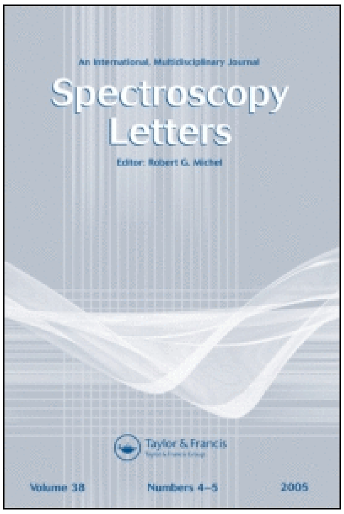

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Centrifugal Distortion Effects in The Microwave Spectrum of Thiomorpholine

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CENTRIFUGAL DISTORTION EFFECTS IN THE MICROWAVE SPECTRUM OF THIOMORPHOLINE

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ABSTRACT

A first order centrifugal distortion analysis has been carried out on the equatorial form of normal thiomorpholine ($\overline{CH_2-CH_2-S-CH_2-CH_2-NH}$). Twenty **eight new Q-branch rotational** transitions with J up to 41 were assigned and measured, and the obtained frequencies combined with the low J transitions previously published to determine the Watson's centrifugal distortion constants.

INTRODUCTION

Experimental studies on centrifugal distortion effects in heavy molecules, particularly saturated ring compounds, conform currently a small section in the microwave spectroscopy literature (1-7). Therefore, the determination of centrifugal distortion constants of another six membered ring molecule should be an useful increase in the amount of experimental data available on this topic.

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With this object the microwave spectrum of high J rotational transitions of the equatorial form of thiomorpholine was investigated.

EXPERIMENTAL

The sample of thiomorpholine was prepared after the method described in ref. (8) and degasified by means of several cooling-vacuum-warming cycles prior to its use. The microwave spectrum was recorded using a conventional 5-kHz Stark modulated spectrometer and a Hewlett-Packard 8460A spectrometer. The measurements were made at room temperature and may be considered accurate within 0.1 MHz.

RESULTS AND DISCUSSION

From the results of the previous study (9), made using rotational transitions with J less than 10, it can be seen that for such J values the rigid rotor model was a very accurate approximation. In fact, it is just from J = 10 that the centrifugal distortion effects become noticeable, and they are truly significative for J higher than 12.

Therefore, for the determination of the Watson's centrifugal distortion coeficients (10), twenty eight new a-type transitions belonging to $14 \leq J \leq 41$ in the 7-19 GHz and 26.5-40 GHz frequency regions were assigned and measured (Table 1). The obtained frequencies along with those reported in ref. (9) were fitted by a least square treatment, and the results can be seen in Table 2. Also, in this table, it is shown a summary of centrifugal distortion constants of another similar six membered ring molecules. All computations were performed in double precision arithmetic on an IBM 360/50 computer at the University of La Plata.

The molecular masses, in a.m.u., of axial piperidine (I), tetrahydropyran (II), morpholine (III) and thiomorpholine (IV) are 85.15, 86.14, 87.12 and 103.18, respectively. It is clear

TABLE 1

Observed Rotational Transitions of Thiomorpholine[a]

$J(K_{-1},K_1) - J'(K'_{-1},K'_1)$	Observed	Calculated
1 (0, 1) - 2 (0, 2)	9543.51 [b]	9543.53
1 (1, 0) - 2 (1, 1)	11144.43 [b]	11144.44
1 (1, 1) - 2 (1, 2)	8944.19 [b]	8944.17
2 (0, 2) - 3 (0, 3)	13506.83 [b]	13506.64
2 (1, 2) - 3 (1, 3)	13150.29 [b]	13150.30
2 (1, 1) - 3 (1, 2)	16289.56 [b]	16289.52
2 (2, 1) - 3 (2, 2)	15066.42 [b]	15066.45
2 (2, 0) - 3 (2, 1)	16626.22 [b]	16626.25
3 (0, 3) - 4 (0, 4)	17330.39 [b]	17330.38
3 (1, 3) - 4 (1, 4)	17199.01 [b]	17199.03
3 (2, 1) - 4 (2, 2)	22394.02 [b]	22394.12
3 (2, 2) - 4 (2, 3)	19678.40 [b]	19678.49
5 (1, 4) - 6 (1, 5)	28420.26 [b]	28420.26
5 (2, 4) - 6 (2, 5)	28143.05 [b]	28143.00
5 (2, 3) - 6 (2, 4)	32097.97 [b]	32098.06
5 (4, 1) - 6 (4, 2)	32581.62 [b]	32581.61
5 (5, 0) - 6 (5, 1)	31571.13 [b]	31571.14
5 (5, 1) - 6 (5, 2)	31478.79 [b]	31478.77
6 (0, 6) - 7 (0, 7)	29025.98 [b]	29025.93
6 (1, 6) - 7 (1, 7)	29023.77 [b]	29023.67
6 (1, 5) - 7 (1, 6)	32233.21 [b]	32233.20
6 (2, 5) - 7 (2, 6)	32142.32 [b]	32142.31
6 (2, 4) - 7 (2, 5)	35910.12 [b]	35910.14
6 (6, 1) - 7 (6, 2)	36696.91 [b]	36696.87
6 (6, 0) - 7 (6, 1)	36721.80 [b]	36721.85
7 (0, 7) - 8 (0, 8)	32946.52 [b]	32946.50
7 (1, 7) - 8 (1, 8)	32946.06 [b]	32946.00
7 (1, 6) - 8 (1, 7)	36113.13 [b]	36113.12
7 (1, 6) - 7 (3, 5)	16788.79 [b]	16788.83
7 (2, 6) - 8 (2, 7)	36087.04 [b]	36087.05
7 (2, 5) - 8 (2, 6)	39546.98 [b]	39547.03
8 (2, 6) - 8 (4, 5)	16888.49 [b]	16888.44

