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Isotopic Dependence of the Hydrogen-Transfer-Triggered Methyl-Group Rotation in Deuterated 5-Methyltropolone

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Abstract

We present here the first experimental study of the microwave spectrum of deuterated 5-methyltropolone, a molecule which exhibits two large-amplitude motions: an intramolecular hydrogen transfer (deuterium transfer in the current case of deuterated 5-methyltropolone) and a methyl torsion. The main goal of this study was to get information on the isotopic dependence of the main tunneling parameters of 5-methyltropolone in the framework of the two dimensional tunneling formalism, which previously has shown some counterintuitive results for isotopic dependence of tunneling parameters in 2-methylmalonaldehyde. Measurements were carried out by Fourier-transform microwave spectroscopy in the 9 GHz to 26 GHz frequency range. Theoretical analysis was carried out using a tunneling-rotational Hamiltonian based on a G_{12}^m extended-group-theory formalism. Our global fit of 384 transitions to 17 molecular parameters gave a weighted root-mean-square deviation of 0.8. The current study on the isotopic dependence of the main tunneling parameters in 5-methyltropolone supports the assumption of possible “leakage” between tunneling parameters in the two-dimensional tunneling formalism in use.

Keywords

hydrogen transfer; internal rotation; large-amplitude motion; microwave spectrum; tunneling Hamiltonian; tunneling splittings

1. Introduction

About a decade ago Y.-C. Chou and J. T. Hougen showed [1] that a high-barrier tunneling formalism originally developed for methylamine [2] could be used to fit the spectra of molecules like 2-methylmalonaldehyde (2-MMA) [3] and 5-methyltropolone (5-MT) [4] where an intramolecular hydrogen transfer in one part of the molecule triggers the internal rotation of a methyl group in another part. Application of the high-barrier tunneling formalism [2] to the studies of the –OH and –OD isotopologues of 2-MMA [1,3] showed an

unexpected anomaly for the CH₃ internal-rotation tunneling parameters in the two species: the change in the pure torsional tunneling splitting parameter, h_{3v} , upon deuteration of the hydroxyl H in 2-MMA was unexpectedly large, and splitting increased instead of the expected decrease [1,2]. One possible explanation proposed [4] for this counterintuitive result of the isotopic dependence on the tunneling parameter was the “leakage” of the large H-transfer tunneling splitting parameter h_{2v} [1,2] in 2-MMA into the much smaller torsional tunneling splitting parameter h_{3v} , caused by some “coupling” of these two motions that was not properly included in the model. From this point of view it was very interesting to look at the result of deuteration of the hydroxyl H in 5-MT. If the “leakage” hypothesis is correct, then the deuteration of the hydroxyl group in 5-MT should produce a much smaller change in the h_{3v} parameter since the h_{2v}/h_{3v} ratio is only 2.2 for 5-MT compared to 188 for 2-MMA and a small leakage of one splitting parameter into the other nearly equal splitting parameter should be much less noticeable.

In this paper, we report the microwave study of the S_0 state of deuterated 5-methyl tropolone, shown in Figure 1 (see Figure 1 of Ref. [4] for the equilibrium structure of 5-MT and the transition state in the tunneling path involving hydrogen transfer). The main goal of the present study is to get information on the isotopic dependence of the main tunneling parameters of 5-methyltropolone in the framework of the two dimensional tunneling formalism [2] used previously to fit the spectra of 2-MMA [1,3] and to shed more light on the anomalies in the tunneling parameters obtained for the 2-MMA molecule.

2. Experimental

5-MT is commercially unavailable and requires custom synthesis. The details of the synthesis procedure may be found in [4]. In the current study deuteration was accomplished by refluxing the normal isotope of 5-MT in D₂O for several hours.

Rotational spectra were measured using two nearly identical Fourier-transform microwave spectrometers equipped with a heated reservoir nozzle [5], one at the College of Charleston (CofC), the other at NIST. Deuterated 5-methyltropolone, 5-MT-OD, was warmed to 110 °C in a reservoir nozzle oriented parallel to the cavity axis. In this configuration, rotational linewidths are approximately 6 kHz. The 5-MT-OD vapor was expanded at a backing pressure of ~150 kPa using a 80%/20% mixture by volume of neon/helium carrier gas. The rotational temperature in the expansion under these conditions is ≈2 K. Initial searches and a part of the measurements were carried out at CofC. Measurements at NIST aimed at extending the data set to higher frequencies above 18 GHz, and aimed at recording more b-type transitions across the tunneling splittings. No previous microwave measurements for this molecule could be found in the literature.

