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Magnetic Susceptibility Anisotropy, Molecular Quadrupole Moment, Molecular g Values, and the Sign of the Electric Dipole Moment in Methylacetylene

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Abstract: The high-field molecular Zeeman effect has been observed for $CH_3C{\equiv}CH$, $CH_3C{\equiv}CD$, and $CD_3{\equiv}CH$ under high resolution. An analysis of the data gives the perpendicular molecular g values of $g_\perp = +0.00350 \pm 0.00015$ for $CH_3C{\equiv}CH$, $g_\perp = +0.00271 \pm 0.00015$ for $CD_3C{\equiv}CH$, and $g_\perp = +0.00367 \pm 0.00015$ for $CH_3C{\equiv}CD$. The parallel molecular g value is $g_{||} = 0.312 \pm 0.002$ for methylacetylene. The magnetic susceptibility anisotropy is found to be $(\chi_\perp - \chi_{||}) = (7.70 \pm 0.14) \times 10^{-6}$ erg/(G^2 mole), and the molecular quadrupole moment in $CH_3C{\equiv}CH$ is $Q_{||} = (+4.82 \pm 0.23) \times 10^{-26}$ esu cm^2. The sign of the electric dipole moment for methylacetylene is found to be $^+CH_3C{\equiv}CH^-$. The elements in paramagnetic susceptibility tensor are $\chi_{||}{}^p = 9.50 \pm 0.03$ and $\chi_\perp{}^p = 158.41 \pm 0.04$ in units of 10^{-6} erg/(G^2 mole). The anisotropy of electronic charge distribution is $\langle 0|\Sigma_i a_i^2|0\rangle - \langle 0|\Sigma_i b_i^2|0\rangle = (33.28 \pm 0.05) \times 10^{-16}$ cm^2. Using an estimated bulk magnetic susceptibility, the total magnetic susceptibility tensor elements are determined, giving $\chi_\perp = -28.9 \pm 2.1$ and $\chi_{||} = -36.6 \pm 2.1$ in units of 10^{-6} erg/(G^2 mole). The second moments of electronic charge distribution are $\langle 0|\Sigma_i a_i^2|0\rangle = (38.72 \pm 0.30) \times 10^{-16}$ cm^2 and $\langle 0|\Sigma_i b_i^2|0\rangle = (5.44 \pm 0.25) \times 10^{-16}$ cm^2. The a axis is the symmetry axis of the molecule. The D–C bond deuterium nuclear quadrupole coupling constant is determined for $CD_3C{\equiv}CH$ to be χ_D(C–D bond) $= +(176 \pm 15)$ kHz. The results are discussed and comparisons are made with other similar molecules.

The rotational Zeeman effect can lead to new information about the ground- and excited-state electronic structure of molecules. The first-order Zeeman effect leads to the measurement of the molecular g values[2a] and the second-order Zeeman effect leads to the measurement of the anisotropy of the magnetic susceptibility.[2b] The measurement of these quantities leads directly to an experimental determination of the molecular quadrupole moments and the second moments of the electronic charge distribution.[3] By measuring the molecular g values in two different center of mass systems (isotopic species), the sign of the electric dipole moment can be obtained.

Methylacetylene is a particularly suitable molecule for the study of the molecular Zeeman effect and an investigation of the electronic structure. The microwave spectra of the parent $CH_3C{\equiv}CH$ and all isotopic species are known,[4,5] and a complete substitutional structure for the molecule is available.[6]

The first-order molecular Zeeman effect in methylacetylene has been observed previously in fields up to 10,000 G by Cox and Gordy.[7] They were unable to measure the very small g value perpendicular to the symmetry axis, $g_\perp$, and they gave values for the g value parallel to the symmetry axis of $|g_{||}| = 0.298 \pm 0.006$ for $CH_3C{\equiv}CH$ and $|g_{||}| = 0.310 \pm 0.01$ for $CH_3C{\equiv}CD$.

We have reexamined the molecular Zeeman effect in methylacetylene under high resolution in magnetic fields up to 30,000 G. The signs and magnitudes of $g_{||}$ and $g_\perp$ are obtained for CH_3CCH, CH_3CCD, and CD_3CCH,

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[1] National Science Foundation Predoctoral Fellow.

