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Theoretical and experimental estimates of the acetylenic deuteron quadrupole coupling constant

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The acetylenic deuteron quadrupole coupling constant in 1-D-3,3-dimethyl-1-butyne was determined in neat liquid and in 20 mol % solution in an inert solvent (C_6H_{12}), by combining NMR relaxation data with Raman line shape analysis of the totally symmetric A_1 mode at 1983 cm^{-1} . The value in the inert solvent was found to be $233 \pm 4\text{ Hz}$, which is significantly higher than previously found value for acetylenic deuteron in acetylene and nonyne, but is in excellent agreement with *ab initio* calculation which was performed using "double zeta plus polarization" basis functions on smaller model molecules.

I. INTRODUCTION

The conversion of ^2H spin lattice relaxation rates of organic molecules to molecular motion parameters requires the knowledge of the precise quadrupole coupling constant (Q_D) of deuteron in the C-D bond in various deuterated molecules.¹⁻³ The most commonly used method for measuring Q_D has been the one which is based on NMR spectral information obtained from deuterated molecules which are oriented in nematic solvents.⁴ This method, when used with appropriate mathematical refinements involving vibrational averaging of internuclear distances and MO calculations for the evaluation of the asymmetry parameter in the case of a deviation from cylindrical symmetry of the C-D bond, is capable of arriving at accurate values of Q_D . However, it has been shown in many instances involving polar molecules that the measured Q_D varies significantly with the type of nematic solvent used.⁵⁻⁷ As suggested by Ragle *et al.*⁸ who determined the Q_D of CDCl_3 in solid complexes with mesitylene, acetone, and ether and found the lowering of Q_D from 166.9 kHz for neat CDCl_3 to 162.0, 151.4, and 149.1 kHz, respectively, the field gradient in the neighborhood of the deuteron may be significantly affected by the polarization of C-D bond due to the medium or solvent effects. That there is indeed a solvent effect on Q_D of the CDCl_3 was further substantiated by the result of the determination of a 20% molar solution of CDCl_3 in cyclohexane by using the technique which utilizes the Raman line shape studies in conjunction with ^2H NMR relaxation.⁹ The Q_D value in this inert solvent was found to be $186 \pm 4\text{ kHz}$, which is significantly higher than any previously reported value in any medium, the values found in three types of nematic solvents ranging from 157.8 to 170.5 kHz.⁵ It is thus becoming increasingly apparent that for the meaningful interpretation of deuteron relaxation studies in solutions, they must be restricted to inert solvents or media in which the solvent effect is minimized and that estimates of Q_D should be made whenever possible by methods which do not involve media in which significant solvent interactions are probable. Another promising way of estimating typical values of Q_D associated with different types of bonding is to perform *ab initio* calculations on small molecules and subsequently use these values

in conjunction with larger molecules of interest. The object of this paper is to demonstrate the feasibility of such an approach by estimating the Q_D value of acetylenic deuteron both theoretically and experimentally.

II. THEORETICAL DEUTERON QUADRUPOLE COUPLING CONSTANTS

Snyder¹⁰ computed the Q_D for a variety of small molecules from *ab initio* wave functions in a "double zeta" basis. He stated that the Q_D values obtained theoretically are about 20% greater than the experimental values which were then known, and that through the use of polarization functions which he applied to some of these molecules the calculated values approach those determined experimentally. In the case of acetylenic deuteron, however, the theoretical value in the C_2D_2 molecule reported by Snyder without the use of polarization is about 25% higher than the experimentally determined values in liquid crystals for acetylene^{11,12} and nonyne.¹³ In this light, we have performed *ab initio* calculations on acetylene and methylacetylene using double zeta plus polarization basis functions as well as double zeta without polarization basis functions for comparison. This was done in anticipation of obtaining an experimental estimate in a neutral solvent of the acetylenic Q_D . Since such an experimental value of Q_D is now available for chloroform in inert solvent, we have also obtained the theoretical estimate of the latter.

These calculations were performed using the "GAMESS" program. The electric field gradients were calculated using the "POLYATOM" (version II) system of programs. The Q_D is converted from the electric field gradients using

$$Q_D (\text{kHz}) = \text{efg (a.u.)} \times 672.0 \text{ kHz/a.u.} \quad (1)$$

based on the quadrupole moment, $Q = 2.860 \times 10^{-3}\text{ b}$, of Reid and Vaida.¹⁴ Two different sets of polarization functions were used. Set No. 1 contains one *p* polarization function at the proton ($\alpha = 1.08$) and one *d* polarization at the carbon ($\alpha = 0.74$), which are the same as those used by Snyder for methyl fluoride.¹⁵ Set No. 2 used one *p* polarization function and one *d* polarization function at the proton ($\alpha_p = 0.88$, $\alpha_d = 1.8$), which are the same as those used by

Snyder for hydrogen molecule,¹⁶ and two *d* polarization functions at the carbon ($\alpha_{d1} = 1.5, \alpha_{d2} = 0.5$), which were used in formaldehyde and carbon monoxide by Neumann and Moskowitz.¹⁷ Table I shows the Q_D results for the acetylenic deuteron in acetylene and methylacetylene.

