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Deuterium Isotope Effects on Molecular Dipole Moments by Microwave Spectroscopy*

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A special parallel-plate microwave spectrometer has been constructed and the effect of deuteration on the dipole moment in the ground vibrational state of seven different molecules has been measured. The molecules studied were: methylacetylene, propane, methyl fluoride, fluoroform, vinylidene fluoride, methylsilane, and methylgermane. With the exception of fluoroform, where an effect of 0.001 D was observed, the magnitude of the isotope effect was found to be of the order of 0.01 D. A simplified interpretation of the isotope effects leads to information about the signs of the dipole moments in these molecules.

INTRODUCTION

LECTRIC dipole moments are one of the more C commonly measured properties of molecules. Little is known, however, about their variation with vibrational and electronic state or their dependence on internuclear distance in polyatomic molecules. One way of obtaining information bearing on these questions is to study the effect of isotopic substitution on dipole moments. An early attempt at determining the effect of deuterium substitution was made by Bell and Coop,¹ using the conventional dielectric-constant technique. However, the observed effect was near the limits of accuracy obtainable in their measurement. Also, dielectric-constant measurement has the inherent disadvantage of being an average over the entire ensemble of states present in the sample and of being subject to effects from intermolecular interactions and impurities. On the other hand, measurements of the Stark effect on rotational energy levels can be made on molecules in known quantum states, essentially isolated from other molecules, and unaffected by any impurities present. Accurate Stark effect measurements can be made by either the molecular-beam method or by using gas-phase microwave spectroscopy. While capable of very great precision, the molecular-beam method is presently practical for a limited class of molecules and microwave spectroscopy is of more general applicability, especially for organic compounds.

Previous microwave studies using conventional spectrometers have indicated that an isotope effect as large as 0.01 D might be caused by deuterium substitution, but in only one investigation² was the observed effect definitely outside experimental error. In this paper we

report a study, utilizing a special microwave spectrometer, of the effect of deuterium substitution on the dipole moment of a number of simple organic molecules.

INSTRUMENTATION

With the exception of the sample cell and Stark fields, the microwave spectrometer employed was a conventional 100-kc/sec Stark modulation instrument using phase-sensitive detection. The absorption cell, which is described in detail elsewhere,³ is of parallel-plate configuration and will produce dipole-moment measurements precise to ± 0.001 D or better for moments in the range of 0.5 to 2.0 D.

The Stark shifts were produced using a large dc electric field with a small ac modulation field superimposed on it. The dc Stark voltages were measured using a precision voltage divider and either a Leeds & Northrup Type K-2 potentiometer or a Type 525 differential voltmeter made by the John Fluke Company. The ac modulation voltage was measured using a Tektronix Type Z differential comparator in a Tektronix Type 545 oscilloscope. The actual electricfield strength in the sample was determined from the applied voltage and an effective electrode spacing. This Stark electrode spacing was obtained from calibrating the absorption cell by observing the Stark effect of the carbonyl sulfide $1 \rightarrow 2$ transition and assuming the Marshall and Weber value⁴ of 0.7124 D for the OCS dipole moment. The voltage measurements and the cell calibration were in all cases sufficiently accurate so as not to limit the over-all accuracy of the dipolemoment measurements.

The limiting accuracy of the measurements given here was determined by the accuracy of the frequency measurements. Over the period of time during which these measurements were taken, two methods of frequency measurement were employed. Initially, the microwave absorptions were displayed on an oscilloscope along with frequency markers derived from a Micro-Now No. 101 frequency multiplier chain and a Collins 51J4 receiver. Later measurements used a

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¹ R. P. Bell and I. E. Coop, Trans. Faraday Soc. **34**, 1209 (1938). ² D. R. Lide, J. Chem. Phys. **33**, 1519 (1960).

⁸ J. S. Muenter, Ph.D. thesis, Stanford University, 1964; J. S. Muenter and V. W. Laurie (to be published). ⁴ S. A. Marshall and J. Weber, Phys. Rev. 105, 1502 (1957).