[2] (a) J. R. Eshbach and M. W. P. Strandberg, *Phys, Rev.*, **85**, 24 (1952); (b) W. Hütnner and W. H. Flygare, *J. Chem. Phys.*, **47**, 4137 (1967).

[3] W. Hüttner, H. K. Lo, and W. H. Flygare, *ibid.*, **48**, 1206 (1968).

[4] R. Trambarulo and W. Gordy, *ibid.*, **18**, 1613 (1950).

[5] L. F. Thomas, E. I. Sherrard, and J. Sheridan, *Trans. Faraday Soc.*, **51**, 619 (1955).

[6] C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

[7] J. T. Cox and W. Gordy, *Phys. Rev.*, **101**, 1298 (1956).

as well as the value of the magnetic susceptibility anisotropy, $(\chi_{\perp} - \chi_{\parallel})$, in methylacetylene. These parameters are then combined to yield the molecular quadrupole moment and the sign of the electric dipole moment for methylacetylene. Finally, by estimating the bulk magnetic susceptibility from other data, the second moments of the charge distribution and the elements of the magnetic susceptibility tensor for methylacetylene are obtained.

We have also determined the deuterium nuclear quadrupole coupling constant in $\mathrm{CD_3C{\equiv}CH}$ in the course of this work.

The results obtained in this work are compared with similar results in other molecules.

Experimental Data and Analysis

A sample of methylacetylene was obtained from K and K Laboratories. The $\mathrm{CH_3C{\equiv}CD}$ was obtained from Volk Radiochemical Co., and the $\mathrm{CD_3C{\equiv}CH}$ from Merck Sharp and Dohme.

The microwave spectrometer and electromagnet used in this work have been described elsewhere.[8] The spectrometer is a relatively standard high-resolution instrument. The electromagnet gives homogeneous magnetic fields of up to 30,000 G over an area of 2 × 72 in. with a gap spacing of 0.6 in., and fields of up to 26,000 G with a gap spacing of 1.1 in.

The energy level expression for a rotating molecule in a magnetic field is given in eq 28 of Hüttner and Flygare.[2b] For a symmetric rotor like methylacetylene, this expression simplifies to

$$E(J,K,M) = E^0 - \mu_0 MH\left[g_{\perp} + (g_{\parallel} - g_{\perp})\frac{K^2}{J(J+1)}\right] - \frac{H^2}{3}\left[\frac{3M^2 - J(J+1)}{(2J-1)(2J+3)}\right]\left\{(\chi_{\perp} - \chi_{\parallel}) - \frac{3K^2}{J(J+1)}(\chi_{\perp} - \chi_{\parallel})\right\} \quad (1)$$

J, K, and M are the rotational quantum numbers, E^0 is the zero-field rigid rotor energy, H is the magnetic field, and μ_0 is the nuclear magneton. This expression does not include the effects of the hydrogen nuclear magnetic moments. These effects are negligible since the coupling of the nuclear spins to the molecular rotation is unobservably small, and the anisotropies in the nuclear magnetic shieldings lead to effects of less than 1 kHz.[2b]

For $\mathrm{CD_3C{\equiv}CH}$ and $\mathrm{CH_3C{\equiv}CD}$, the effects of nuclear quadrupole coupling must be considered. The deuterium nucleus will be uncoupled from the molecular rotation if[9]

$$\chi_{\mathrm{D}} \ll (g_I + g_J)\mu_0 H \quad (2)$$

g_I is the deuterium nuclear g value, χ_{D} is the deuterium nuclear quadrupole coupling constant, and g_J is the rotational g value. The deuterium nuclear quadrupole coupling constant in $\mathrm{H_3CC{\equiv}CD}$ along the symmetry axis is known to be $\chi_{\mathrm{D}} = (208 \pm 10)$ kHz.[10]