It is seen from Table I that inclusion of polarization functions leads to substantial lowering of the calculated Q_D . In discussing the effects of polarization functions, Snyder¹⁰ stated that the addition of *p* and *d* polarization functions to the deuteron results in better agreement between experimental and theoretical values than the addition of *p* polarization functions alone. Thus the use of set No. 2 should result in better values. However, irrespective of which set is used, the effect of substitution of hydrogen in acetylene by methyl groups results in only a slight increase, on the order of one percent.

Ab initio calculations were also performed on chloroform using the double zeta basis functions for the carbon and proton and the set basis functions for the chlorine from Veillard.¹⁹ The addition of either set of the polarization functions above to chloroform resulted in nonconvergence. The addition of a *p* polarization function to the proton ($\alpha = 0.88$) (set No. 3) did show convergence and the results are shown in Table II.

In this case the inclusion of polarization also leads to lowering of Q_D value but to a substantially lesser extent than in the acetylenic case. The value of 187 kHz is in remarkable agreement with the experimental value of 186 ± 4 kHz obtained in an inert solvent.

It was shown by Gordon²¹ that for molecules with a quadrupolar nucleus lying on a threefold or higher axis of symmetry the information about molecular reorientation dynamics furnished by Raman polarized and depolarized bands and nuclear quadrupolar relaxation can be related in the liquid and gaseous states. For any deuteron satisfying the above mentioned condition, and in the extreme narrowing limit (valid for small molecules in solution), the spin relaxation time (T_1) is related to the angular correlation time for the reorientation of the principal axis on which it is located ($\tau_{\theta 1}$) by the equation¹

$$\frac{1}{T_1} = \frac{3\pi^2}{2} Q_D^2 \tau_{\theta 1} \quad (2)$$

$\tau_{\theta 1}$ can be determined from the relative intensity distribution of the depolarized component of a totally symmetric Raman rotation vibration band. Hence, by measuring the deuteron spin relaxation time (T_1) at the same temperature and concentration in any solvent for a molecule satisfying

TABLE II. Theoretical acetylenic deuteron coupling constants in deuteriochloroform.

Molecule	Quadrupole coupling constant (kHz)	
	DZ	DZ + set No. 3
CDCl ₃ ^a	193	187

^a Same bond lengths as in Ref. 20.

the abovementioned conditions, the Q_D can be determined from Eq. (2).

This relationship between $\tau_{\theta 1}$ and T_1 was experimentally exploited by Wright and Rogers²² to determine the Q_D of CDCl₃ and CDBr₃ in neat liquids. In their work they assumed Lorentzian line shapes which implies exponential correlation functions and calculated $\tau_{\theta 1}$ from the relation

$$\tau_{\theta 1} = 1/2\pi c\omega_{\text{reor}}, \quad (3)$$

where c is the speed of light and ω_{reor} is the difference between the half-widths at half-heights of the polarized and depolarized spectra.

The values of Q_D reported by these authors involved considerable uncertainties. We found in our work⁹ that it was possible to reduce considerably the uncertainties by increasing the number of scans for each determination, thus statistically lowering the standard deviation. Furthermore, we found that the Fourier inversion method leads to better precision and most likely better accuracy. This method does not assume Lorentzian line shape or any kind of functionality of the mathematical form of the reorientational correlation function, $\langle R \rangle$. Theory leads to the following formulation of $\langle R \rangle$:

$$\langle R \rangle = F^{-1} I_{\text{aniso}} / F^{-1} I_{\text{iso}}, \quad (4)$$

where I_{aniso} and I_{iso} are the anisotropic and isotropic components of which the polarized Raman band is a convolution, and F^{-1} indicates an inverse Fourier transform. Equation (4) makes no assumption as to the line shape or functionality of the curve thus generated, and numerical integration of the area under the curve (zeroth moment) results in a value yielding $\tau_{\theta 1}$. The practical problems associated with this procedure and how they can be overcome are described in detail in Ref. 9.