TABLE I. Dipole moments.

	Compound	Transi- tion ^a	Dipole moment µ ^b	$\Delta \mu^{c}$
I–a	CH₃C≡CH	$0 \rightarrow 1 \\ 1 \rightarrow 2$	0.7804 0.7809	•••
Ib	CH₃C≡CD	$\begin{array}{c} 0 \longrightarrow 1 \\ 1 \longrightarrow 2 \end{array}$	0.7689 0.7668	$-0.0115 \\ -0.0141$
I-c	CD₃C≡CH	1→2	0.7841	+0.0032
I-d	CD₃C≡CD	1→2	0.7722	-0.0087
II-a	CH ₃ CH ₂ CH ₃	$\begin{array}{c}1_{01} \longrightarrow 1_{10}\\2_{02} \longrightarrow 2_{11}\\3_{03} \longrightarrow 3_{12}\end{array}$	$0.0841 \\ 0.0849 \\ 0.0853$	•••
II–b	$CH_{3}CD_{2}CH_{3}$	$\begin{array}{c}1_{01} \rightarrow 1_{10}\\2_{02} \rightarrow 2_{11}\\3_{03} \rightarrow 3_{12}\end{array}$	$\begin{array}{c} 0.0941 \\ 0.0948 \\ 0.0955 \end{array}$	$^{+0.0100}_{-0.0099}_{+0.0102}$
II–c	$\mathrm{CD}_3\mathrm{CH}_2\mathrm{CD}_3$	$\begin{array}{c}2_{02} \rightarrow 2_{11}\\3_{03} \rightarrow 3_{12}\end{array}$	0.0749 0.0767	$-0.0100 \\ -0.0086$
III-a	CHF ₃	$\begin{array}{c} 0 \longrightarrow 1 \\ 1 \longrightarrow 2 \end{array}$	1.6461 1.6458	•••
III–b	CDF_3	$\begin{array}{c} 0 \longrightarrow 1 \\ 1 \longrightarrow 2 \end{array}$	1.6468 1.6471	$^{+0.0007}_{+0.0013}$
IV-a	CH₃F	0→1	1.8471	•••
IV-b	CD₃F	0→1	1.8583	+0.0112
V-a	H ₂ C=CF ₂	$\substack{1_{01} \rightarrow 2_{02} \\ 1_{11} \rightarrow 2_{12}}$	$1.3843 \\ 1.3862$	•••
V-b	$D_2C=CF_2$	$\begin{array}{c}1_{01} \longrightarrow 2_{02}\\1_{11} \longrightarrow 2_{12}\end{array}$	1.3905 1.3916	$^{+0.0062}_{+0.0054}$
VI-a	CH₃SiH₃	0→1	0.7351	•••
VI-b	CH ₃ SiD ₃	0→1	0.7236	-0.0115
VII-a	CH3 ⁷⁰ GeH3 CH3 ⁷⁴ GeH3	$1 \rightarrow 2$ $1 \rightarrow 2$	$\begin{array}{c} 0.6425\\ 0.6420\end{array}$	•••
VII-b	CH3 ⁷⁰ GeD3 CH3 ⁷⁴ GeD3	$1 \rightarrow 2$ $1 \rightarrow 2$	0.6295 0.6298	$-0.0130 \\ -0.0122$
VII-c	CD3 ⁷⁰ GeH3 CD3 ⁷⁴ GeH3	$1 \rightarrow 2$ $1 \rightarrow 2$	0.6548 0.6539	$^{+0.0123}_{+0.0119}$

^a All symmetric-top transitions are K=0.

^b All values are relative to the ${}^{16}\text{O}{}^{19}\text{C}{}^{82}\text{S}$ ground state taken to be 0.7124 D. • $\Delta \mu \equiv \mu_D - \mu_H$.

phase-stabilized klystron with recorder presentation and markers derived from a frequency counter. In both cases, the frequencies were compared to the time base of a Hewlett-Packard 524D frequency counter, whose stability is at least 10 times greater than the precision of the measurements. The frequency measuring precision was limited by the absorption linewidth. Increased frequency stability and recorder presentation allowed more consistent results and enabled the study of molecules with moments greater than 1 D to be studied without loss of absolute accuracy.

