Molecular g-Values and Magnetic Susceptibility Anisotropy Parameters of D_2-Ketene. Sign of the Dipole Moment of Ketene

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The rotational Zeeman-effect of D_2CCO has been observed under high resolution. In addition to g-factors and susceptibility anisotropies the sign of the electric dipole moment has been determined after having remeasured the same parameters for normal ketene under identical conditions.

Molecular g-values and magnetic susceptibility anisotropies have been measured for ketene by several workers [1–4]. However no work has been reported on similar measurements for dideuteroketene (D_2C_2O). We have measured the g-factors and magnetic susceptibility anisotropies for D_2C_2O and determined the sign of the dipole moment.

Dideuteroketene prepared from hexadeuteroacetone by L. Nemes using a modified Williams-Hurd ketene lamp, was kindly made available to us by M. Winnewisser. The Zeeman measurements were carried out in the frequency range from 20 to 70 GHz using phase stabilized BWO's ** as radiation sources and a conventional 33 KHz Stark modulated spectrometer as described elsewhere [5]. The absorption cell was cooled to $-70\,^{\circ}$C.

Five of the measured lines given in Table 1 were found to present a convenient measurable effect with the application of the magnetic field in both $\Delta M = 0$ and $\Delta M = \pm 1$ cases. They are: $0_{00} - 1_{01}$, $1_{10} - 2_{11}$, $1_{11} - 2_{12}$, $2_{11} - 3_{12}$ and $2_{12} - 3_{13}$. Some of the observed Zeeman splittings with the corresponding magnetic fields along with the calculated g-values and magnetic susceptibility anisotropies are listed in Table 2. The molecular Zeeman effect equations used to fit these splittings are given by Hüttner and Flygare [6]. In order to determine the sign of the electric dipole moment for ketene we found it necessary to remeasure the g-values for normal ketene [3–4] under identical conditions. Table 4 lists these measurements. The sign of the g-factors have been determined by using the method described in a recent work [12, 13] which can be summarized as follows: By means of INDO wavefunctions [14] it is possible to determine the ground state expectation values for the sums of the squares of the electron coordinates. These values combined with the measured susceptibility anisotropies α, β and with the gas-phase bulk susceptibility $\overline{\chi}$ permit to determine the molecular g-factors and their relative signs. In this paper we assume a value for the gas bulk susceptibility as determined by Pascal rule [15] or by the method described in Reference [16]. In Table 5 the measured g-factors and the relative signs are compared with those calculated using different values of the bulk susceptibility $\overline{\chi}$. The signs are in agreement with those reported by Hüttner and alias [4].

Table 1. Frequency in MHz of the observed transition in D_2CCO. Transitions labeled with * have been used for the Zeeman investigations.

Transition	Obs. Frequency
$0_{00}-1_{01}$	17 673.528 *
$1_{11}-2_{12}$	34 777.559 *
$1_{10}-2_{11}$	35 913.804 *
$2_{02}-3_{03}$	53 013.036
$2_{12}-3_{13}$	52 165.079 *
$2_{11}-3_{12}$	53 869.419 *
$2_{20}-3_{21}$	53 019.845
$2_{21}-3_{22}$	53 012.583

For the determination of the sign of the electric dipole moment the Eq. (1) [7–9]

$$\frac{g_{aa}^{D}}{A^{D}} - \frac{g_{aa}^{H}}{A^{H}} = -\frac{8\pi M_p}{\hbar |e|}(\Delta b\,\mu_b + \Delta c\,\mu_c) \qquad (1)$$

and the cyclic permuted ones have been used. The molecular parameters needed for this determination are listed in Table 6. The resulting electric dipole moment, reported in Table 7, is found to be with

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** (with point-contact multipliers for the frequencies over 54 GHz).

Table 2. Molecular g-values and magnetic susceptibility anisotropy parameters of d_2-ketene. The listed data are only part of the 54 observations used for the least square fitting procedure. The errors given on the results are standard errors of this procedure. $\alpha = 2\chi_{aa} - \chi_{bb} - \chi_{cc}$, $\beta = 2\chi_{bb} - \chi_{cc} - \chi_{aa}$. Fields are in KGauss and frequencies in KHz.

Transition	Field	M1	M2	Frequency Observed	Difference Calculated	Delta (Obs-Cal)
$0_{00}-1_{01}$	25588	0	0	58	56	2
$0_{00}-1_{01}$	24521	0	1	495	497	−2
		0	−1	−551	−549	−2
$1_{10}-2_{11}$	25588	−1	−1	1229	1218	11
		0	0	64	56	8
		1	1	−1277	−1272	−5
$1_{10}-2_{11}$	24510	−1	0	2317	2333	−16
		0	1	1193	1216	−23
		1	2	−47	−54	7
		−1	−2	0	2	−2
		0	−1	−1131	−1114	−17
		1	0	−2398	−2382	−16
$1_{11}-2_{12}$	25588	−1	−1	1282	1264	18
		0	0	59	41	18
		1	1	−1210	−1226	16
$1_{11}-2_{12}$	24550	−1	0	2296	2301	−5
		0	1	1102	1092	10
		1	2	−144	−157	13
		−1	−2	91	83	8
		0	−1	−1031	−1054	23
		1	0	−2243	−2230	−13
$2_{11}-3_{12}$	25563	−2	−2	617	623	−6
		−1	−1	319	318	1
		0	0	11	9	2
		1	1	−299	−304	5
		2	2	−607	−621	14
$2_{12}-3_{13}$	25567	−2	−2	656	661	−5
		−1	−1	326	326	0
		0	0	0	7	−7
		1	1	−297	−296	−1
		2	2	−572	−583	11

$g_{aa} = -0.2195 \pm 0.0005$, $\alpha = -5.15 \pm 0.5\ 10^{-6}$ erg/G²·mole,
$g_{bb} = -0.0329 \pm 0.0005$, $\beta = 0.13 \pm 0.4\ 10^{-6}$ erg/G²·mole.
$g_{cc} = -0.0230 \pm 0.0005$,

Table 3. Frequency in MHz of the observed transitions in H_2CCO. All these transitions have been used for the Zeeman investigation.

