

## Dipole Moments of Methyl-Substituted Cyclohexanone

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The structure of cyclohexanone from electron diffraction study and microwave spectrum has been reported previously.<sup>1-3</sup> The dipole moment of cyclohexanone was measured to be 2.87 (4) Debye from the Stark displacements of a few microwave transitions.<sup>2</sup> The geometry of cyclohexanone was further improved by least-squares analysis of both by the gas-phase electron diffraction and microwave data.<sup>3</sup> The heavy atom structural parameters for the chair form of its ground state are reported.<sup>4</sup> The Microwave spectra of 4-thiacyclohexanone in the ground state and eight vibrationally excited states have also been studied and the data are consistent with a chair conformation for the ring.<sup>5</sup>

The microwave spectrum of 3-methylcyclopentanone has been studied and the dipole components  $|\mu_a| = 2.97(2)$ ,  $|\mu_b| = 1.00(3)$ ,  $|\mu_c| = 0.18(5)$ , and  $|\mu_{tot}| = 3.14(3)$  D were reported.<sup>6</sup> These were consistent with a twisted-ring conformation with a methyl group in the equatorial position. The conformation of 3-, 4-methyl cyclohexanone in its ground state has been reported to be a chair form with the methyl group in the equatorial position.<sup>7,8</sup>

The resonance enhanced multiphoton ionization (REMPI) method has been applied to methyl- and ethyl- derivatives of cyclohexanone to investigate the various conformers as well as cyclic ketone and cyclic ether including oxygen.<sup>9-11</sup> The structural information was compared with *ab initio* density functional theory to calculate not only the structure of cyclohexanone, but the vibrational spectra of isotopomers of cyclohexanone as well. The information was compared with electron diffraction structure and liquid-phase IR spectra.<sup>12</sup>

The dominant conformations of methyl cyclohexanone and their interconversion rate at room temperature in which the methyl group is either axial or equatorial to the six membered rings have been also reported as well as the interconversion rate of ethyl rotor of ethylcyclohexanone.<sup>13</sup>

While the dipole moments of 3- and 4-methylcyclohexanones are reported previously, the dipole moment of 2-methylcyclohexanone has not been reported.<sup>14-16</sup> In this paper, the dipole moment of 2-methylcyclohexanone has been measured using the second-order Stark effects in the microwave region.

Since all the experimental dipole moments for the methyl-substituted cyclohexanones are reported, these are compared with those calculated using Gaussian03.<sup>17</sup> The geometric parameters of each molecule were calculated by applying the Møller-Plesset (MP2) perturbation theory, 6-311++G(2d,2p) basis set.

The induced dipole moments of the methyl, ethyl cyclohexa-

none are calculated on the assumption that the dipole moment is located mostly at the C=O bond and the values of induced dipole moments are relatively in good agreement with the *ab initio* results.

### Experimental

The rotational spectrum of 2-methylcyclohexanone was measured by using Fourier Transform Microwave Spectrometer (FTMS) with a pulsed gas nozzle described previously.<sup>18-20</sup> The sample was purchased from Aldrich Chemical Company. About 1 - 2 atm of Ar gas was bubbled through a liquid sample of 2-methylcyclohexanone placed just upstream of a pulsed gas valve. The nozzle is perpendicular to the microwave cavity axis and typical linewidth of about 20 kHz (FWHM) resulting from Doppler broadening were observed and center frequencies were reproducible to  $\pm 2$  kHz. Two parallel plates supplied DC voltage was chosen for the Stark electric field. To determine the dipole moment, DC voltages of up to  $\pm 8$  kV were applied with opposite polarities to two steel-mesh parallel plates that were 30 cm apart, straddling the microwave cavity. At each voltage, a Stark-shifted transition of 2-methylcyclohexanone and OCS were measured sequentially. The calibration of the electric field was performed using the frequency shift of  $\Delta M_J = 0$  component of OCS transition ( $J = 0 - 1$ )<sup>21</sup> and the dipole moment of OCS of 0.71519 (3) D reported by Reinartz.<sup>22</sup>