The χ_{D} along the symmetry axis in $\mathrm{D_3CC{\equiv}CH}$ has not been measured up to this time. Therefore, we have observed the zero-field $J = 0 \rightarrow J = 1$ transition in $\mathrm{D_3CC{\equiv}CH}$ in a large L-band absorption cell[11] in order to determine the value of χ_{D} in the $\mathrm{D_3CC{\equiv}CH}$ molecule. The theory of the nuclear quadrupole coupling with three equivalent $I_1 = I_2 = I_3 = 1$ spin nuclei has been given previously.[12] We observed the $J = 0 \rightarrow J = 1$ transition under high resolution and achieved a partially resolved multiplet. The unresolved spectra were fit by adding Lorentzian line shapes to yield the value of χ_{D} along the symmetry axis in $\mathrm{D_3CC{\equiv}CH}$. The result was

$$\chi_{\mathrm{D}}(\mathrm{C_3\ axis}) = (55 \pm 5)\ \mathrm{kHz} \quad (3)$$

If we assume that the C–D bond is cylindrically symmetric, we can find the value of χ_{D} along the C–D bond axis from

$$\chi_{\mathrm{D}}(\mathrm{C_3\ axis}) = \frac{\chi_{\mathrm{D}}(\mathrm{CD\ bond})}{2}(3\cos^2\theta - 1) \quad (4)$$

where θ is the C–C–H angle which is known[6] to be 110° 14′. The results give χ_{D} along the C–D bond in $\mathrm{D_3CC{\equiv}CH}$ of

$$\chi_{\mathrm{D}} = (176 \pm 15)\ \mathrm{kHz} \quad (5)$$

We now know the values of $\chi_{\mathrm{D}}(\mathrm{C_3}$ axis) in both $\mathrm{D_3CC{\equiv}CH}$ and $\mathrm{H_3CC{\equiv}CH}$. However, in both molecules, the spins are uncoupled (as eq 2 is satisfied) to within the limits of our resolution at 25,000 G. We have found appreciable coupling remaining in $\mathrm{H_3C\text{-}C{\equiv}{}^{14}N}$ at 25,000 G where $\chi_{\mathrm{N}} = -4212$ kHz.[13] Thus, as χ_{D} in both $\mathrm{D_3CC{\equiv}CH}$ and $\mathrm{H_3CC{\equiv}CD}$ is a factor of 20 smaller in magnitude than χ_{N} in $\mathrm{H_3CC{\equiv}N}$, we feel confident in using the uncoupled basis and first-order theory. However, there are still diagonal corrections to eq 1 due to the nonzero values of χ_{D} along the symmetry axes.[9] The diagonal correction to eq 1 in $\mathrm{H_3CC{\equiv}CD}$ is

$$E_{\mathrm{Q}}(JKMIM_I) = \frac{C}{2}[J(J+1) - 3M^2][I(I+1) - 3M_I^2] \quad (6)$$

C, for the $J = 1$, $K = 0$ state, is

$$C = -\frac{\chi_{\mathrm{D}}(\mathrm{C_3\ axis})}{10} = -21\ \mathrm{kHz} \quad (7)$$

The diagonal correction to eq 1 in $\mathrm{D_3CC{\equiv}CH}$ is

$$E_{\mathrm{Q}}(JKMI,M_I,I_2M_{I2}I_3M_{I3}) = \frac{C}{2}\sum_{\substack{I_i=I_1\\ I_2\\ I_3}}[J(J+1) - 3M^2][I_i(I_i+1) - 3M_{I_i}] \quad (8)$$

C, for the $J = 1$, $K = 0$ state, is

$$C = -\frac{\chi_{\mathrm{D}}(\mathrm{C_3\ axis})}{10} = -5.5\ \mathrm{kHz} \quad (9)$$

The $J = 0 \rightarrow J = 1$ $\Delta M = 0$, $\Delta M = \pm 1$, and $\Delta K = 0$ transitions were observed in $\mathrm{H_3CC{\equiv}CH}$, $\mathrm{H_3CC{\equiv}CD}$, and $\mathrm{D_3CC{\equiv}CH}$. The $\mathrm{H_3CC{\equiv}CH}$ spectrum at the

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[8] W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *J. Chem. Phys.*, **50**, 1714 (1969).

[9] C. K. Jen, *Phys. Rev.*, **76**, 1494 (1949).

[10] V. W. Weiss and W. H. Flygare, *J. Chem. Phys.*, **45**, 8 (1966).

[11] W. H. Flygare and V. W. Weiss, *ibid.*, **45**, 2785 (1966).

[12] M. Mizushima and T. Ito, *ibid.*, **19**, 739 (1951), and references cited therein.

[13] J. M. Pochan, R. G. Stone, and W. H. Flygare, *ibid.*, in press.

high magnetic fields was analyzed with eq 1. The $H_3C-C\equiv CD$ and $D_3CC\equiv CH$ spectra were analyzed with eq 1 corrected for the small first-order effects described above due to the deuterium nuclear quadrupole coupling.

