The Effect of Deuteration on the Molecular Dipole Moments of Haloacetylenes

N. Heineking, U. Andresen, and H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie
der Christian-Albrechts-Universität zu Kiel

Z. Naturforsch. **44a,** 848–852 (1989); received July 18, 1989

The dipole moments of chloro-, bromo-, and iodoacetylene, and those of the respective deuterated species, have been accurately determined using microwave Fourier transform spectrometers equipped with Stark cells. In each case, deuteration resulted in a change of the value of the dipole moment of about 0.012 D. The results provide strong evidence that the orientation of the dipole moment vector of iodoacetylene is opposite to that of the other haloacetylenes.

Introduction

Isotopic substitution of a hydrogen atom in a polyatomic molecule normally leads to a considerable decrease in the effective bond length [1]. Associated with this is a small variation of the molecular dipole moment, as has been found, among many others, for fluoroacetylene [2, 3] and propyne [4]. From the observation, that the sign of this variation obviously depends on the orientation of the dipole moment, Schäfer and Christiansen [5] have concluded it might be possible to determine unambiguously the molecular dipole moment of iodoacetylene (which by accident is very small, so that its orientation cannot be determined by chemical intuition) by evaluation of the effect of deuteration on its dipole moment. We have now measured the dipole moments of iodoacetylene and deuteroiodoacetylene, and those of bromo-, deuterobromo-, chloro-, and deuterochloroacetylene.

Experimental

The monohaloacetylenes form a group of gaseous compounds stable under experimental conditions, i.e., temperatures around 230 K and pressures of 0.1–1 Pa. All of them react more or less readily with oxygen. They are obtained by elimination reactions from appropriate ethylene halogenides or, in the case of iodoacetylene, by a substitution reaction, though in low yield. The preparations are described in more detail in [6] and [7].

The initial experiments were on the $J=2-1$ rotational transition of normal iodoacetylene (HCCI). For these measurements, a conventional X-band Stark cell was used in one of our early microwave Fourier transform (MWFT) spectrometers. However, resolution of the various Stark components was not possible, partly due to field inhomogeneity. Therefore, a special Stark cell was designed [8]: to achieve a more homogeneous electric DC field, we decided to place a septum 8 mm thick in a 4 m J-band rectangular waveguide (34.85 mm × 17.80 mm inner cross section). With this cell we measured the $J=1-0$ rotational transition of HCCI at field strengths up to 12.5 kV/cm. A listing of these recordings is given in Table 1a. Because of the high field used, the polarizability anisotropy had to be

Table 1a. Observed frequencies of Stark satellites of the $J=1-0$ rotational transition of iodoacetylene.

$2F'$	$2F''$	$2M_F$	Voltage (V)	Field (V/cm) [a]	ν_{obs} (MHz)	$\nu_{obs-calc}$ (MHz)
7	5	1 [b]	2000.	5 221.	6469.846	−0.009
7	5	1 [b]	4300.	11 224.	6470.791	0.004
7	5	1 [b]	4800.	12 529.	6471.080	0.001
5	5	5 [b]	2000.	5 221.	5997.886	0.009
5	5	1	4000.	10 441.	–	–
5	5	3	4000.	10 441.	5998.452	0.011
5	5	5	4000.	10 441.	5998.872	0.002
5	5	1	4800.	12 529.	–	–
5	5	3	4800.	12 529.	5998.833	−0.001
5	5	5	4800.	12 529.	5999.451	−0.002
3	5	1 [b]	2500.	6 526.	6676.579	−0.007
3	5	1 [b]	4000.	10 441.	6677.121	−0.008
3	5	1	4800.	12 529.	6677.524	0.002
3	5	3	4800.	12 529.	6677.441	−0.003

[a] Septum spacing was 0.3831 cm.
[b] The other M_F-components were not considered.