One of the molecules studied, propane, must be singled out because of its very small dipole moment. Because of this small moment, the absorptions are relatively weak and dipole-moment measurements were made at -78° C in a conventional X-band Stark cell.

The same methods of Stark voltage application and measurements were employed with this cell. While the relative accuracy of a dipole-moment measurement in the X-band cell was less, absolute accuracy was not lost in this case due to the small moment. The absolute value of the isotope shift for the dipole moment of propane was as well determined as the other isotope shifts studied. All measurements in the parallel-plate cell were carried out at room temperature.

COMPOUNDS STUDIED

Table I lists the isotopic species of the compounds studied. In most cases, the isotopic purity was in excess of 90%. However, since microwave spectroscopy observes a given species independently of the presence of other molecules, isotopic or chemical purity does not influence the dipole measurements.

The compounds I-a, II-a, and III-a were purchased from Matheson Company, Inc. and IV-a was purchased from Columbia Organics, Inc. I-c and III-b were prepared by Merck of Canada. I-b and I-d were prepared by the reaction of D₂O with the sodium salt of I-a and I-c, respectively. II-b and II-c were kindly prepared by D. Feigl in the laboratory of H. S. Mosher of Stanford University. IV-b was prepared⁵ by refluxing $CD_{3}I$ with an excess of KF in N, N-dimethylformamide. V-a was provided by the E. I. duPont de Nemours and Company, Inc. through the courtesy of R. J. Plunkett and V-b was provided by N. Craig, Oberlin College. Trichloromethylsilane, obtained from Peninsular Chemical Company, was reduced with LiAlH4 and LiAlD₄ to obtain VI-a and VI-b, respectively. VII-a and VII-b were produced by reacting CH₃I and CD₃I, respectively, with GeH₃Na. VII-b was obtained by reducing CH₃GeI₃ with LiAlD₄.

EXPERIMENTAL PROCEDURE

Since it is the change of moment on deuteration which is being investigated, the experimental conditions used for studying different species of the same molecule were kept as constant as possible. All the data given are for transitions exhibiting second-order Stark effect in molecules in their ground vibrational state. The measurements of the same transitions of different species of the same molecule were carried out during the same period of time with a cell calibration carried out both before and after the dipole-moment measurements. To provide an internal verification of the measurement, two or more transitions were measured for each species whenever possible.

To obtain a dipole moment from the observed data, the measured frequency shifts $\Delta \nu$ for a given Stark field *E* were assumed to be given by

$$\Delta \nu = A \mu^2 E^2 + B \mu^4 E^4 + \cdots$$
 (1)

 $^{{}^{\}mathfrak{s}}$ We should like to thank Professor J. I. Brauman for suggesting this preparation.



To obtain the desired accuracy, the fourth-power term had to be included since it contributed as much as 1% to $\Delta\nu$ at the largest fields used. However, higherpower terms were negligible. If Eq. (1) is divided by AE^2 , one obtains

$$\Delta \nu / A E^2 = \mu^2 + B \mu^4 E^2 / A. \tag{2}$$

This shows that plotting $\Delta \nu / AE^2$ vs E^2 will give a straight line with the zero-field intercept being μ^2 . Since only the slope of this plot depends on the fourthorder term, the dipole-moment correct to fourth order may be determined knowing only A, where A is the usual second-order Stark coefficient⁶ depending on the rotational constants and the transition involved. Since B is also calculable from the molecular rotational constants, an alternate procedure is to calculate both A and B and to solve Eq. (1) for μ^2 . However, this is a considerably more tedious process, especially for asymmetric tops, and since no loss of accuracy is involved, the method of plotting $\Delta \nu / AE^2$ versus E^2 was used. Figure 1 illustrates a typical plot. Here the dipole-moment measurement is for the $J=1 \rightarrow J=2$ transition, M=0, of $CH_3C\equiv CH$. It may be seen that the intercept is easily well determined enough to give a value for μ^2 accurate to ± 0.001 D.² It might also be noted that at the highest field used, the fourth-order contribution is 0.5% of $\Delta \nu / AE^2$.