We have chosen (CH₃)₃CC≡CD (1-D-3,3-dimethyl-1-butyne) as a compound for the experimental estimation of acetylenic Q_D because it satisfies the symmetry condition mentioned above, with the reasonable assumption that the methyl groups are undergoing free rotation. The undeuterated molecule shows a strong absorption peak in Raman²³ which corresponds to the totally symmetric A_1 mode at 2109 cm⁻¹. Deuteration moves the absorption peak down to 1983 cm⁻¹ and into a clear portion of the entire spectrum. The peak is perfectly symmetric and lends itself to the facile analysis of the line shape.

TABLE I. Theoretical acetylenic deuteron coupling constants.

Molecule	Quadrupole coupling constants (kHz)		
	DZ	DZ + set No. 1	DZ + set No. 2
CH≡CD ^a	259	245	231
CH ₃ -C≡CD ^b	261	247	234

^a Same bond lengths as in Ref. 10.

^b Same bond lengths as in Ref. 18.

III. EXPERIMENTAL

A. Preparation of $(\text{CH}_3)_3\text{CC}\equiv\text{CD}$

The starting compound 3,3-dimethyl-1-butyne was commercially purchased from Aldrich. Preparation of deuterated compound was carried out under liquid nitrogen temperature using ammonia, sodium, and D_2O .^{24,25} The product was fractionally distilled, and its purity was found to be greater than 99% using gas chromatography.

B. NMR

Solutions of neat $(\text{CH}_3)_3\text{CC}\equiv\text{CD}$ and $(\text{CH}_3)_3\text{CC}\equiv\text{CD}/\text{C}_6\text{H}_{12}$ (20 mol %) were degassed and sealed in flat bottom cylindrical tubes for T_1 measurements. At the beginning and the end of each T_1 measurement the temperature at the coil of the magnet was checked in order to detect any possible temperature fluctuation; none was observed. T_1 measurements were made (the 180- τ -90 inversion recovery pulse sequence was employed) on a JEOL FX 90Q NMR spectrometer operating at 13.69 MHz in FT mode. For each sample using 11 different τ values with 20 scans each, 18–20 separate measurements were made. Through this procedure the statistical errors of obtained values were reduced to within an acceptable range.

C. Raman

Samples made from the same stock solutions as those used in the NMR relaxation measurements were sealed in capillary tubes and transversely irradiated with the blue line (4880 Å) of a Spectraphysics argon ion laser (model 165).

The scattered light was collected and focused onto the entrance slit of SPEX 1403 double monochromator equipped with holographic grating blazed at 1800 g/mm. The scattered radiation at the entrance slit was analyzed for its polarization characteristic and then scrambled prior to its entry into the monochromator. The monochromator is equipped with a chilled photomultiplier tube (RCA3103402) operating in the photon counting mode. The tube is coupled to a discrimination amplifier whose output is fed to a digital photometer (SPEXDPC-2). A data log computer system receives the real time data from the digital photometer, and thus each individual spectrum is stored. The system is capable of a multiscanning process which improves signal to noise ratio when at least five scans are collected for the depolarized band. All spectra were stored on floppy disks. A temperature control procedure was carried out, using a thermocouple, to maintain $25 \pm 0.5^\circ\text{C}$ for all samples. A focused laser could be source of local heating so the thermocouple was placed in the sample cell as close to the focal cylinder as possible. The tube was irradiated at the power identical to that of the actual experiment for 30 minutes. No temperature change was observed in the sample.

As a further evaluation of possible temperature effects, the anisotropic correlation function, which is known to be temperature dependent,^{22,26} was generated for each sample of interest at different laser power settings ranging from 250 to 900 mW. The area under these correlation functions was calculated and found to vary by less than 2%. All of the spectra were obtained at a spectral slit width of 1.64 cm^{-1} . A

TABLE III. Reorientational times ($\tau_{\theta 1}$), deuteron relaxation times (T_1), and quadrupole coupling constants of 1-D-3,3-dimethyl-1-butyne at 26°C .

State	$\tau_{\theta 1}$ (ps)	T_1 (s)	Q_D (kHz)
Neat	1.45 ± 0.03	0.94 ± 0.01	223 ± 3
20 mol % in cyclohexane	1.70 ± 0.04	0.73 ± 0.01	233 ± 4

correctly chosen slit width should give no instrumental error contribution to the band^{26,27} width and therefore this possible error factor is eliminated. The number of scans for the polarized band was 5 and for the depolarized band 15 and 20 for neat and 20 mol % samples, respectively.