Reprint requests to Prof. Dr. H. Dreizler, Abt. Chemische Physik, Institut für Physikalische Chemie der Universität Kiel, Ludewig-Meyn-Str. 8, D-2300 Kiel.

0932-0784 / 89 / 0900-0848 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1 b. Observed frequencies of Stark satellites of the $J = 1 - 0$ rotational transition of iodoacetylene-d.

$2F'$	$2F''$	$2M_F$	Voltage (V)	Field (V/cm) [a]	ν_{obs} (MHz)	$\nu_{obs-calc}$ (MHz)
7	5	1	2004.	5 231.	5938.382	−0.006
7	5	3	2004.	5 231.	5938.382	−0.007
7	5	5	2004.	5 231.	5938.382	−0.006
7	5	1	4004.	10 452.	5938.577	−0.012
7	5	3	4004.	10 452.	5938.577	−0.014
7	5	5	4004.	10 452.	5938.577	−0.019
7	5	1	4801.	12 532.	5938.707	0.001
7	5	3	4801.	12 532.	5938.707	−0.002
7	5	5	4801.	12 532.	5938.707	−0.009
5	5	5 [b]	2009.	5 244.	5466.532	0.016
5	5	5 [b]	3999.	10 439.	5466.795	0.025
3	5	1	2009.	5 244.	6145.377	0.005
3	5	3	2009.	5 244.	6145.377	0.005
3	5	1	3999.	10 439.	6145.562	0.007
3	5	3	3999.	10 439.	6145.562	0.007
3	5	1	4996.	13 041.	6145.657	−0.006
3	5	3	4996.	13 041.	6145.657	−0.006

[a] Septum spacing was 0.3831 cm.
[b] The other M_F-components were not considered.

included in the analysis. However, the internal consistency of the analysis now turned out to be better than that of the calibration measurements, which used the $J, K_-, K_+ = 1, 1, 0 - 1, 1, 1$ rotational transition of formic aldehyde. Therefore, we recorded the $J = 1 - 0$ transition of normal bromoacetylene (HCCBr) near 8 GHz, this time using field strengths lower than 3 kV/cm. These measurements (in Table 2 a) were later compared to those using a similarly designed X-band cell [9] (inner cross section 22.86 mm × 10.16 mm, septum thickness 5 mm), which in turn had been calibrated with the $J = 1 - 0$ transition of carbonyl sulphide. Next, we measured the Stark shifts of the hyperfine components of the $J = 1 - 0$ transition of deutero-iodoacetylene, DCCI. These recordings are summarized in Table 1 b. For this species, resolution of the M_F-components turned out to be impossible even at 13 kV/cm, for the dipole moment was even smaller than that of HCCI. The opposite was observed for DCCBr (Tables 2 b and c): clearly the various Stark components of this species shifted "faster" than the corresponding ones of HCCBr (see Figure 1). However, the difference between the dipole moments was nearly the same for HCCI/DCCI and HCCBr/DCCBr, namely 0.0123 Debye. When we later completed the calibration measurements on HCCBr in X-band, we also recorded the $J = 1 - 0$ transition of DCCCl (Table 3 b), and remeasured the Stark shifts of HCCCl

Table 2 a. Observed frequencies of Stark satellites of the $J = 1 - 0$ rotational transition of bromo(79)acetylene.