Measurements were made in the frequency range from 9 GHz to 26 GHz and transitions up to $J=17$ and $K_a=7$ were observed. Some $K=0$ transitions were clearly broadened, presumably by quadrupole or spin-spin and spin-rotation hyperfine interactions, but this broadening was not investigated in detail and these transitions were simply given an uncertainty of 10 kHz. Very weak transitions were assigned an uncertainty of 4 kHz. The

normal lines were assigned an uncertainty of 2 kHz. All lines were weighted in our fits by the inverse square of their assigned uncertainties.

3. Effective Hamiltonian

We use here the same high-barrier tunneling-formalism Hamiltonian as for 2-MMA [1,3] and 5-MT [4], which is described in detail in Refs. [1,2]. Previously this formalism was successfully applied to methylamine [6,7,8,9], for which it was originally developed [2]. We also used the same fitting program, i.e., a slightly modified version [3,6] of the program obtained from N. Ohashi [10]. The reader is referred to Ref. [2] and references therein for a detailed description of this formalism. The Hamiltonian operator is defined as (we repeat here only the linear and quadratic terms which are used in the fit of 5-MT spectrum):

$$H = h_v + h_j J^2 + h_k J_z^2 + (f_+ J_+^2 + f_- J_-^2) + q J_z + (r_+ J_+ + r_- J_-) \quad (1) \\ + (1/2)[s_+(J_+ J_z + J_z J_+) + s_-(J_- J_z + J_z J_-)]$$

Hamiltonian matrix elements of the various operators are expanded in Fourier series whose n -th term represents a tunneling process from molecular framework 1 to molecular framework n (see [1,2] for definition of the frameworks). In the notation adopted, the subscript $n = 1$ corresponds to non-tunneling motion. The even subscripts $n = 2, 4, 6 \dots$ designate tunneling involving hydroxyl hydrogen transfer which is accompanied by 60° internal rotation of the methyl group. The odd subscripts $n = 3, 5, 7 \dots$ refer to tunneling involving only torsional motion of the methyl group. In the Hamiltonian (1), the non-tunneling value of h_v corresponds to an absolute energy offset for all levels, while the tunneling values of h_v represent the tunneling frequencies in the nonrotating molecule for each symmetrically inequivalent tunneling path. Thus, the parameter h_{2v} associated with the tunneling from framework 1 to framework 2 corresponds to the hydroxyl hydrogen transfer followed by 60° internal rotation of the methyl group, whereas the parameter h_{3v} associated with the tunneling from framework 1 to framework 3 corresponds to the internal rotation of the methyl group by 120° . These two parameters, h_{2v} and h_{3v} , which represent the main tunneling splittings in the spectrum of 5-MT, will be in the focus of our attention from the point of view of isotopic dependence upon deuteration of the hydroxyl H atom. The physical interpretation of other Hamiltonian parameters from Eq. (1) may be found in [4].

4. Spectral fits

Since there was no previous microwave study reported for deuterated 5-MT, we had to perform an initial search for the 5-MT-OD transitions based on some assumptions. Initial values for rotational constants in our tunneling-Hamiltonian fits were taken from a low-level *ab initio* calculation, with the centrifugal distortion constants as well as the ρ value taken from our previous study of the normal isotopologue of 5-MT [4]. We assumed that the pure torsion parameter h_{3v} should not change much in comparison with the normal 5-MT isotopologue [4] whereas the decrease in the hydrogen transfer tunneling parameter h_{2v} was taken to be equal to the corresponding decrease in the case of 2-MMA [3]. The scans around initial predictions for $K=0$ R-type transitions revealed a sequence of multiplets, which were

attributed to tunneling-split components for the deuterated 5-MT vibrational ground state. One of these multiplets is shown in Fig. 2 where the splitting pattern of the $6_{06} - 5_{05}$ transition of 5-MT-OD is compared with the corresponding splitting pattern for 5-MT-OH. The overall splitting for 5-MT-OD is observed to be slightly less than in the case of 5-MT-OH as expected (note also that the B_1/B_2 and E_2 tunneling components are not fully resolved in the case of 5-MT-OD). After initial assignment of several $K=0$ R-type transitions of 5-MT-OD the usual iterative procedure of predictions and new measurements gave us the final fit described in the next paragraph.