IV. RESULTS AND DISCUSSION

Listed in Table III are the results of the reorientational times and deuteron relaxation times of neat 1-D-3,3-dimethyl-1-butyne and of its 20 mol % solution in cyclohexane. Each T_1 value is an average of 18 separate determinations and each $\tau_{\theta 1}$ value is an average of no less than 19 separate determinations using the data processing procedure previously described.⁹

The Q_D values calculated from the τ_{θ} and T_1 data are also given in Table III. Analogous to the results for chloroform, the Q_D value for the acetylenic deuteron determined in an inert solvent is larger than that obtained for the neat liquid. The value obtained in cyclohexane is also larger (10%–15%) than those found for acetylene and nonyne in liquid crystal solvents. Comparison of the Q_D values for acetylene¹² and nonyne¹³ obtained in the same liquid crystal solvent indicated that hydrocarbon substituents on acetylene did not greatly affect the electric field gradients at the deuteron. The results of the theoretical calculations on acetylene and propyne should be representative of the acetylenic Q_D value in all unsubstituted acetylenic hydrocarbons in general and in 3-3-dimethyl-1-butyne in particular. The experimental value of $233 \pm 4\text{ kHz}$ obtained for 3,3-dimethyl-1-butyne is in excellent agreement with the theoretical values obtained with the set No. 2 basis functions. Similarly, as was stated earlier, there is also excellent agreement between the theoretical Q_D value for chloroform and the experimental value determined in an inert solvent. Thus, it appears that as the theoretical calculations become more refined and the experimental determination of Q_D becomes more devoid of solvent effects, the theoretical and experimental estimates of Q_D converge.

¹A. Abragam, *The Principles of Nuclear Magnetism* (Oxford, New York, 1961).

²D. E. Woessner, *J. Chem. Phys.* **37**, 647 (1962).

³W. T. Huntress, Jr., *J. Chem. Phys.* **48**, 3524 (1968).

⁴J. M. Emsley and J. C. Lindon, *NMR Spectroscopy Using Liquid Crystal Solvents* (Pergamon, New York, 1975).

⁵G. C. Lickfield, J. F. McKenna, A. L. Beyerlein, and G. B. Savitsky, *J. Magn. Reson.* **51**, 301 (1983).

- ⁶G. C. Lickfield, S. E. Emery, R. V. Gregory, T. C. Chen, A. L. Beyerlein, and G. B. Savitsky, *J. Magn. Reson.* **54**, 305 (1983).
- ⁷J. Jokisaari, P. Diehl, J. Amrein, and E. Ijas, *J. Magn. Reson.* **52**, 193 (1983).
- ⁸J. L. Ragle, G. Minott, and M. Mokarram, *J. Chem. Phys.* **60**, 3184 (1974).
- ⁹R. V. Gregory, M. R. Asdjodi, H. G. Spencer, A. L. Beyerlein, and G. B. Savitsky, *J. Chem. Phys.* **81**, 4790 (1984).
- ¹⁰L. C. Snyder, *J. Chem. Phys.* **68**, 291 (1978).
- ¹¹F. S. Millet and B. P. Dailey, *J. Chem. Phys.* **56**, 3249 (1972).
- ¹²S. E. Emery, G. C. Lickfield, A. L. Beyerlein, and G. B. Savitsky, *J. Magn. Reson.* **56**, 323 (1984).
- ¹³J. F. McKenna, K. Seidman, A. L. Beyerlein, and G. B. Savitsky, *J. Magn. Reson.* **29**, 181 (1980).
- ¹⁴R. V. Reid, Jr. and M. L. Vaida, *Phys. Rev. A* **7**, 1841 (1973).
- ¹⁵L. C. Snyder, *J. Chem. Phys.* **68**, 340 (1978).
- ¹⁶L. C. Snyder, *J. Chem. Phys.* **61**, 5032 (1974).
- ¹⁷D. B. Neumann and J. W. Moskowitz, *J. Chem. Phys.* **50**, 2216 (1969).
- ¹⁸C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).
- ¹⁹A. Veillard, *Theoret. Chim. Acta (Berlin)* **12**, 405 (1968).
- ²⁰M. Jen and D. R. Lide, Jr., *J. Chem. Phys.* **36**, 2525 (1962).
- ²¹R. G. Gordon, *J. Chem. Phys.* **42**, 3658 (1965).
- ²²A. Wright and M. T. Rogers, *J. Chem. Phys.* **63**, 909 (1975).
- ²³F. F. Cleveland and M. J. Murray, *Research Publications, Illinois Institute of Technology, Molecular Spectra II*, **6** (No. 1), 34 (1948).
- ²⁴A. Murray III and D. L. Williams, *Organic Synthesis with Isotopes, Part II* (Interscience, New York, 1958), p. 1434.
- ²⁵B. S. Rabinovitch and F. Slooney, *J. Am. Chem. Soc.* **75**, 2652 (1953).
- ²⁶F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.* **56**, 404 (1972).
- ²⁷I. Laulicht and S. Meirman, *J. Chem. Phys.* **59**, 2521 (1973).