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Dipole Moment of 3-Methylcyclohexanone

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The structures of methyl- and ethyl- derivatives of cyclohexanone have been studied using a variety of methods.[1-3] The microwave spectra of 4-, 3- and 2-methylcyclohexanone for the ground state and a few excited states have been observed and analyzed in the frequency region of 18.0 GHz to 26.5 GHz.[1,3-5] The methyl group internal rotation has not been seen in either molecule, and a minimum of 2.5 kcal/mol for the rotational barrier height was assumed for 4-methylcyclohexanone.

There have been some resonance enhanced multiphoton ionization (REMPI) studies of methyl- and ethyl- derivatives of cyclohexanone and cyclopentanone molecules.[6] In addition to microwave spectrum, there has been employed REMPI (resonance enhanced multi photon ionization) method to investigate the conformers of methyl- and ethyl-substituted cyclic ketone and cyclic ether including oxygen. In [2+1] REMPI process, molecule occurs (3s ← n) Rydberg transition so that transition origin is shifted to blue or red depending on the position and the orientation of substituent on the ring. An *ab initio* density functional theory has been applied to calculate not only the structure of cyclohexanone, but the unpolarized vibrational spectra of isotopomers of cyclohexanone as well.[7] The structural information was compared with electron diffraction structure and liquid-phase IR spectra.[8,9]

The microwave spectrum of 4-ethylcyclohexanone is also reported and confirmed the structure of its ground state.[10] To measure the dipole moment of 3-methylcyclohexanone in the gas phase, the rotational spectrum of 3-methylcyclohexanone in the ground state is measured in the frequency region of 5 GHz to 18 GHz. The improved spectroscopic constants and dipole moment of 3-methylcyclohexanone are reported in this paper.

Experimental

The rotational spectrum of 3-methylcyclohexanone was measured by using FTMS (Fourier Transform Microwave Spectrometer) with a pulsed gas nozzle described previously.[11,12] The sample of 3-methylcyclohexanone was obtained from Aldrich Company. About 1 - 2 atm of Ar gas was bubbled through a liquid sample of 3-methylcyclohexanone just upstream of a pulsed gas valve. The nozzle is perpendicular to the microwave cavity axis and typical linewidths of about 20 kHz (FWHM) resulting from Doppler broadening were observed and center frequencies were reproducible to ±2 kHz. Two parallel plates supplied DC voltage up to 8 kV was chosen for the Stark electric field.

Result

Thirty-two *a*-type, forty-two *b*-type, and fourteen *c*-type transitions have been observed and listed in Table 1. The rotational and centrifugal distortion constants were fit using a Watson S-reduced Hamiltonian,[13]

$$H = \{(B+C)/2\} P^2 + \{A-(B+C)/2\} P_z^2 + \{(B-C)/2\} (P_x^2 - P_y^2) - D_J P^4 - D_{JK} P^2 P_z^2 - D_K P_z^4 + d_1 P^2(P_+^2+P_-^2) + d_2 (P_+^4+P_-^4),$$

where A, B, C are the rotational constants, D_J *etc* are five P4 centrifugal distortion constants. The fitted spectroscopic constants are shown in Table 2.

The second-order Stark effects were measured on 8 M components of 3 transitions 2_{11}-1_{01}, 3_{03}-2_{02}, and 3_{13}-2_{12}. Perturbation theory to second order is sufficient to account for the Stark splitting with the accuracy of most measurements which are made with an imposed field of a few thousand volts/centimeter. When there is no 1st order effect, one often finds it advantageous to apply several thousand volts/centimeter to obtain sufficiently large displacements for precise measurement of Δν. To determine the dipole moment, DC voltages of up to +/−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 3-ethylcyclohexanone and OCS were measured sequentially as a function of electric field. The calibration of the electric field was performed using the frequency shift of $\Delta M_J = 0$ component of OCS transition (J = 0-1) and the dipole moment of OCS (0.71521 D) reported by Muenter.[14,15] The second-order Stark effects ($\Delta\nu/\varepsilon^2$) for 8 M components from 3 transitions of 3-methylcyclohexanone were determined. The second-order Stark effects for 2 M_J components of 2_{11}-1_{01} transition were shown in Figure 1. A least-squares fit of $\Delta\nu/\varepsilon^2$ using the calculated second-order coefficients gave $|\mu_a| = 2.527(1)$, $|\mu_b| = 1.795(3)$, $|\mu_c| = 0.836(5)$, and $|\mu_{tot}| = 3.210(2)$ D. The experimental values of $\Delta\nu/\varepsilon^2$ are listed in Table 3. The measured $\Delta\nu/\varepsilon^2$ are in good agreement with the calculated.