$2F'$	$2F''$	$2M_F$	Voltage (V)	Field (V/cm) [a]	ν_{obs} (MHz)	$\nu_{obs-calc}$ (MHz)
5	3	1	400.83	1558.56	7969.919	0.002
5	3	3	400.83	1558.56	7969.627	−0.003
5	3	1	450.56	1751.92	7970.368	0.001
5	3	3	450.56	1751.92	7970.007	0.003
5	3	1	500.62	1946.57	7970.874	−0.001
5	3	3	500.62	1946.57	7970.428	0.003
5	3	1	550.22	2139.44	7971.428	−0.003
5	3	3	550.22	2139.44	7970.882	−0.002
5	3	1	600.75	2335.91	7972.051	0.000
5	3	3	600.75	2335.91	7971.393	−0.004
3	3	1	400.83	1558.56	8131.656	−0.002
3	3	3	400.83	1558.56	8132.252	0.000
3	3	1	450.56	1751.92	8131.944	0.011
3	3	3	450.56	1751.92	8132.684	0.000
3	3	1	500.62	1946.57	8132.239	−0.004
3	3	3	500.62	1946.57	8133.174	0.002
3	3	1	550.22	2139.44	8132.585	0.002
3	3	3	550.22	2139.44	8133.698	−0.006
3	3	1	600.75	2335.91	8132.972	0.010
3	3	3	600.75	2335.91	8134.300	−0.000

$2F'$	$2F''$	$2M_F$	Voltage (V)	Field (V/cm) [b]	ν_{obs} (MHz)	$\nu_{obs-calc}$ (MHz)
5	3	1	500.73	1307.05	7969.409	0.000
5	3	3	500.73	1307.05	7969.208	−0.001
5	3	1	800.36	2089.17	7971.278	−0.003
5	3	3	800.36	2089.17	7970.766	0.005
1	3	1	500.73	1307.05	7840.167	0.003
1	3	1	800.36	2089.17	7841.686	0.001
1	3	1	1001.26	2613.57	7843.089	−0.002

[a] Septum spacing was 0.2571_8 cm, calibrated against OCS.
[b] Septum spacing was determined to be 0.3831 cm, using the dipole moment evaluated from the above measurements.

Table 2 b. Observed frequencies of Stark satellites of the $J = 1 - 0$ rotational transition of bromo(79)acetylene-d.

$2F'$	$2F''$	$2M_F$	Voltage (V)	Field (V/cm) [a]	ν_{obs} (MHz)	$\nu_{obs-calc}$ (MHz)
5	3	1	500.70	1306.97	7279.820	0.006
5	3	3	500.70	1306.97	7279.566	−0.001
5	3	1	700.95	1829.68	7281.225	0.007
5	3	3	700.95	1829.68	7280.736	0.007
5	3	1	902.11	2354.76	7283.097	−0.008
5	3	3	902.11	2354.76	7282.275	−0.006
3	3	1	500.70	1306.97	7441.694	0.001
3	3	3	500.70	1306.97	7442.198	0.003
3	3	1	800.11	2088.51	7443.089	0.007
3	3	3	800.11	2088.51	7444.370	0.001
1	3	1	301.45	786.87	7149.827	0.006
1	3	1	500.70	1306.97	7150.583	−0.001
1	3	1	1002.65	2617.20	7154.149	−0.002

[a] Septum spacing was 0.3831 cm.

Table 2c. Observed frequencies of Stark satellites of the $J=1-0$ rotational transition of bromo(81)acetylene-d.

$2F'$	$2F''$	$2M_F$	Voltage (V)	Field (V/cm) [b]	ν_{obs} (MHz)	$\nu_{obs-calc}$ (MHz)
5	3	1	500.67	1306.89	7244.746	0.001
5	3	3	500.67	1306.89	7244.503	0.001
5	3	1	801.96	2093.34	7246.992	split [c]
5	3	3	801.96	2093.34	7246.378	split [c]
3	3	1	500.67	1306.89	7379.822	0.000
3	3	3	500.67	1306.89	7380.346	0.011
3	3	1	801.96	2093.34	7381.234	0.009
3	3	3	801.96	2093.34	7382.553	0.005
3	3	1	1001.18	2613.36	7382.503	−0.007
3	3	3	1001.18	2613.36	7384.600	split [c]
1	3	1	500.67	1306.89	7136.642	0.001
1	3	1	801.96	2093.34	7138.497	−0.002
1	3	1	1001.18	2613.36	7140.182	−0.007

[b] Septum spacing was 0.3831 cm.