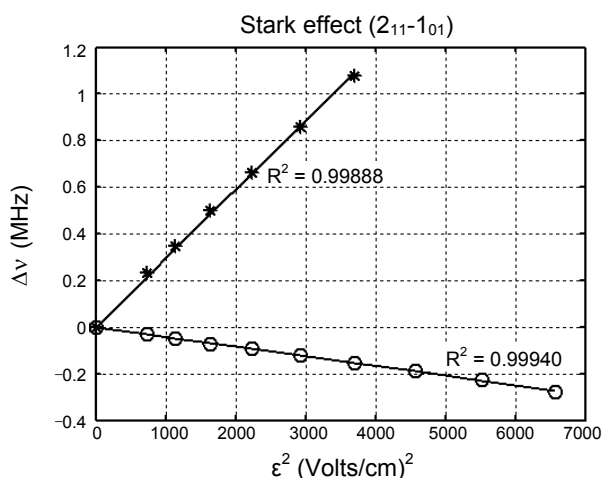
### Results

The rotational spectrum of 2-methylcyclohexanone in the frequency region from 5 to 18 and 18 to 26.5 GHz was observed and analyzed to determine the spectroscopic constants using by a Watson A-reduced Hamiltonian<sup>23</sup> in the ground state.<sup>16</sup> Table 1 summarizes all the rotational and distortion constants of substituted cyclohexanones reported so far in its ground state. The second-order Stark effects ( $\Delta v/\epsilon^2$ ) for 8 M components from 3 transitions of 2-methylcyclohexanone were obtained and shown in Fig. 1. The experimental values of  $\Delta v/\epsilon^2$  are listed in Table 2. All the dipole moment components are calculated from the least-squares fit of  $\Delta v/\epsilon^2$  using the second-order coefficients given in Table 3. The dipole components of  $|\mu_a| = 2.168$ ,  $|\mu_b| = 1.932$ ,  $|\mu_c| = 0.997$  and  $|\mu_{tot}| = 3.070$  D is obtained for the 2-methylcyclohexanone. The dipole moments for other derivatives of cyclohexanone are also listed in Table 3 for comparison. The dipole components show that the geometric conformers of substituted cyclohexanone in the position of  $\alpha$ ,  $\beta$ , and  $\gamma$  are

**Table 1.** Spectroscopic constants for methyl, ethyl derivatives of cyclohexanone (MHz)

	CHO	2-MCHO	3-MCHO	4-MCHO	4-ECHO
A	4197.67	2875.29379 (21)	3091.53436 (23)	4034.31770 (58)	3660.3669 (20)
B	2503.86	1999.33928 (13)	1720.95803 (12)	1455.47596 (20)	931.6707 (3)
C	1754.97	1299.18958 (13)	1204.69635 (13)	1174.07431 (22)	796.8889 (3)
D <sub>J</sub>		0.0001268 (24)	0.00010687 (18)	0.0001422 (23)	0.000053 (4)
D <sub>JK</sub>		0.0003295 (38)	0.00023839 (51)	0.0009288 (80)	-0.000301 (14)
D <sub>K</sub>		0.0000264 (65)	-0.00023198 (70)	-0.0032980 (65)	0.002293 (421)
d <sub>1</sub>		0.0000178 (6)	-0.00001992 (65)	-0.0000060 (11)	
d <sub>2</sub>		0.0003088 (24)	-0.00000947 (21)	-0.0000016 (5)	

All the values are in MHz and uncertainties given in parentheses represent one standard deviation in the least-squares fit. <sup>a</sup>Reference 3. <sup>b</sup>Reference 16. <sup>c</sup>Reference 15. <sup>d</sup>Reference 14. <sup>e</sup>Reference 24.