The $J = 0 \rightarrow J = 1$, $\Delta M = \pm 1$ transitions in $H_3C-C\equiv CH$, $H_3CC\equiv CD$, and $D_3CC\equiv CH$ were doublets whose center frequencies were shifted from the zero-field frequency by $H^2/15h\ (\chi_\perp - \chi_\parallel)$ Hz. Several traces of the doublets were obtained for each molecule. The doublet splitting was on the order of 130 kHz in a field of 25,000 G. These splittings give the following g values.

$$\begin{array}{lll} H_3CC\equiv CH & |g_\perp| = 0.00350 \pm 0.00015 & \\ H_3CC\equiv CD & |g_\perp| = 0.00367 \pm 0.00015 & (10) \\ D_3CC\equiv CH & |g_\perp| = 0.00271 \pm 0.00015 & \end{array}$$

We will show below that these g values have positive signs. The molecular g values given here are the smallest ever reported.

The $(\chi_\perp - \chi_\parallel)$ value obtained from the shift of the doublet center was combined with the $(\chi_\perp - \chi_\parallel)$ value obtained from an examination of the $J = 0 \rightarrow 1$, $\Delta M = 0$ and $J = 1 \rightarrow 2$, $K = 0$, $\Delta M = 0$ transitions. The result of the several measurements is

$$\begin{aligned} (\chi_\perp - \chi_\parallel) &= (1.279 \pm 0.023) \times 10^{-29}\ \text{erg/G}^2 \\ &= (7.70 \pm 0.14) \times 10^{-6}\ \text{erg/(G}^2\ \text{mole)} \end{aligned} \qquad (11)$$

$(\chi_\perp - \chi_\parallel)$ is the same for all isotopic species since it is invariant with respect to a change in origin of the coordinate system.

By working out the explicit energy level expressions from eq 1, it is easy to show that both the magnitude of $g_\parallel$ and the relative signs of $g_\parallel$ and $g_\perp$ can be obtained from the Zeeman pattern of the $J = 1 \rightarrow 2$, $K = 1$, $\Delta M = \pm 1$ transition. This transition was observed in $H_3CC\equiv CH$ at high fields and the strongest of the six $\Delta M = \pm 1$ components are shown in Figure 1. We will show below that $g_\parallel$ is positive and, therefore, the ΔM transitions in Figure 1 are assigned on this basis. The splitting between the $\Delta M = 1 \rightarrow 2$ and $\Delta M = 0 \rightarrow -1$ components is given by $2\mu_0 g_\perp H + (6H^2/35)(\chi_\perp - \chi_\parallel)$, and the splitting between the $\Delta M = -1 \rightarrow -2$ and $\Delta M = 0 \rightarrow 1$ components is given by $2\mu_0 g_\perp H - (6H^2/35)\cdot(\chi_\perp - \chi_\parallel)$. Since $(\chi_\perp - \chi_\parallel)$ is positive, it is obvious from Figure 1 that $g_\perp$ is positive.

We will now show that $g_\parallel$ is in fact positive. From the 6-MHz splitting between the weak $1 \rightarrow 0$ and $-1 \rightarrow 0$ components (not shown in Figure 1), and from the $J = 1 \rightarrow 2$, $K = 1$, $\Delta M = 0$ transition, the magnitude of $g_\parallel$ was found to be

$$|g_\parallel| = 0.312 \pm 0.002 \qquad (12)$$

which is in agreement with the earlier work of Cox and Gordy.[7] $g_\parallel$ is determined primarily by the methyl group protons. The $-C\equiv CH$ part of the molecule contributes to $g_\parallel$ only if low-lying excited electronic states exist in which the molecule is bent. Thus $g_\parallel$ in methylacetylene should be approximately the same as $g_\parallel$ in the methyl halides. In methyl iodide, $g_\parallel$ is known to be $+0.310 \pm 0.016$.[14] The sign of $g_\parallel$ in H_3CI is obtained as the M states are identified by the strong nuclear Zeeman effect and the sign of the g value of the iodine nucleus is known.[14] Therefore, $g_\parallel$ in methylacetylene must be positive also.

