Notes

Dipole Moment of 4-Methylcyclohexanone

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The structures of methyl- and ethyl- derivatives of cyclohexanone have been studied using variety of methods.[1-3] The microwave spectra of 4- and 3-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] In those studies the most stable conformer was shown to be in the chair form with the methyl group in the equatorial position. The dipole moment components calculated with respect to the *a*-, *b*-, and *c*- principal axes in the 3-methylcyclohexanone conformers were also used to determine the most stable conformation.[3]

The various rotamer conformations associated with the hindered ethyl group rotor in ethyl-substituted cyclohexanones have also been studied by $[2 + 1]$ resonance-enhanced multiphoton ionization (REMPI) via the $3s \leftarrow n$ Rydberg transition.[4] Many different isomers have been trapped in a supersonic expansion and spectroscopically identified by comparing peak intensities with those calculated by both molecular and *ab initio* MO methods. Although many researchers have used REMPI to study geometric and configurational isomers, conformers, and rotamers of a variety of compounds, the relative intensities and the calculated energy levels were all required to confirm their final assignments.

In addition to the REMPI studies, there have been studies of vibrational spectra of cyclohexanone and its isotopomers. *Ab initio* density functional theory (DFT) calculations of cyclohexanone in its chair conformation and of the unpolarized vibrational absorption spectra of four of its isotopomers have been reported and compared with the electron diffraction structure and liquid-phase IR spectra.[5-7]

To measure the dipole moment of 4-methylcyclohexanone in the gas phase, the rotational spectrum of 4-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 4-methylcyclohexanone are reported in this paper.

Experimental Section

The rotational spectrum of 4-methylcyclohexanone was measured by using the Fourier Transform Microwave Spectrometer with a pulsed gas nozzle described previously.[8,9]

About 1-2 atm of Ar gas was bubbled through a liquid sample of 4-methylcyclohexanone (Aldrich Chemical Co.)

at just upstream of a pulsed gas valve. Typical linewidths of about 20 kHz (FWHM) were observed and center frequencies were reproducible within $+/-$ 2 kHz.

Results and Discussion

Thirty-six *a*-dipole and twenty-one *c*-dipole transitions were measured to determine the spectroscopic constants.

Table 1. Observed transition frequencies for 4-methylcyclohexanone[a]

Transition $(J' K_p' K_o' \leftarrow J'' K_p'' K_o'')$	υ_{obs}	$\Delta\upsilon_{obs\text{-}cal}$
a-type		
2 0 2 1 0 1	5237.3024	0.0011
2 1 2 1 1 1	4977.6986	0.0004
3 0 3 2 0 2	7802.3142	0.0008
3 1 3 2 1 2	7453.4073	-0.0003
3 1 2 2 1 1	8296.5544	0.0019
3 2 2 2 2 1	7888.6585	0.0006
3 2 1 2 2 0	7974.9772	-0.0025
4 0 4 3 0 3	10307.6659	-0.0043
4 1 4 3 1 3	9914.7822	-0.0007
4 1 3 3 1 2	11034.0589	0.0004
4 2 3 3 2 2	10501.2204	0.0024
4 2 2 3 2 1	10711.6720	0.0029
4 3 2 3 3 1	10558.8193	0.0003
4 3 1 3 3 0	10565.1558	0.0089
5 0 5 4 0 4	12746.4029	0.0021
5 1 5 4 1 4	12359.2817	-0.0043
5 1 4 4 1 3	13744.3237	0.0009
5 2 4 4 2 3	13099.3039	-0.0066
5 2 3 4 2 2	13500.2505	0.0024
5 3 3 4 3 2	13212.1807	0.0019
5 3 2 4 3 1	13234.1411	-0.0016
5 4 2 4 4 1	13196.2343	-0.0023
5 4 1 4 4 0	13196.5718	-0.0051
6 0 6 5 0 5	15126.1691	0.0030
6 1 6 5 1 5	14785.9591	0.0008
6 1 5 5 1 4	16416.6676	-0.0017
6 2 5 5 2 4	15679.5532	-0.0080
6 2 4 5 2 3	16329.0512	0.0044
6 3 4 5 3 3	15869.6765	-0.0009
6 3 3 5 3 2	15927.3474	-0.0030
6 4 3 5 4 2	15850.9855	0.0046
6 4 2 5 4 1	15852.5038	-0.0015
7 0 7 6 0 6	17466.4638	0.0024
7 1 7 6 1 6	17195.3606	0.0001
7 1 6 7 1 7	7665.6774	-0.0021
7 2 6 7 0 7	12858.6095	0.0035