TABLE 1 - Continued

$J(K_{-1},K_1) - J'(K'_{-1},K'_1)$	Observed	Calculated
8 (0, 8) - 9 (0, 9)	36867.87 [b]	36867.95
8 (1, 8) - 9 (1, 9)	36867.87 [b]	36867.84
9 (5, 5) - 9 (3, 6)	17926.74 [b]	17926.87
9 (3, 6) - 9 (3, 7)	18529.14 [c]	18529.05
14 (7, 7) - 14 (7, 8)	10758.20 [c]	10758.21
17 (8, 9) - 17 (8,10)	17891.71 [c]	17891.67
17 (9, 8) - 17 (9, 9)	7271.34 [c]	7271.44
18 (6,12) - 18 (8,11)	32659.15 [c]	32659.17
18 (9, 9) - 18 (9,10)	12787.09 [c]	12787.17
19 (10, 9) - 19 (10,10)	7895.46 [c]	7895.36
20 (8,12) - 20 (10,11)	32447.30 [c]	32447.27
21 (9,12) - 21 (9,13)	31428.70 [c]	31428.64
21 (11,10) - 21 (11,11)	8497.36 [c]	8497.26
22 (11,11) - 22 (11,12)	14674.66 [c]	14674.51
23 (12,11) - 23 (12,12)	9078.40 [c]	9078.37
24 (12,12) - 24 (12,13)	15571.35 [c]	15571.33
25 (13,12) - 25 (13,13)	9639.60 [c]	9638.68
26 (13,13) - 26 (13,14)	16439.44 [c]	16439.29
27 (14,13) - 27 (14,14)	10181.95 [c]	10182.00
28 (13,15) - 28 (13,16)	32181.05 [c]	32181.06
28 (14,14) - 28 (14,15)	17279.70 [c]	17279.75
29 (15,14) - 29 (15,15)	10706.05 [c]	10706.03
30 (15,15) - 30 (15,16)	18093.77 [c]	18093.87
31 (16,15) - 31 (16,16)	11212.21 [c]	11212.33
33 (17,16) - 33 (17,17)	11701.36 [c]	11701.37
35 (18,17) - 35 (18,18)	12173.51 [c]	12173.57
37 (19,18) - 37 (19,19)	12629.28 [c]	12629.27
39 (20,19) - 39 (20,20)	13068.91 [c]	13068.75
40 (21,19) - 40 (21,20)	7049.75 [c]	7049.77
41 (20,21) - 41 (20,22)	31963.25 [c]	31963.27
41 (21,20) - 41 (21,21)	13492.27 [c]	13492.27

[a] All frequencies are in MHz.

[b] From ref. (9).

[c] This work.

TABLE 2

Molecular Constants and Watson's Centrifugal Distortion Coefficients of Several Six Membered Ring Molecules

	Axial Piperidine [a]	Tetrahydropyran [a]	Equatorial Morpholine [b]	Equatorial Thiomorpholine [c]
A (MHz)	4494.433±0.026	4673.502±0.009	4925.006±0.013	4198.504±0.006
B (MHz)	4395.421±0.024	4495.074±0.009	4625.140±0.014	3061.148±0.004
C (MHz)	2535.759±0.024	2601.281±0.009	2684.244±0.015	1961.009±0.003
d_J (kHz)	11.23 ±1.60	2.516 ±0.301	0.73 ±0.54	-0.87 ±0.06
d_{JK} (kHz)	251.5 ±66.5	171.2 ±3.4	110.88 ±7.58	-4.20 ±0.45
d_K (kHz)	-108.9 ±28.4	-74.13 ±1.45	-48.03 ±3.24	-0.65 ±0.20
$d_{EJ} \cdot 10^6$	-1.304 ±0.311	-0.3242 ±0.0201	-0.01 ±0.03	0.47 ±0.03
$d_{EK} \cdot 10^6$	-57.48 ±14.92	-37.87 ±0.73	-23.52 ±1.58	1.16 ±0.17
Lines fitted	68	68	78	63
Standard Dev. (MHz)	0.114	0.126	0.096	0.072
Highest J value	25	32	46	41

[a] From ref. (6) [b] From ref. (7) [c] This work

from Table 2, that the absolut values of centrifugal distortion coefficients go down from I to IV. This tendency is expected to hold for molecules with very similar structures as in this case.

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