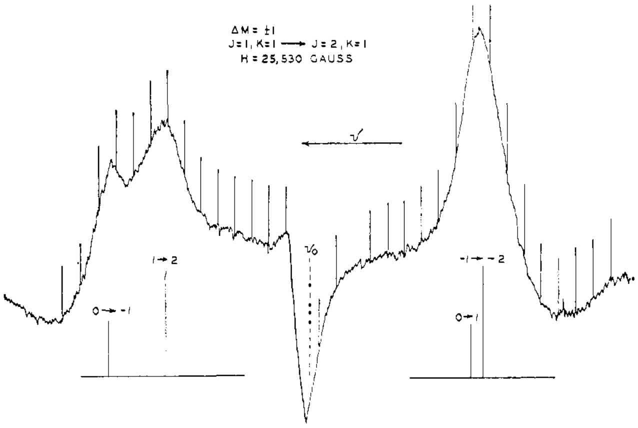

Figure 1. The center four of the six $J = 1$, $K = 1 \rightarrow J = 2$, $K = 1$, $\Delta M = \pm 1$ components in $CH_3C\equiv CH$ at 25,530 G. The $\Delta M = \pm 1$ components are shown by the bars below the spectra. This spectrum unambiguously assigns the sign of $g_\perp$ relative to $g_\parallel$ (see text). The markers are every 50 kHz.

The strong Stark components near the zero-field frequency, ν_0, as shown in Figure 1 was unexpected initially. The magnetic field for the spectrum shown in Figure 1 is perpendicular to the electric vector of the microwaves giving $\Delta M = \pm 1$ selection rules. However, the electric field used for Stark modulation is parallel to the microwave electric vector. When both fields are present, the projection of J along either the magnetic or the electric field axes is no longer a constant. To obtain the Stark component frequencies and intensities a secular equation must be solved. This was done and the results were in agreement with experiment. It is easy to see how the Stark component near ν_0 arises. The $J = 1$, $M = 0$ level and the $J = 2$, $M = 0$ level are unchanged to first order by an electric or magnetic field. It is the transition between these two levels that appears near ν_0 when the electric field is strong enough to give appreciable $\Delta M = 0$ transition intensity.

Molecular Properties in Methylacetylene from the Zeeman Effect Parameters

The expression for the molecular quadrupole moment of a symmetric top is[3]

$$\begin{aligned} Q_\parallel &= \frac{|e|}{2}\sum_n Z_n(3a_n^2 - r_n^2) - \frac{|e|}{2}\langle 0|\sum_i (3a_i^2 - r_i^2)|0\rangle \\ &= \frac{\hbar|e|}{4\pi M_p}\left(\frac{g_\perp}{B} - \frac{g_\parallel}{A}\right) + \frac{4mc^2}{|e|}(\chi_\perp - \chi_\parallel) \end{aligned} \qquad (13)$$

Here the a axis is the symmetry or parallel axis of the molecule. Using the second expression for $Q_\parallel$ we find for the normal species of methylacetylene

$$Q_\parallel = +(4.82 \pm 0.23) \times 10^{-26}\ \text{esu cm}^2 \qquad (14)$$

The sign of the electric dipole moment in methylacetylene can be found from the g values given in eq 10 and the relation[2,15]

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[14] D. Vander Hart and W. H. Flygare, *Mol. Phys.*, in press.

[15] C. H. Townes, G. C. Dousmanis, R. L. White, and R. F. Schwartz, *Discussions Faraday Soc.*, 19, 56 (1955).

$$\frac{g_\perp'}{B'} - \frac{g_\perp}{B} = -\frac{8\pi M_P}{\hbar|e|}Z\mu_z \qquad (15)$$

B and B' are the rotational constants for two isotopic species and μ_z is the electric dipole moment of the molecule. Z is the coordinate of the center of mass of the primed isotopic species in a coordinate system which originates at the center of mass of the unprimed species. Taking CD_3CCH as the unprimed species and CH_3CCD as the primed species we find that $Z = 0.1774$ Å. We have chosen positive Z to be the direction from the CD_3 group to the C≡C triple bond. From the g values, we now calculate μ_z and find

$$\mu_z = -(0.70 \pm 0.20) \times 10^{-18} \text{ esu cm} \qquad (16)$$

The magnitude of μ_z in eq 16 is in good agreement with the accepted value for the methylacetylene dipole moment of $|\mu| = (0.75 \pm 0.01) \times 10^{-18}$ esu cm.[16] From the sign of μ_z, the polarity of the molecule is $^+CH_3CCH^-$.