A final least-squares fit of 384 5-MT-OD transitions to 17 parameters was carried out, giving a root-mean-square (rms) deviation of 2.8 kHz. The list of measured rotational transitions in the ground vibrational state of 5-MT-OD is deposited in the supplementary material. The data set contains 320 $K=0$ and 27 $K=2$ a -type transitions, which connect energy levels within each vibrational tunneling state, as well as 37 $|K|=1$ b -type transitions, which go across the tunneling splittings, as shown in Fig. 3. The diagram in Fig. 3 shows the position of 5-MT-OD relative to other molecules exhibiting a methyl-group rotation triggered by some back-and-forth large-amplitude motion elsewhere in the molecule (see Ref. [4] for a detailed discussion of the concept of this diagram). The $K=0$ transitions include 17 Q -branch lines. The transitions are evenly distributed among the four symmetry-related species of the molecule. Thus, the current dataset for 5-MT-OD contains the same types of transitions as the dataset for the normal isotopologue [4], including $|K|=1$ b -type transitions, which go across the tunneling splittings, and thus are crucial for precise determination of the h_{2v} and h_{3v} parameters associated with the hydrogen transfer and torsion tunneling processes. All these data are fit to a weighted rms deviation of 0.8, which from our point of view is excellent.

The molecular parameters from our final fit are shown in Table 1, where molecular parameters of the normal 5-MT isotopologue from Ref. [4] are also given for comparison. The left column contains linear combinations of the three usual rotational constants, the five quartic centrifugal distortion constants, an off-diagonal rotational constant s_1 (see Eq. (1)), and the value of the usual internal-rotation moment-of-inertia ratio ρ . The right column contains parameters associated with the large-amplitude tunneling motions. The parameters h_{nv} for $n=2$ and 4 represent the nearest-neighbor and next-next-nearest neighbor tunneling frequencies associated with the D-transfer (or H-transfer in the case of the normal 5-MT isotopologue) motion plus corrective internal rotation. Table 1 shows that $|h_{2v}|/|h_{4v}| \approx 1839$, very close to the corresponding value of $|h_{2v}|/|h_{4v}| \approx 1800$ in 5-MT-OH, and this large ratio justifies the high-barrier tunneling formalism used here. Also, it is observed that deuteration decreases all h_{nv} parameters connected with $n=2$ or 4 by at least an order of magnitude which is intuitively clear due to the increase in the effective mass participating in the tunneling motion associated with these parameters. The parameter h_{nv} for $n=3$ represents the next-nearest-neighbor tunneling frequency associated with the pure internal rotation motion of the methyl group. As a final point, we note in passing, as in the case of 5-MT-OH, that no parameters of the type q_n occur in Table 1 for 5-MT-OD. Thus, we have almost the same set of parameters for the 5-MT-OH and 5-MT-OD species. At the same time, it should be noted, presumably because of a smaller dataset for 5-MT-OD, that the f_2 , h_{3k} , r_3

coefficients, which are present in the parameter set for 5-MT-OH, are not determined statistically in the case of the current 5-MT-OD dataset.

5. Discussion

The studies of the –OH and –OD isotopologues of 2-methylmalonaldehyde [1,3] using the two-dimensional high barrier tunneling formalism developed for methylamine by Ohashi and Hougen [2] revealed an unexpected problem with the methyl torsion tunneling parameter h_{3v} which is associated with the pure torsional A-E splitting in the spectrum. The change from -111.5 MHz to -348.2 MHz [3] upon deuteration of the hydroxyl H in 2-MMA represents a significant increase of the pure torsional splitting $3|h_{3v}|$ and seems to be unexpectedly large and in the “wrong” direction. It is expected that deuteration at a position far removed from methyl torsion would have a rather small effect on the pure torsion barrier height. In addition, making the molecule heavier upon deuteration should result in a decrease in the A-E splitting because of the increase in the effective mass of the motion.

One possible explanation proposed [4] for these counterintuitive results of the isotopic dependence of torsion tunneling parameters in 2-MMA was the “leakage” of the large H-transfer tunneling splitting parameter h_{2v} into the much smaller torsional tunneling splitting parameter h_{3v} , caused by some “coupling” of these two motions that was not properly included in the model. From this point of view it was interesting to look at the effect of deuteration of the hydroxyl H in 5-MT on the h_{3v} parameter associated with the pure torsion motion in this molecule. As is seen from Table 1, the h_{3v} parameter changed rather insignificantly from -295.0 MHz in the case of the –OH isotopologue to -287.7 MHz for the –OD isotopologue. Thus, for 5-MT we observe intuitively “correct” behavior of the h_{3v} parameter. This result supports the “leakage” hypothesis [4] according to which deuteration of the hydroxyl group in 5-MT should produce a much smaller change in the h_{3v} parameter since the h_{2v}/h_{3v} ratio is only 2.2 for 5-MT compared to 188 for 2-MMA and a small leakage of one splitting parameter into the other nearly equal splitting parameter should be much less noticeable.