For the calibration of the effective plate spacing, the frequencies of the two Stark components of the OCS transition at 24 352.92 Mc/sec were measured as a function of the voltage applied to the Stark electrodes. These data were plotted in the same manner as in the dipole-moment determinations, but the Stark electrode spacing was treated as a parameter which was adjusted to yield an OCS dipole moment⁴ of 0.7124 D.

Table I lists the dipole moments obtained. The accuracy of the measurements may be best judged by observing the values obtained for different transitions of the same species. The accuracy of a given determination is dependent on several factors such as the absorption intensity, frequency, and dipole-moment size. In all cases, with the exception of propane, a sufficient frequency displacement was measured that $\Delta \nu$ was determined to at least one part in a thousand or better and it is felt that an error of ± 0.002 D for all dipole moments reported here is a conservative estimate. In the case of CF₃H, where the isotope effect is only ~ 0.001 D, a very careful study was made and the error here was reduced sufficiently that the value reported is considered good to 0.001 D and the direction of the istope effect correct.

DISCUSSION

In considering the nature of the isotope effects, it is convenient to expand the dipole moment as

$$\mu = \mu_{e} + \sum_{i} (\partial \mu / \partial Q_{i})_{e} Q_{i}$$
$$+ \sum_{i} \sum_{j} [(\partial^{2} \mu / \partial Q_{i}) \partial Q_{j}]_{e} Q_{i} Q_{j} + \cdots, \quad (3)$$

where Q_i are the normal coordinates and μ_o and the derivatives are evaluated at the equilibrium configuration of the nuclei. The dipole moment of a given vibrational state can then be expressed in terms of the expectation values of the various normal-coordinate terms and the difference in dipole moments among isotopic species can be expressed in terms of isotope effects on the normal coordinates.⁷ Bell and Coop¹ have discussed the effect for a diatomic molecule and Halevi⁸ has extended their treatment to NH₃. They consider that as a first approximation the isotope effect is due to the change in the mean configuration of the molecule and neglect quadratic and higher powers of the normal coordinates. For a diatomic molecule this approximation gives

$$\mu_{\rm D} - \mu_{\rm H} = (\partial \mu / \partial r)_{s} (\langle r_{\rm D} \rangle - \langle r_{\rm H} \rangle), \qquad (4)$$

where $\langle r \rangle$ is the average internuclear distance for the isotopic species considered. For polyatomic molecules a more complicated expression will generally be required, but in the case of deuterium substitution in a CH bond in molecules such as CH₃C=CH it might be

⁶S. Golden and E. B. Wilson, J. Chem. Phys. 16, 669 (1948).

⁷ There are also other effects such as the breakdown of the Born-Oppenheimer approximation, but except possibly for CF_3H these are expected to be an order of magnitude smaller than those reported here; cf. S. M. Blinder, J. Chem. Phys. **32**, 105, 582 (1960); **35**, 974 (1964).

⁸ E. A. Halev, Trans. Faraday Soc. 54, 1441 (1958).