Transition	Obs. Frequency
$0_{00}-1_{01}$	20 209.214
$1_{11}-2_{12}$	40 039.061
$1_{10}-2_{11}$	40 793.837
$2_{12}-3_{13}$	60 058.089
$2_{11}-3_{12}$	61 190.308

Table 4. Molecular g-values and magnetic susceptibility anisotropy parameters of ketene. The listed data are only part of the 58 observations used for the least square fitting procedure. The errors given on the results are standard errors of this procedure. Fields are in KGauss and frequencies in KHz.

Transition	Field	M1	M2	Frequency Observed	Difference Calculated	Delta (Obs-Cal)
$0_{00}-1_{01}$	25739	0	0	62	61	1
$1_{11}-2_{12}$	23982	−1	−1	2458	2465	−7
		0	0	39	38	1
		1	1	−2421	−2428	7
$1_{11}-2_{12}$	19032	−1	−1	1954	1953	1
		0	0	14	24	−10
		1	1	−1933	−1930	−3
$1_{10}-2_{11}$	23982	−1	−1	2423	2420	3
		0	0	50	53	−3
		1	1	−2495	−2472	−23
$1_{10}-2_{11}$	25739	−1	−1	2604	2595	9
		0	0	63	61	2
		1	1	−2680	−2656	−24
$2_{12}-3_{12}$	25916	−2	−2	1356	1366	−10
		−1	−1	673	678	−5
		0	0	13	7	6
		1	1	−640	−644	4
		2	2	−1275	−1278	3
$2_{11}-3_{12}$	25916	−2	−2	1320	1322	−2
		−1	−1	672	669	3
		0	0	15	10	5
		1	1	−657	−653	−4
		2	2	−1315	−1322	7
$0_{00}-1_{01}$	24510	0	1	545	546	1
		0	−1	−602	−601	−1
$1_{11}-2_{12}$	14671	−1	0	2556	2572	−16
		0	1	1060	1068	−8
		1	2	−429	−449	20
		−1	−2	424	421	3
		0	−1	−1038	−1054	16
		1	0	−2559	−2543	16

$g_{aa} = -0.4322 \pm 0.0004$, $\alpha = -5.53 \pm 0.4\ 10^{-6}$ erg/G²·mole,
$g_{bb} = -0.0362 \pm 0.0007$, $\beta = 0.03 \pm 0.3\ 10^{-6}$ erg/G²·mole.
$g_{cc} = -0.0252 \pm 0.0005$,

Table 5. g-Factors calculated for two different values of the bulk susceptibility $\overline{\chi}$ in comparison with the measured ones. $\overline{\chi}$ values are in 10^{-6} erg/G²·mole.

	Calculated		Measured (this paper)
g_{aa}	−1.204	−0.410	-0.4322 ± 0.0004
g_{bb}	−0.068	−0.039	-0.0362 ± 0.0007
g_{cc}	−0.061	−0.033	-0.0252 ± 0.0005
$\overline{\chi}$	−16 *	−22 **	—

* Obtained by applying the Pascal-rule considering the value of the bulk susceptibility for the ethylene and carbon-mono-oxide. The same value can be obtained using the method proposed in [16].

** Corrected value to reproduce the measured g-factors.

Table 6. Molecular Parameters for H_2CCO and D_2CCO.

	Molecular Parameters	
d_2-Ketene	$A = 141502$ MHz $B = 9121.239$ MHz $C = 8552.294$ MHz	a
Ketene	$A = 282081.$ MHz $B = 10293.972$ MHz $C = 9915.240$ MHz	b

Δa = (Change in center of mass along the C=O bond) 0.0829 Å [c].
$\mu = 1.414 \pm 0.01$ D [d].

[a] M. Winnewisser, private Communication.
[b] J. W. C. Johns, S. M. R. Stone, and G. Winnewisser, J. Mol. Spectr. **42**, 523 [1972].
[c] Structure used in the calculation is from R. A. Beaudet, Dissertation, Harvard University 1961.
[d] H. E. Johnson and M. W. P. Strandberg, J. Chem. Phys. **20**, 687 [1952].

the negative end on the oxygen atom and with the positive end on the carbon atom.

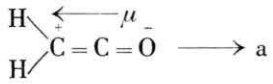


Table 7. Results from the application of formula (1).

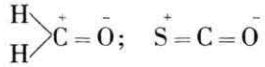
From g^{D}_{bb} and g^{H}_{bb} $\mu = -1.4 + 0.7$ D,
from g^{D}_{cc} and g^{H}_{cc} $\mu = -2.2 + 0.9$ D.

Using the formula (1) with g^{D}_{aa} and g^{H}_{aa} the result should be zero. We obtain

$$\left(\frac{g^{D}_{aa}}{A^{D}} - \frac{g^{H}_{aa}}{A^{H}}\right)\frac{\hbar\,|e|}{8\pi M_p} = -0.024 \text{ D Å}.$$

This value can be taken as crosscheck for this calculations.

As the direction going from C-atom to O-atom was considered as positive, the sign of the dipole moment will be therefore negative. This result is consistent with that obtained for other molecules containing the C = O group [10–11]:



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