This “leakage” hypothesis has recently received some theoretical consideration [12] (developed by Ohashi and Hougen) which connects the “leakage” problem to the non-orthogonality of the vibrational basis set functions used in the high-barrier tunneling formalism [2]. According to this theoretical treatment [12], tunneling parameters h_{2v} and h_{3v} obtained from a fit are connected with the physically meaningful «true» tunneling matrix elements $\langle 1||h_v||2 \rangle$ and $\langle 1||h_v||3 \rangle$ defined in terms of basis functions strictly localized near a given framework by the following approximate relations:

$$h_{2v} = (1 - \Delta_2) \langle 1||h_v||2 \rangle - \Delta_1 \langle 1||h_v||3 \rangle \quad (2)$$

$$h_{3v} = -\Delta_1 \langle 1||h_v||2 \rangle + \langle 1||h_v||3 \rangle \quad (3)$$

where $\langle 1|2\rangle$, $\langle 1|3\rangle$ are corresponding tunneling overlap integrals; and $\langle 1|h_v||s\rangle = \langle 1|h_v - h_0||s\rangle$ ($s = 2, 3$), is a modified tunneling matrix element independent of any constant shift in the energy origin ($h_0 = \langle 1|h_v|1\rangle$). From Eqs. (2) and (3) it is seen that h_{2v} parameter contains the contribution from $\langle 1|h_v||3\rangle$ «true» tunneling matrix element and h_{3v} parameter contains the contribution from $\langle 1|h_v||2\rangle$ «true» tunneling matrix element which are proportional to tunneling overlap integral. It is these contributions we call here «leakage» of one tunneling splitting parameter into another tunneling splitting parameter. These contributions become possible because of nonzero tunneling overlap integrals $\langle i|j\rangle$ which means that the set of framework functions $\{|i\rangle\}$, which represents the same vibrational state localized on each of the frameworks i for $i = 1, 2, 3, \dots$, is not an orthonormal set (since the overlap integrals $\langle i|j\rangle$ with $i \neq j$ are not zero). Thus it can be said that the «leakage» problem is produced by the non-orthogonality of the vibrational basis set functions used in the high-barrier tunneling formalism. The readers are referred to Ref.[12] for more comprehensive discussion of cross-contamination of the fitting parameters in tunneling treatments.

8. Conclusions

We have observed for the first time the rotational spectra of the -OD isotopologue of 5-methyltropolone. The 384 microwave lines of 5-MT-OD measured and fit to experimental error in this work have confirmed one more time the ability of the high barrier tunneling formalism [2] to handle microwave measurements at the kHz level of accuracy. In contrast to the case of the 2-methylmalonaldehyde [1,3] the results for the isotopic dependence of the main tunneling parameters upon hydroxyl H deuteration in 5-MT revealed no counterintuitive behavior of the h_{3v} parameter associated with the pure torsional large amplitude motion in this molecule. This result supports the «leakage» explanation of the 2-MMA anomaly [4] according to which deuteration of the hydroxyl group in 5-MT should produce a much smaller change in the h_{3v} parameter in comparison with the 2-MMA case [1,3] since the h_{2v}/h_{3v} ratio is only 2.2 for 5-MT compared to 188 for 2-MMA and a small leakage of one splitting parameter into the other nearly equal splitting parameter should be much less noticeable.

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Appendix A. Supplementary Data

Table S1.

Measured rotational transitions of deuterated 5-methyltropolone in the ground vibrational state.