expected that the carbon-hydrogen stretching mode makes a major contribution to the dipole-moment change. Thus, in comparing the dipole moment of $CH_3C \equiv CH$ and $CH_3C \equiv CD$, in the simplest approximation Eq. (4) might be used. It has been shown⁹ that the average length of CH bonds is consistently 0.003 to 0.004 Å longer than for CD bonds in the ground vibrational state. Using $\langle r_{\rm H} \rangle - \langle r_{\rm D} \rangle = 0.003 - 0.004$ Å and the dipole-moment change $\mu_{\rm H} - \mu_{\rm D} = 0.012$ D, given in Table I, Eq. (4) gives $(\partial \mu / \partial r)_e = 4-3$ D/Å. This is a value considerably larger than what might be expected,¹⁰ indicating that Eq. (4) is probably an insufficient approximation. A similar conclusion is reached by considering the other isotope effects reported here. However, it is probably true that it is vibrations involving motion of the hydrogen atom that contribute the major part of the isotope effect and that the failure of Eq. (4) is due to contributions of higher-order terms. At this point it might be noted that the increase of 0.009 ± 0.001 D found by Lide² for (CH₃)₃CD over (CH₃)₃CH is the same within experimental error as the isotope effect reported here for $(CH_3)_2CD_2$. This indicates that to *first* order CH bending is not important, but second derivatives involving bending probably makes significant contributions.

Although the magnitudes of the isotope effects cannot be interpreted in a simple way to obtain quantitative values for the dipole-moment derivatives, the direction of the shifts can be used to obtain information. The simplest assumption is that the direction¹¹ of the isotope effect is the same whenever deuterium is substituted for ordinary hydrogen. This assumption is consistent with the observation that for all cases studied the isotope shifts are always of opposite sign whenever opposite ends of a molecule are deuterated. In this approximation, whenever deuterium substitution is made on the positive end of a molecule, an isotope shift on the absolute value of the dipole moment would occur that would be opposite to that observed for substitution on the negative end of the molecule. If an isotopic shift were observed for a molecule whose polarity were known, it would then be possible to de-

termine the sign of the dipole moment of a molecule by observing its isotope effect and comparing it to the known molecule. Taking the dipole moment of CH₃F to be such that the F is at the negative end, we see from the isotope shift that deuteration of the positive end causes an increase in the absolute magnitude of the dipole moment. Then, if our assumption is correct, increase of a dipole moment on deuteration can be taken to indicate that substitution has been made on the positive end of a molecule, whereas a decrease in the dipole moment would indicate substitution on the negative end. Their observed isotope shifts then indicate that CF_3H and $H_2C=CF_2$ have F as the negative end. The acetylenic hydrogen in methylacetylene is also indicated to be at the negative end of the molecule. These conclusions are in accord with usual chemical ideas and are not surprising.

Of more interest are propane and isobutane where the total dipole moments are very small, and chemical intuition does not give a clear preference for the sign. According to the simple interpretation of the isotope effects the methyl groups are at the negative end of the molecule. This is in accord with some recent evidence¹² that methyl groups might be electron withdrawing in saturated systems. In the case of methylsilane and methylgermane, simple electronegativity ideas might be taken to predict that the methyl group is the negative end, whereas the isotope shifts give the opposite result. However, the properties of silicon and germanium compounds do not in general seem to fit into any simple ideas¹³ of electronegativity, and the sign of the dipole moment indicated by the isotope shifts cannot be ruled out on the basis of electronegativity consideration.

Although the interpretation of deuterium isotope effects on dipole moments given here seems quite reasonable, more data will be necessary before its reliability or the extent to which it is applicable can be fully determined. However, it is clear that studies of isotope effects constitute a valuable source of information about molecular dipole moments, and that further investigation will lead to new insight.

⁹V. W. Laurie and D. R. Herschbach, J. Chem. Phys. 37, 1687 (1962).

¹⁰ For example, compare the value $\partial \mu / \partial r = \pm 0.8$ D/Å for the CH of acetylene from infrared intensity data: D. F. Eggers, I. Hisatune, and L. Van Alten, J. Phys. Chem. 59, 1124 (1955).

¹¹ Direction is meant in the vector sense.

¹² (a) H. Kwart and T. Takeshita, J. Am. Chem. Soc. **86**, 1161 (1964); (b) R. C. Fort and P. von R. Schleyer, *ibid.* **86**, 4194 (1964); (c) H. D. Holtz and L. M. Stock, *ibid.* **87**, 2404

^{(1965).} ¹³ See, for example, E. C. Thomas and V. W. Laurie, J. Chem. Phys. 44, 2602 (1966) and references cited therein.