[c] These lines appeared doubled by the septum displacement and were not used for the fit.

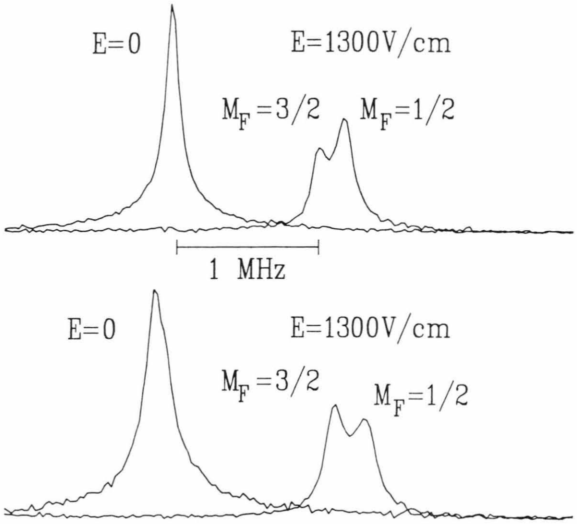

Fig. 1. Hyperfine components $J, F=1, 5/2-0, 3/2$ of bromo(79)-acetylene (upper traces) and deuterobromo(79)acetylene (lower traces) without DC electric field and with field of 1300 V/cm. Sample rate was 100 MHz, 2048 data points were supplemented by 2048 zeros prior to Fourier transformation. Zero field recordings are scaled to 200% to account for degeneracy of M_F-components. For each trace, $2 \cdot 10^6$ individual experiment cycles have been performed (lower right trace: $5 \cdot 10^6$ cycles).

(Table 3a) – which had already been thoroughly studied by Ebenstein et al. [10] –, and found again the same difference in the dipole moments. A similar value had also been found for fluoroacetylene [2, 3], and also for propyne [4].

Table 3a. Observed frequencies of Stark satellites of the $J=1-0$ rotational transition of chloro(35)acetylene.

$2F'$	$2F''$	$2M_F$	Voltage (V)	Field (V/cm) [a]	ν_{obs} (MHz)	$\nu_{obs-calc}$ (MHz)
5	3	1	250.46	973.87	11 374.083	−0.003
5	3	3	250.46	973.87	11 373.871	−0.009
5	3	1	300.34	1167.82	11 374.808	0.000
5	3	3	300.34	1167.82	11 374.523	−0.010
5	3	1	350.05	1361.11	11 375.651	0.002
5	3	3	350.05	1361.11	11 375.312	0.001
3	3	1	200.60	780.00	11 353.142	−0.001
3	3	3	200.60	780.00	11 353.557	−0.003
3	3	1	250.46	973.87	11 353.511	0.000
3	3	3	250.46	973.87	11 354.155	−0.002
3	3	1	300.34	1167.82	11 353.955	−0.006
3	3	3	300.34	1167.82	11 354.880	0.001
3	3	1	350.05	1361.11	11 354.494	0.006
3	3	3	350.05	1361.11	11 355.727	0.007
1	3	1	200.60	780.00	11 389.250	0.006

[a] Septum spacing was 0.2571_8 cm, calibrating against OCS.

Table 3b. Observed frequencies of Stark satellites of the $J=1-0$ rotational transition of chloro(35)acetylene-d.

