=1.015$ Å, while in ice $d=1.01$ Å. This close agreement with experiment proves that SCF-MO-LCAO orbitals are useful for calculating field gradients and also suggests that hydrogen bond formation is more important because it produces an elongation of the OD bond than because of electronic structural changes, although both effects are additive.

It is well known that stronger hydrogen bonds have longer OD distances. Therefore, our results predict smaller coupling constants for stronger bonds. This effect was observed by Chiba⁷ for different O₁-D \cdots O₂ bonds and in fact our computed values of Table II can be plotted almost exactly over the curves in Fig. 6 of his paper.

Finally, it is also interesting that the quadrupole spin-lattice relaxation time for the nuclear magnetic resonance of deuterons in liquid D₂O⁸ could also be explained with a reduced coupling constant due to hydrogen bonding.

The author thanks Dr. Norah V. Cohan for helpful correspondence.

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Second and Fourth Moments of the Polyethylene Chain

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(Received 30 August 1965)

TWO years ago the present author developed a method for calculating even moments, in particular the fourth moment $\langle r^4 \rangle$, of the end-to-end distance of chain molecules, by taking into account the interdependence of internal rotations about neighboring skeletal bonds.¹ This is an extension of methods for calculating the mean-square end-to-end distance, i.e., the second moment $\langle r^2 \rangle$, developed previously by several authors.²⁻⁶ The expressions derived for the polyethylene chain are

$$\langle r^2 \rangle / b^2 = \zeta_1 n + \zeta_0, \quad (1)$$

$$\langle r^4 \rangle / b^4 = \eta_2 n^2 + \eta_1 n + \eta_0, \quad (2)$$

where b is the length of the C-C bond, n is the number of C-C bonds, and ζ 's and η 's are constants which depend on the bond angle and hindrance to internal rotations, but are independent of n . Both the expressions are subject to a common approximation that terms of the orders of magnitude of μ_1^n , μ_2^n , \cdots , are neglected as small compared to unity, where all μ 's are quantities smaller than unity. Therefore these expressions are valid for large n only.

Very recently Flory and Jernigan presented exact methods for calculating these and related quantities.⁷ Their treatments are not restricted to the end-to-end vector, but are applicable to any vector determined unambiguously by rotational angles about skeletal bonds. These authors cast doubt upon the stated approximation and hence the entire treatment of our previous work.¹

We are thus in a position to compare numerical results obtained by both the methods and to assess the validity of the stated approximation. Numerical calculations are made for the same model for the polyethylene chain, with the same values of geometrical and statistical-mechanical parameters, as used by Flory and Jernigan, i.e., the GG' -eliminated, three-states [*trans* ($\theta^{(T)}=0^\circ$), *gauche* ($\theta^{(G)}=120^\circ$), and another *gauche* ($\theta^{(G')}=-120^\circ$)] rotational isomeric model,^{8,9} with the bond angle $\pi-\omega=112^\circ$ and with the statistical weight $\sigma=0.56$ of the *gauche* conformation relative to the *trans*. For these values of the parameters, we obtain $(\langle r^2 \rangle / nb^2)_{n \rightarrow \infty} = \zeta_1 = 7.3366$ while Flory and Jernigan reported a very little higher value 7.34, based on the same expression, i.e., ζ_1 . These authors appear to have used a somewhat lower value of σ than 0.56 as indicated in their paper. Values of other quantities for the same values of the parameters are: $\zeta_0 = -40.625$, $\eta_2 = 89.709$,