The bulk magnetic susceptibility of methylacetylene has not been measured. However, we can estimate the susceptibility from susceptibility data for other molecules. The success of Pascal's rules in estimating bulk magnetic susceptibilities indicates that the susceptibility is very nearly an additive property. If this is the case, then the difference between the susceptibilities of phenylacetylene and benzonitrile should be equal to the difference between the susceptibilities of methylacetylene and methylcyanide. This difference is -3.4×10^{-6} erg/(G^2 mole).[17] Since $\chi = -27.6$ for methylcyanide,[17] methylacetylene should have a value of $\chi = 31.6 \times -10^{-6}$ erg/(G^2 mole). Similarly, using the difference between the susceptibilities of toluene and benzene and the susceptibility of acetylene,[17] one obtains $\chi = -32.1 \times 10^{-6}$ erg/(G^2 mole) for methylacetylene. Thus we feel that a good estimate of χ for methylacetylene is

$$\chi = (-31.5 \pm 2.0) \times 10^{-6} \text{ erg/(G}^2\text{ mole)} \qquad (17)$$

Using the expressions for the magnetic susceptibility tensor elements,[18] we can combine our molecular g values, magnetic susceptibility anisotropy, and estimated bulk susceptibility to give (in units of 10^{-6} erg/(G^2 mole))

$$\begin{aligned} \chi_{aa} &= -36.6 \pm 2.1 \\ \chi_{bb} = \chi_{cc} &= -28.9 \pm 2.1 \end{aligned} \qquad (18)$$

$$\begin{aligned} \chi_{aa}^{d} &= -46.1 \pm 2.1 \\ \chi_{bb}^{d} = \chi_{cc}^{d} &= -187.3 \pm 2.1 \end{aligned} \qquad (19)$$

$$\begin{aligned} \chi_{aa}^{P} &= 9.50 \pm 0.03 \\ \chi_{bb}^{P} = \chi_{cc}^{P} &= 158.41 \pm 0.04 \end{aligned} \qquad (20)$$

The a axis is the symmetry axis of the molecule, χ_{aa}^{d} is the diamagnetic contribution to the magnetic susceptibility about the a axis, and χ_{aa}^{P} is the paramagnetic contribution to the magnetic susceptibility about the a axis. The total susceptibility χ_{aa} is the sum of χ_{aa}^{d} and χ_{aa}^{P}.

From the molecular quadrupole moment and the known molecular substitutional structure,[6] we obtain $\langle 0|\Sigma(a_i^2 - b_i^2)|0\rangle = (33.28 \pm 0.05) \times 10^{-16}$ cm^2 through the use of eq 13. This result may then be combined with χ_{aa}^{d} (which is proportional to $\langle 0|\Sigma_i b_i^2|0\rangle$ to give

$$\begin{aligned} \langle 0|\sum_i a_i^2|0\rangle &= (38.72 \pm 0.30) \times 10^{-16} \text{ cm}^2 \\ \langle 0|\sum_i b_i^2|0\rangle = \langle 0|\sum_i c_i^2|0\rangle &= (5.44 \pm 0.25) \times 10^{-16} \text{ cm}^2 \end{aligned} \qquad (21)$$

for the second moments of the electronic charge distribution in $H_3CC{\equiv}CH$.

Discussion

The value of the symmetry axis g value, $g_{\|}$, given here for methylacetylene in eq 12 is within the experimental error of the corresponding value of $g = 0.3133 \pm 0.0002$ found in methane.[19] As the absolute sign of the above g value in methane and our value of $g_{\|}$ in eq 12 cannot be measured by the present experiments, we can refer to the work on H_3CI[14] where a positive $g_{\|}$ was found to assign the positive signs for both CH_4 and $H_3CC{\equiv}CH$.

The positive g value perpendicular to the symmetry axis (see eq 10) in methylacetylene was unexpected. According to Cederberg, Anderson, and Ramsey, the value of $g_\perp$ in acetylene is negative.[20] Therefore, we expected $g_\perp$ to also be negative in $H_3CC{\equiv}CH$. However, the opposite or positive sign is correct for methylacetylene.