**Figure 1.** Observed 2nd order Stark effect for the 2<sub>11</sub>-1<sub>01</sub> transition.**Table 2.** Measured Stark Coefficients of 2-methylcyclohexanone

Transition	M	Δv/ε <sup>2a</sup>	obs-calc <sup>b</sup>
2 <sub>11</sub> -1 <sub>01</sub>	0	-0.4156	-0.01856
2 <sub>11</sub> -1 <sub>01</sub>	1	2.9520	0.00314
3 <sub>13</sub> -2 <sub>02</sub>	0	-0.06317	0.00008
3 <sub>13</sub> -2 <sub>02</sub>	1	1.5810	-0.02627
3 <sub>13</sub> -2 <sub>02</sub>	2	6.6280	0.01098
3 <sub>13</sub> -2 <sub>12</sub>	0	-0.03149	0.00043
3 <sub>13</sub> -2 <sub>12</sub>	1	0.5071	0.00616
3 <sub>13</sub> -2 <sub>12</sub>	2	2.0760	-0.02389

<sup>a</sup>Observed second order Stark coefficients (Δv/ε<sup>2</sup>) in units of 10<sup>-4</sup> MHz/(V/cm)<sup>2</sup>. <sup>b</sup>Calculated Stark coefficients with dipole components of |μ<sub>a</sub>| = 2.168(21), |μ<sub>b</sub>| = 1.932(13), |μ<sub>c</sub>| = 0.997(2) and |μ<sub>tot</sub>| = 3.070(17) D.

in agreement with the chair conformers with the substituted group in equatorial position and this result is consistent with the analysis of REMPI spectra.<sup>7,8</sup> The calculated dipole moments from *ab initio* MP2 method with 6-311++g (2d,2p) basis set are also listed in Table 3 and they are consistent within a few hundredth of Debye. The experimental dipole moments from 3.07 D for 2-methylcyclohexanone to 3.32 D for 4-ethylcyclohexanone show a nice trend of methyl- and ethyl- substitution effects on the cyclohexanone.

According to Jose L. Alonso's unpublished data, the dipole moment of cyclohexanone was μ<sub>a</sub> = 3.102 D, μ<sub>c</sub> = 0.955 D and

**Table 3.** Experimental dipole moments of cyclohexanone and methyl, ethyl derivatives of cyclohexanone (uncertainties given in parentheses)

	CHO <sup>a</sup>	2-MCHO <sup>b</sup>	3-MCHO <sup>c</sup>	4-MCHO <sup>d</sup>	4-ECHO <sup>e</sup>
μ <sub>a</sub>	3.102	2.168 (21)	2.527 (1)	3.032 (5)	3.11058 (0082)
μ <sub>b</sub>	-	1.932 (13)	1.795 (3)	-	0.48085 (0601)
μ <sub>c</sub>	0.955	0.997 (2)	0.836 (5)	1.207 (14)	1.05935 (0230)
μ <sub>tot</sub>	3.246	3.070 (17)	3.210 (2)	3.263 (7)	3.32102 (0137)
μ <sub>calc</sub> <sup>f</sup>	3.269	3.076	3.246	3.298	3.364

<sup>a</sup>Reference 5. <sup>b</sup>Reference 16. <sup>c</sup>Reference 15. <sup>d</sup>Reference 14. <sup>e</sup>Reference 24. <sup>f</sup>*ab initio* calculation results calculated by applying the Møller-Plesset (MP2) perturbation theory, 6-311++G(2d,2p) basis set.

**Table 4.** Projected dipole moment of substituted cyclohexanone. (μ<sub>c=O</sub> = 3.246 D)<sup>a</sup>

	CHO <sup>b</sup>	2-MCHO	3-MCHO	4-MCHO	4-ECHO
μ <sub>a</sub>	3.102	2.185 (0.017)	2.523 (0.004)	2.931 (0.101)	2.890 (0.221)
μ <sub>b</sub>	-	1.972 (0.040)	1.706 (0.089)	-	0.451 (0.030)
μ <sub>c</sub>	0.955	1.369 (0.372)	1.124 (0.228)	1.395 (0.188)	1.408 (0.349)
μ <sub>ind</sub> <sup>c</sup>		-0.375	-0.301	0.213	0.414

<sup>a</sup>Induced dipole components are in parentheses. <sup>b</sup>Experimental dipole moments of cyclohexanone from L. Jose, Alonso, unpublished data. <sup>c</sup>Induced dipole moment with μ<sub>c=O</sub> = 3.246 D.