$2F'$	$2F''$	$2M_F$	Voltage (V)	Field (V/cm) [a]	ν_{obs} (MHz)	$\nu_{obs-calc}$ (MHz)
5	3	1	150.76	586.20	10 378.654	0.006
5	3	3	150.76	586.20	10 378.551	−0.002
5	3	1	200.13	778.17	10 379.193	0.010
5	3	3	200.13	778.17	10 379.018	−0.005
5	3	1	250.45	973.83	10 379.879	0.002
5	3	3	250.45	973.83	10 379.642	−0.002
5	3	1	299.67	1165.22	10 380.696	−0.002
5	3	3	299.67	1165.22	10 380.398	0.004
3	3	1	200.13	778.17	10 358.768	−0.005
3	3	3	200.13	778.17	10 359.253	−0.001
3	3	1	250.45	973.83	10 359.191	−0.013
3	3	3	250.45	973.83	10 359.957	0.007
3	3	1	299.67	1165.22	10 359.724	0.007
3	3	3	299.67	1165.22	10 360.773	0.001
1	3	1	100.52	390.85	10 394.147	−0.001
1	3	1	180.86	703.24	10 394.724	0.001
1	3	1	250.45	973.83	10 395.481	−0.016
1	3	1	299.67	1165.22	10 396.208	0.001

[a] Septum spacing was 0.2571_8 cm, calibrated against OCS.

Results and Discussion

For the analysis, we set up the matrix of the Hamiltonian in the coupled basis $|JIFM_F\rangle$. This matrix is diagonal in M_F but not in J and F. Therefore, the Hamiltonian may be separated into individual M_F-blocks. Each M_F-block is set up simultaneously for both J values of the transition under investigation,

Table 4. Zero field recordings used to determine rotational and quadrupole coupling constants of HCCBr and HCCCl.

$2F'$	$2F''$	ν_{obs} (MHz)	$H-C\equiv C-{}^{79}Br$
5	3	7 968.207	B = 4000.069 MHz
3	3	8 130.612	eQq = 648.125 MHz
1	3	7 893.183	(c_I = 0.007 MHz fixed)
			$H-C\equiv C-{}^{35}Cl$
5	3	11 372.414	B = 5684.210 MHz
3	3	11 352.480	eQq = −79.740 MHz
1	3	–	(c_I = 0.0013 MHz fixed)

Table 5. Compilation of the molecular parameters determined in this work. The dipole moment of OCS has been taken from [14] to be 0.715196 D.

Species	Dipole moment [D]	Polarizability anisotropy [nm^3]
HCCI	0.02525(3)	0.0038(3)
DCCI	0.01290(7)	0.004 fixed
HCC^{79}Br	0.23006(4) 0.232(4) [15]	
DCC^{79}Br	0.24231(6)	
DCC^{81}Br	0.24216(9)	
HCC^{35}Cl	0.43992(14) 0.440079(1) [10]	
DCC^{35}Cl	0.45249(21)	

Table 6. Comparison of the isotope effect on the dipole moments (in Debye) of various acetylenic compounds.

Molecule	Dipole moment of		Difference
	deuterated species	parent species	
type $^+H-C\equiv C-X^-$			
HCCF (Laser Stark)	0.73292(2) [3]	0.7207(3) [2]	+0.0122(4)
HCC^{35}Cl**, $J=1-0$	0.45249(21) *	0.43992(14)*	+0.01257(25)
HCC^{79}Br, $J=1-0$	0.24231(6) *	0.23006(4)*	+0.01225(7)
type $^-H-C\equiv C-X^+$			
HCCI, $J=1-0$	0.01290(7) *	0.02525(3) *	−0.01235(8)
HCCCH$_3$**,			
$J=1-0$	0.7689 [4]	0.7804 [4]	−0.0115
$J=2-1$, $K=0$	0.7668 [4]	0.7809 [4]	−0.0141
HCCCD$_3$**, $J=1-0$	0.7722 [4]	0.7841 [4]	−0.0119

* This work.
** For these molecules, the sign of the dipole moment has been determined using the Zeeman-effect.

considering the matrix elements of the rigid rotor contribution, the centrifugal distortion, the nuclear spin interaction, the electric dipole interaction and the polarizability anisotropy. After diagonalization of the Hamiltonian matrix, the eigenvalues are matched to the J and F quantum numbers according to the resulting eigenvectors.