The induced dipole moment of the methyl group is calculated assuming that the carbonyl group is the major contributor to the dipole moment of the molecule. The calculated induced dipole moment of the methyl group is 0.382 D using the simple vector model and the dipole moment of cyclohexanone (3.246 D). The dipole moment of 3-methylcyclohexanone is compared with that of 4-methylcyclohexanone (3.263 D).[4] The introduc-

Table 1. Observed transition frequencies for 3-methylcyclohexanone

Transition ($J'K'_pk'_o - J''K''_pk''_o$)		ν_{obs}[a]	$\Delta\nu_{obs-calc}$[b]	Transition ($J'K'_pk'_o - J''K''_pk''_o$)		ν_{obs}[a]	$\Delta\nu_{obs-calc}$[b]
a-type				b-type			
2 0 2	1 0 1	5730.8043	0.0021	4 4 1	4 3 2	11231.4502	−0.0013
2 1 2	1 1 1	5335.0447	0.0014	4 4 0	4 3 1	11110.7329	0.0006
2 1 1	1 1 0	6367.5666	0.0012	5 1 5	4 0 4	13252.0526	0.0007
3 0 3	2 0 2	8332.7415	−0.0032	5 0 5	4 1 4	12830.3222	−0.0033
3 1 3	2 1 2	7934.3190	−0.0019	5 1 4	4 2 3	12608.9286	−0.0006
3 1 2	2 1 1	9464.9343	−0.0012	5 2 3	4 3 2	8853.7843	−0.0044
3 2 2	2 2 1	8776.9456	−0.0012	5 1 4	5 0 5	7415.4367	0.0006
3 2 1	2 2 0	9221.1521	0.0003	5 2 4	5 1 5	9037.1758	0.0017
4 0 4	3 0 3	10759.5890	0.0008	5 3 3	5 2 4	9029.9180	−0.0002
4 1 4	3 1 3	10473.8916	0.0039	5 3 2	5 2 3	6494.1525	−0.0003
4 1 3	3 1 2	12434.1134	0.0017	5 4 2	5 3 3	11237.4349	−0.0011
4 2 3	3 2 2	11607.5865	−0.0018	5 4 1	5 3 2	10798.1006	0.0004
4 2 2	3 2 1	12548.3285	0.0022	5 5 1	5 4 2	14412.4121	0.0050
4 3 2	3 3 1	11898.7559	0.0006	5 5 0	5 4 1	14392.7596	−0.0034
4 3 1	3 3 0	12003.5690	0.0012	6 1 6	5 0 5	15543.0514	0.0008
4 1 3	4 1 4	5039.6271	0.0048	6 1 5	5 2 4	15992.7168	0.0032
5 0 5	4 0 4	13121.0148	−0.0031	6 2 4	5 3 3	12986.0496	0.0054
5 1 5	4 1 4	12961.3622	0.0028	6 3 3	5 4 2	7822.2510	0.0020
5 1 4	4 1 3	15206.1412	0.0020	6 1 5	6 0 6	9672.7812	0.0004
5 2 4	4 2 3	14361.7021	0.0009	7 2 6	6 3 3	8560.0771	0.0005
5 2 3	4 2 2	15851.2544	0.0001	7 3 4	6 4 3	11932.5027	−0.0054
5 3 3	4 3 2	14888.7095	0.0014	7 4 3	6 5 2	6989.2472	0.0008
5 3 2	4 3 1	15224.9647	0.0017	7 1 6	7 0 7	11910.3607	0.0013
5 4 2	4 4 1	14894.6883	−0.0043	7 2 5	7 1 6	7902.8387	0.0036
5 4 1	4 4 0	14912.3249	−0.0060	7 3 4	7 2 5	6133.5197	0.0023
5 1 4	5 1 5	7284.4027	0.0006	7 4 4	7 3 5	11612.5097	−0.0019
6 0 6	5 0 5	15488.1428	0.0020	7 4 3	7 3 4	9390.2500	0.0031
6 1 6	5 1 5	15412.0159	−0.0008	8 2 7	8 1 8	14312.9631	0.0003
6 1 5	6 1 6	9617.8706	−0.0003				
7 1 6	7 1 7	11888.4406	−0.0014				
8 1 7	8 1 8	14051.8154	−0.0013				
8 2 6	8 2 7	9931.0156	0.0007				
b-type				c-type			
2 1 2	1 0 1	6705.6213	0.0023	2 1 1	1 0 1	8254.4003	−0.0023
2 2 0	1 1 1	11116.0518	0.0001	2 2 1	1 1 1	10995.5459	−0.0032
2 2 1	1 1 0	10479.2859	−0.0017	2 2 0	1 1 0	10599.7871	−0.0031
3 2 1	2 1 2	15002.1584	−0.0018	3 1 2	2 0 2	11988.5367	0.0008
3 2 2	2 1 1	12888.6748	0.0059	3 2 2	2 1 2	14437.4555	0.0030
3 1 3	2 0 2	8909.1384	0.0007	3 2 1	2 1 1	13453.3788	0.0021
3 0 3	2 1 2	7357.9295	0.0016	4 1 3	3 0 3	16089.8961	−0.0068
4 1 4	3 0 3	11050.2806	0.0000	4 2 2	3 1 2	16536.7649	−0.0025
4 0 4	3 1 3	10183.1921	−0.0031	4 3 2	4 2 2	6997.4665	0.0009
4 2 3	3 1 2	15031.3254	0.0037	4 4 1	4 3 1	11108.4702	−0.0027
4 1 3	3 2 2	9010.3797	0.0014	5 3 3	5 2 3	6034.9203	0.0009
4 2 3	4 1 4	7636.8318	−0.0005	5 4 2	5 3 2	10778.2011	−0.0014
4 3 2	4 2 3	8502.9089	−0.0024	6 4 3	6 3 3	10118.3895	−0.0024
4 3 1	4 2 2	7120.4442	0.0001	6 4 3	7 3 4	9061.7729	0.0014