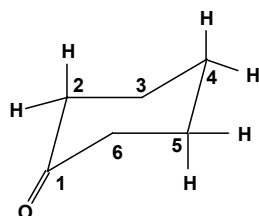
μ<sub>tot</sub> = 3.246 D.<sup>4</sup> All the results show that the dipole moment of cyclohexanone is most likely to be 3.246 D instead of 2.87 D as reported in Reference 2.

Since the dipole moment of cyclohexanone is located mostly at the carbonyl bond, and the bond moment of μ<sub>c=O</sub> = 3.246 D was assumed and projected to the principal axis of the methyl-substituted cyclohexanones to give μ<sub>ap</sub> = 2.185 D, μ<sub>bp</sub> = 1.972 D, μ<sub>cp</sub> = 1.369 D for 2-methyl cyclohexanone. The induced dipole moment can be calculated by comparing the projected dipole component with the experimental value. In the same way, the C=O bond dipole moment was projected to the principal axis for other derivatives and the induced dipole moments are given in parentheses in Table 4. The difference between the experimental dipole moment in Table 4 and projected dipole components is mostly from the substituted group attached at the ring

**Table 5.** Structural parameters for cyclohexanone<sup>a</sup>

	CHO <sup>b</sup>	2-MCHO (MP2)	3-MCHO (MP2)	4-MCHO (MP2)	4-ECHO (MP2)
C1-O	1.222 (1.229)	1.222	1.222	1.222	1.222
C1-C2	1.513 (1.503)	1.513	1.512	1.512	1.512
C2-C3	1.536 (1.542)	1.536	1.536	1.535	1.536
C3-C4	1.527 (1.545)	1.527	1.527	1.528	1.529
O-C1-C2	122.60 (122.35)	122.40	122.67	122.66	122.72
C6-C1-C2	114.77 (115.30)	114.98	114.70	114.65	114.50
C1-C2-C3	110.20 (111.50)	109.84	109.93	110.20	110.43
C2-C3-C4	110.02 (110.80)	110.74	111.05	111.93	111.91
C3-C4-C5	111.02 (110.80)	110.79	111.68	109.73	109.56
O-C1-C2-C3	124.66 (128.30)	121.67	124.38	125.13	124.98
C6-C1-C2-C3	53.32 (51.70)	55.74	53.31	52.87	52.99
C1-C2-C3-C4	54.28 (53.00)	54.75	53.92	54.38	54.37
C2-C3-C4-C5	57.62 (56.30)	56.76	57.65	57.05	56.71

<sup>a</sup>*ab initio* calculation results calculated by applying the Møller-Plesset (MP2) perturbation theory, 6-311++G(2d,2p) basis set. <sup>b</sup>Experimental structural parameters are in parentheses.

**Figure 2.** Definition of structural parameters for cyclohexanone.

in the equatorial position. These induced moments of all the substituted cyclohexanones are listed in parentheses in Table 4. The induced dipole moments from 0.213 D for 4-methylcyclohexanone to 0.414 D for 4-ethylcyclohexanone<sup>24</sup> are reasonable considering the methyl group effect.

To compare the structural parameters, *ab initio* method using various basis sets were tried and the MP2 method with 6-311++G(2d,2p) basis set produced the best experimental geometry of cyclohexanone. The numbering scheme is defined in Fig. 2 and the calculated structural parameters are listed in Table 5. All the structural parameters for the six membered ring parts are very close and are consistent with the structures from the previous studies.<sup>7, 8, 14-16</sup> The structural similarity from the heavy atom parts of the cyclohexanone between the derivatives also supports that the induced moments are from the methyl- and ethyl-substitutions.

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