[a]units in MHz

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Table 1. Continued

Transition $(J'\,K_p'\,K_o' \leftarrow J''\,K_p''\,K_o'')$	υ_{obs}	$\Delta\upsilon_{obs\text{-}cal}$
c-type		
2 2 1 2 1 1	7736.4919	-0.0008
2 1 1 1 0 1	8400.7380	-0.0051
2 2 0 1 1 0	13298.7923	0.0038
2 2 1 1 1 1	13558.3998	0.0043
2 2 0 2 1 2	8602.4849	-0.0069
3 1 2 2 0 2	11459.9886	-0.0056
3 2 2 2 1 2	16469.3561	0.0010
3 2 1 2 1 1	15733.2674	0.0004
4 1 3 3 0 3	14691.7419	0.0025
4 2 3 4 1 3	6795.7577	0.0001
4 3 2 4 2 2	13349.7192	0.0002
5 2 4 5 1 4	6150.7450	-0.0003
5 3 3 5 2 3	13061.6479	-0.0017
6 1 5 5 2 3	9546.4215	0.0027
6 0 6 5 1 4	9744.1740	-0.0009
6 2 5 6 1 5	5413.6379	0.0006
6 3 4 6 2 4	12602.2796	-0.0006
7 3 5 7 2 5	11956.2179	0.0024
8 1 7 7 2 5	14679.6370	0.0003
8 3 6 8 2 6	11130.3771	-0.0003
9 3 7 9 2 7	10148.1955	-0.0004

[a]units in MHz

Table 2. Spectroscopic constants for 4-methyl cyclohexanone[a]

Rotational constants[a]			Ref. 1
A	4034.31770	(58)	4034.39 (6)
B	1455.47596	(20)	1455.46 (1)
C	1174.07431	(22)	1174.06 (1)
D_J	0.0001422	(23)	-
D_{JK}	-0.0009288	(80)	-
D_K	0.003298	(65)	-
d_1	-0.0000060	(11)	-
d_2	-0.0000016	(5)	-

[a]All the values are in MHz and uncertainties (one σ) are given in parentheses.

The ground state spectrum was fit using a Watson S-reduced Hamiltonian (I^r representation) to obtain the rotational and centrifugal distortion constants.[10] The observed transition frequencies and difference from the calculated values are listed in Table 1 and the derived spectroscopic constants are given in Table 2. These constants are in good agreement with those obtained by Li.[1] There was no evidence for methyl group internal rotation splitting in these transitions, and a minimum of 2.5 kcal · mol^{-1} for the rotational barrier height was estimated for 4-methylcyclohexanone.[1]

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 4-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 $(J = 0\text{-}1)$[11] and the dipole moment of OCS (0.71521 D) reported by Muenter.[12] To select transitions that adequately

Table 3. Measured Stark Coefficients of 4-methylcyclohexanone

Transition	|M|	$\Delta\nu/\varepsilon^{2\,a}$	obs-calc (%)[b]
$2_{11}-1_{01}$	0	-1.505	1.48
$2_{11}-1_{01}$	1	2.111	-0.04
$2_{02}-1_{01}$	0	-1.214	-1.14
$2_{02}-1_{01}$	1	1.396	-0.12
$3_{13}-2_{12}$	0	-0.09215	-3.57
$3_{13}-2_{12}$	1	0.6292	-1.77
$3_{13}-2_{12}$	2	2.846	-0.06

[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 $\mu_a = 3.032(5)$, $\mu_c = 1.207(14)$, and $\mu_{tot} = 3.263(7)$ D.

meet the second order perturbation, each component was examined to eliminate transitions that do not vary strictly with the square of the electric field (ε^2). The second-order Stark effects ($\Delta\nu/\varepsilon^2$) for 7 M components from 3 transitions of 4-methylcyclohexanone were determined. A least-squares fit of $\Delta\nu/\varepsilon^2$ using the calculated second-order coefficients gave $|\mu_a| = 3.032(5)$, $|\mu_c| = 1.207(14)$, and $|\mu_{tot}| = 3.263$ D. The value of $|\mu_b|$ dipole component was held to zero in the fitting due to the *ac* symmetry plane of 4-methylcyclohexanone. The experimental values of $\Delta\nu/\varepsilon^2$ are listed in Table 3. The agreement between the experimental and calculated values of $\Delta\nu/\varepsilon^2$ was good; the rms deviation was 0.71%. When μ_b^2 was not fixed to zero, the least-squares fit determined a slightly negative value ($\mu_b^2 = -0.0264$ D^2). The zero dipole moment component along the *b*-axis also confirmed the *ac*-symmetry plane in this molecule.

The dipole moment of cyclohexanone was reported to be 2.87 D in the gas phase by MW measurements of the Stark effect, and 2.90 D in a 1,4-dioxane solution by Debye's method.[2] We assumed that the dipole moment of cyclohexanone is located mostly at the C=O bond, and the bond moment of $\mu_{C=O} = 2.87$ D was projected to the principal axis to give $|\mu_a| = 2.59$ and $|\mu_c| = 1.23$ D. The difference of the *a*-dipole moment component is as large as 0.44 D, and it is mostly from the methyl group attached at carbon 4 in the equatorial position. The induced moment of about 0.44 D by the methyl group can be compared with the dipole moment of 0.37 D for toluene.

The dipole moment components also confirm that the ground state conformation of 4-methylcyclohexanone is a chair form with the methyl group in the equatorial position.

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