The sign of the electric dipole moment obtained in this work ($^+H_3CC{\equiv}CH^-$) was expected and predicted from many viewpoints involving both π-bond[21] and σ-bond arguments.[22] This sign was also predicted by observing the direction of the *change* in the molecular dipole moment in $H_3CC{\equiv}CH$ with deuteration to $D_3CC{\equiv}CH$ and $H_3CC{\equiv}CD$.[23] The dipole moment of $D_3CC{\equiv}CH$ was found to increase and the value in $H_3CC{\equiv}CD$ was found to decrease relative to the parent $H_3CC{\equiv}CH$ molecule. By comparing this trend with the corresponding trend in the H_3CF–D_3CF dipole moment changes, and by assuming a $^-FCH_3^+$ dipole moment sign, Laurie and Muenter concluded that the sign in methylacetylene was ($^+H_3CC{\equiv}CH^-$).[23] We have now confirmed that analysis by the direct observation presented in this work. The correct sign of the dipole moment was also recently computed from a LCAO-MO-SCF wave function composed of a minimal basis of Slater orbitals where it was found that the π-system polarization gave rise to the dipole moment and its sign.[24]

The value of the C–D bond deterium nuclear quadrupole coupling constant in $D_3CC{\equiv}CH$ given in eq 5 appears to be the first direct measurement of this value for a methyl group in the gas phase. A value of χ_D(CD bond) = 165 kHz is reported for the methyl group in toluene-α-d_3 from nmr liquid-crystal work.[25] This number is in excellent agreement with our result of (176

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[16] S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **21**, 308 (1953).

[17] Landolt-Börnstein, "Zahlenwerte und Funktionen," Vol. 2, Part 10, J. Bartels, *et al.*, Ed., Springer-Verlag, Berlin, 1951.

[18] W. H. Flygare, *J. Chem. Phys.*, 42, 1563 (1965).

[19] C. H. Anderson and N. F. Ramsey, *Phys. Rev.*, **149**, 14 (1966).

[20] J. W. Cederberg, C. H. Anderson, and N. F. Ramsey, *ibid.*, **136**, A960 (1964).

[21] A. Lofthus, *J. Am. Chem. Soc.*, **79**, 24 (1957).

[22] M. J. S. Dewar, "Hyperconjugation," The Press Co., New York, N. Y. 1962.

[23] V. W. Laurie and J. S. Muenter, *J. Am. Chem. Soc.*, 88, 2883 (1966).

[24] M. D. Newton and W. N. Lipscomb, *ibid.*, 89, 4261 (1967).

[25] J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.*, 43, 3442 (1965).

± 15) kHz. Our result of $\chi_D = (176 \pm 15)$ kHz should be characteristic of a methyl group deuterium coupling constant, and it appears to be smaller than the calculated estimate of (210 ± 30) kHz which was obtained for DCH_3 using an extended basis-set LCAO-MO-SCF wave function for methane.[26] A more recent theoretical estimate of 175 kHz is cited for CD_4 by Pyykko and Pedersen[27] which is in good agreement with our result.

The magnetic susceptibility anisotropy in methylacetylene, given as $\chi_\perp - \chi_{||} = (7.70 \pm 0.14) \times 10^{-6}$ erg/(G^2 mole), is only slightly larger than the value reported for $FC{\equiv}CH$ of[28] $\chi_\perp - \chi_{||} = (5.19 \pm 0.12) \times 10^{-6}$ erg/(G^2 mole). These small anisotropies for $FC{\equiv}CH$ and $CH_3C{\equiv}CH$ are in sharp contrast to the large anisotropy estimated for the $-C{\equiv}CH$ group from proton chemical shift data.[29,30] Our results also seem to indicate that $\chi_\perp - \chi_{||}$ in acetylene is considerably smaller than predicted by other estimates.[31]

The molecular quadrupole moment of $Q_{||} = +(4.82 \pm 0.23) \times 10^{-26}$ esu cm^2 obtained here for methylacetylene is somewhat larger than the value of $+(3.96 \pm 0.14) \times 10^{-26}$ esu cm^2 found for fluoroacetylene.[28] The principal contributions to the molecular quadrupole moment come from the electrons in outer portions of the molecule. The CH bonds contribute positively to the value of $Q_{||}$ in methylacetylene, thus indicating that electrons tend to be pulled in from the hydrogen nuclei toward the center of molecule.