[a]Units in MHz. [b]$\Delta\nu = \nu_{obs} - \nu_{calc}$.

tion of a methyl group at the 3-position on the cyclic ketone lessens slightly the dipole moment of the molecule. This shift of dipole moment from 3-methylcyclohexanone is consistent with the trend shown in the cyclopentanone case, where the dipole moment of 3-methylcyclohexanone (3.14 D) is smaller than that of cyclopentanone (3.30 D).[16,17]

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Table 2. Spectroscopic constants for 3-methylcyclohexanone

Rotational constants[a]		
A	3091.53436	(23)
B	1720.95803	(12)
C	1204.69635	(13)
D_J	0.00010687	(18)
D_{JK}	0.00023839	(51)
D_K	−0.00023198	(70)
d_1	−0.00001992	(65)
d_2	−0.00000947	(21)

[a]Uncertainties given in parentheses represent one standard deviation in the least-squares fit in units MHz.

Table 3. Measured Stark coefficients of 3-methylcyclohexanone

Transition	|M|	[a]$\Delta\nu/\varepsilon^2$	obs-calc[a]
2_{11}-1_{01}	0	−0.7767	−0.08180
2_{11}-1_{01}	1	2.558	0.01802
3_{03}-2_{02}	0	−0.1192	0.08451
3_{03}-2_{02}	1	0.1678	−0.2448
3_{03}-2_{02}	2	1.042	0.07328
3_{13}-2_{12}	0	−0.02364	0.006927
3_{13}-2_{12}	1	0.3399	−0.2801
3_{13}-2_{12}	2	1.442	−0.02624

[a]Observed second order Stark coefficients ($\Delta\nu/\varepsilon^2$) in units of 10^{-4} MHz/(V/cm)^2. [b]Calculated with dipole components of $|\mu_a| = 2.527(1)$, $|\mu_b| = 1.795(3)$, $|\mu_c| = 0.836(5)$, and $|\mu_{tot}| = 3.210(2)$ D.

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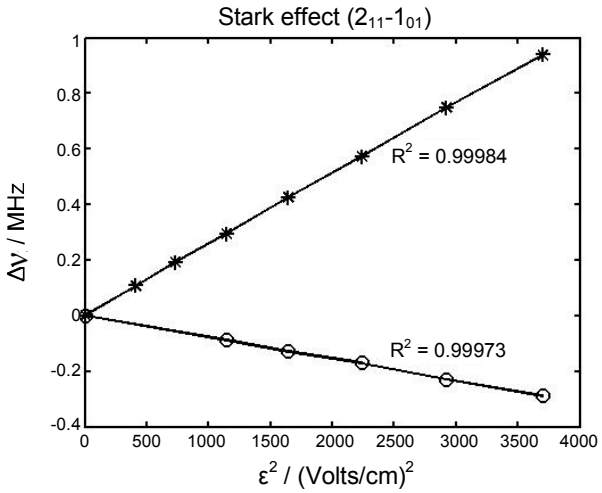


Figure 1. Observed 2nd order Stark effect for the 2_{11}-1_{01} transition.

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