During the fits of the dipole moments (and, in the case of HCCI, the polarizability anisotropy), the rotational constants, centrifugal distortion constants, quadrupole coupling constants, and spin-rotation coupling constants have been held fixed. The values for these constrained parameters have been taken from [6], [7] and [11], or have been determined from zero field recordings during the course of this work (see Table 4). We used the transition frequencies of the individual Stark components rather than the Stark displacements. The prediction and fitting programme is described in more detail in [8]. The dipole moments determined in this work are summarized in Table 5.

In [4], Muenter et al. have compared the dipole moments of a variety of deuterated species to those of their parent compounds, and have found isotopic effects of the order of 0.01 Debye for most, but not all of them. In particular, they found an isotopic decrease of ~0.012 D upon acetylenic deuteration of propyne and propyne-d$_3$. If we confine our argument on acetylenic protons, we can now state that for all of these, the isotopic effect on the dipole moment is very nearly the same in size. However, while deuteration of iodoacetylene also results in a decrease of the dipole moment, there is an increase for bromo- and chloroacetylene (and, according to [2] and [3], for fluoroacetylene). For chloroacetylene, the sign of the dipole moment has been determined by Allen et al. [12] from the Zeeman effect, and found to have the positive charge at the hydrogen atom. On the other hand, Shoemaker et al. [13] have determined the orientation of the molecular dipole moment in propyne from Zeeman effect studies on CH$_3$CCD and CD$_3$CCH. According to their results, in this case the acetylenic hydrogen is located at the negatively charged end of the molecule. It is highly likely that the same applies to iodoacetylene, whereas the opposite is true in the case of bromo-, chloro-, and fluoroacetylene. A compilation of the dipole moments of various acetylenic compounds and their deuterated species is presented in Table 6.

Acknowledgements

We thank M. Andolfatto for the preparation of the samples, and our mechanics workshop for manufacturing the Stark cells and many other important parts of our spectrometers. – Funds provided by the Deutsche Forschungsgemeinschaft, the Fonds der Chemie, and the Land Schleswig-Holstein are gratefully acknowledged. The calculations were carried out at the computer center of the Universität Kiel.

[1] V. W. Laurie and D. R. Herschbach, J. Chem. Phys. **37,** 1687 (1962).
[2] T. Tanaka, C. Yamada, and E. Hirota, J. Mol. Spectrosc. **63,** 142 (1976).
[3] K. Matsumura, K. Tanaka, C. Yamada, and T. Tanaka, J. Mol. Spectrosc. **80,** 209 (1980).
[4] J. S. Muenter and V. W. Laurie, J. Chem. Phys. **45,** 855 (1966).
[5] E. Schäfer and J. J. Christiansen, J. Mol. Struct. **97,** 101 (1983).
[6] N. Heineking, M. Andolfatto, C. Kruse, W. Eberstein, and H. Dreizler, Z. Naturforsch. **43a,** 755 (1988).
[7] N. Heineking, M. Andolfatto, U. Keussen, A. Mues, and H. Dreizler, Z. Naturforsch. **44a,** 735 (1989).
[8] J. Gripp and H. Dreizler, Z. Naturforsch. **43a,** 133 (1988).
[9] E. Fliege and H. Dreizler, Z. Naturforsch. **42a,** 72 (1987).
[10] W. L. Ebenstein, C. Hanning, S. L. Shostak, and J. S. Muenter, J. Chem. Phys. **87,** 1948 (1987).
[11] U. Andresen, N. Heineking, and H. Dreizler, J. Mol. Spectrosc., to be published.
[12] W. C. Allen and W. H. Flygare, Chem. Phys. Lett. **15,** 461 (1972).
[13] R. L. Shoemaker and W. H. Flygare, J. Amer. Chem. Soc. **91,** 5417 (1969).
[14] K. Tanaka, H. Ito, K. Harada, and T. Tanaka, J. Chem. Phys. **80,** 5893 (1984).
[15] H. Jones, J. Sheridan, and O. L. Stiefvater, Z. Naturforsch. **32a,** 866 (1977).