It is also interesting to speculate on the nature of the additivity of the values of the second moment of the electronic charge distribution in molecules. The value of $\langle c^2 \rangle = (5.44 \pm 0.25) \times 10^{-16}$ cm^2 found here for methylacetylene is remarkably similar to the out-of-plane value of $\langle c^2 \rangle = (5.6 \pm 0.5) \times 10^{-16}$ cm^2 reported for acetaldehyde.[32] Both molecules have the same number of electrons and the same number of two protons out of the skeletal plane along the *b* axis in methylacetylene and the *c* axis in acetaldehyde. Previously we have suggested some simple rules for determining the value of the second moment of the electronic charge distribution perpendicular to the skeletal plane.[33,34] These rules are (1) one unit contribution for each first-row atom in the plane, (2) one-fourth unit contribution for each hydrogen atom in the plane, and (3) one unit contribution for each hydrogen atom out of plane.

Using these rules we can predict the value of $\langle c^2 \rangle$ in formic acid from the above result of $\langle c^2 \rangle = 5.6$ in acetaldehyde. Subtracting 2.0 for the two out of plane protons in acetaldehyde predicts $\langle c^2 \rangle = 5.6 - 2.0 = 3.6$ for formic acid which is in excellent agreement with the experimental value for formic acid of $\langle c^2 \rangle = (3.5 \pm 0.2) \times 10^{-16}$ cm^2 reported by Kukolich and Flygare.[35] Further examples of the validity of these simple rules are found in a discussion of linear molecules by Flygare, Shoemaker, and Hüttner.[36]

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[26] T. Caves and M. Karplus, *J. Chem. Phys.*, 45, 1670 (1966); see also ref 17.

[27] P. Pyykko and B. Pedersen, *Chem. Phys. Letters*, 2, 297 (1968).

[28] R. L. Shoemaker and W. H. Flygare, *ibid.*, 2, 610 (1968).

[29] J. A. Pople, *Proc. Roy. Soc.* (London), A239, 541, 550 (1957).

[30] H. Heel and W. Zeil, *Z. Electrochem.*, **64**, 962 (1960); and W. Zeil and H. Buchert, *Z. Physik. Chem.* (Frankfurt), 38, 147 (1963).

[31] J. A. Pople, *J. Chem. Phys.*, 37, 60 (1962).

[32] W. Hüttner and W. H. Flygare, *Trans. Faraday Soc.*, in press.

[33] R. L. Shoemaker and W. H. Flygare, *J. Chem. Phys.*, in press.

[34] D. Sutter and W. H. Flygare, *J. Am. Chem. Soc.*, **91**, 4063 (1969).

[35] S. G. Kukolich and W. H. Flygare, *ibid.*, **91**, 2433 (1969).

[36] W. H. Flygare, R. L. Shoemaker, and W. Hüttner, *J. Chem. Phys.*, **50**, 2414 (1969).

Reactions of Accelerated Carbon Ions and Atoms with Benzene. Product Distribution as a Function of Charge and Kinetic Energy[1]

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Abstract: Monoenergetic beams of $^{14}C^+$ ions (from 15- to 0.1-keV kinetic energy), and beams of 5- and 0.5-keV carbon atoms, were allowed to impinge on a target of solid benzene at −196°. About 28% of the ions striking the benzene have been accounted for as identified C_2, C_6, C_7, C_8, C_{12}, and C_{13} hydrocarbons. The appearance of the known products was essentially unaffected by either the kinetic energy or the charge state of the impinging ions or atoms.

This report describes further efforts toward an understanding of the processes occurring when energetically "hot" carbon ions and atoms strike a benzene target. The principal interest in this subject was generated by the early reports that both recoiling carbon atoms, from the $^{14}N(n,p)^{14}C$ reaction,[2] and accelerated $^{14}C^+$ ions (KE = 5 keV)[3,4] lead to both benzene-^{14}C and toluene-^{14}C, the latter with about 15% of its radio-

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[2] A. P. Wolf, C. R. Redvanly, and R. C. Anderson, *Nature*, **176**, 831 (1956).

[3] R. M. Lemmon, F. Mazzetti, F. L. Reynolds, and M. Calvin, *J. Am. Chem. Soc.*, 78, 6414 (1956).

[4] R. M. Lemmon, R. T. Mullen, and F. L. Reynolds in "Chemical Effects of Nuclear Transformations," Vol. II, International Atomic Energy Agency, Vienna, 1961, p 27.