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
6	0	E2+1	5	0	E2+1	0.0020	9501.2421	-0.0021
6	0	B1	5	0	B2	0.0020	9501.2421	-0.0067
6	0	E1+1	5	0	E1+1	0.0020	9501.3599	-0.0028
6	0	A1	5	0	A2	0.0020	9501.5246	-0.0020
7	2	E1-1	7	0	E1+1	0.0100	9597.2597	0.0075
7	2	E2+1	7	0	E2+1	0.0100	9597.4853	0.0065
7	2	A1	7	0	A2	0.0100	9599.5398	0.0047
7	2	B1	7	0	B2	0.0100	9600.0885	0.0050
6	2	B2	5	2	B1	0.0020	10105.1350	-0.0009
6	2	A2	5	2	A1	0.0020	10105.2840	-0.0017
6	2	E2+1	5	2	E2+1	0.0020	10105.7480	0.0000
6	2	E1-1	5	2	E1-1	0.0020	10105.9640	0.0002
6	4	B1	5	4	B2	0.0020	10316.4570	0.0011
6	4	A1	5	4	A2	0.0020	10316.5680	-0.0010
6	3	A1	5	3	A2	0.0020	10326.5933	-0.0006
6	3	B1	5	3	B2	0.0020	10326.7090	-0.0001
6	3	E1+1	5	3	E1+1	0.0020	10342.4800	0.0009
6	3	E2-1	5	3	E2-1	0.0020	10344.2910	-0.0004
6	3	E2+1	5	3	E2+1	0.0020	10401.1690	0.0003
6	3	E1-1	5	3	E1-1	0.0020	10402.8740	-0.0024
6	3	A2	5	3	A1	0.0020	10418.6103	0.0007
6	3	B2	5	3	B1	0.0020	10418.7030	0.0011
8	2	E1-1	8	0	E1+1	0.0100	10568.8628	0.0070
8	2	E2+1	8	0	E2+1	0.0100	10569.2094	0.0072
8	2	A2	8	0	A1	0.0100	10570.9914	0.0050
6	1	E2+1	5	1	E2+1	0.0020	10733.3220	-0.0025
6	1	A2	5	1	A1	0.0020	10733.3490	-0.0004
6	1	B2	5	1	B1	0.0020	10733.4620	-0.0020
7	1	E1+1	6	1	E1+1	0.0020	10772.2099	-0.0010
7	1	A2	6	1	A1	0.0020	10772.2384	0.0009
7	1	E2-1	6	1	E2-1	0.0020	10772.3676	-0.0001
7	1	B2	6	1	B1	0.0020	10772.7371	0.0011
6	2	E1+1	5	2	E1+1	0.0020	10823.7086	-0.0010
6	2	E2-1	5	2	E2-1	0.0020	10823.8231	0.0003
6	2	B1	5	2	B2	0.0020	10824.3160	0.0030
6	2	A1	5	2	A2	0.0020	10824.3638	-0.0014
7	0	B2	6	0	B1	0.0020	10924.7157	-0.0018
7	0	E2+1	6	0	E2+1	0.0020	10924.9083	-0.0015

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
7	0	E1+1	6	0	E1+1	0.0020	10925.0686	-0.0008
7	0	A2	6	0	A1	0.0020	10925.2276	-0.0012
7	2	B1	6	2	B2	0.0020	11724.8296	-0.0008
7	2	A1	6	2	A2	0.0020	11725.0166	0.0007
7	2	E2+1	6	2	E2+1	0.0020	11725.0898	0.0007
7	2	E1-1	6	2	E1-1	0.0020	11725.2436	-0.0009
7	3	A2	6	3	A1	0.0020	12055.3448	-0.0008
7	3	B2	6	3	B1	0.0020	12055.4812	-0.0003
7	4	B1	6	4	B2	0.0020	12055.9846	0.0014
7	4	A1	6	4	A2	0.0020	12056.1118	-0.0011
7	4	E2+1	6	4	E2+1	0.0020	12061.3649	0.0028
7	4	E1-1	6	4	E1-1	0.0020	12061.4995	-0.0021
7	4	E1+1	6	4	E1+1	0.0020	12061.6303	-0.0023
7	4	E2-1	6	4	E2-1	0.0020	12061.6450	0.0011
7	3	E1+1	6	3	E1+1	0.0020	12064.3133	0.0008
7	4	B2	6	4	B1	0.0020	12066.8691	0.0005
7	4	A2	6	4	A1	0.0020	12066.9960	0.0015
8	0	E2+1	7	1	E2-1	0.0040	12166.5369	0.0000
8	0	B1	7	1	B2	0.0040	12222.7412	-0.0001
7	3	E2+1	6	3	E2+1	0.0020	12242.0890	0.0000
7	3	E1-1	6	3	E1-1	0.0020	12243.7513	-0.0002
8	1	E1+1	7	1	E1+1	0.0020	12247.6377	-0.0004
8	1	A1	7	1	A2	0.0020	12247.6998	-0.0018
8	1	E2-1	7	1	E2-1	0.0020	12247.8982	0.0007
8	1	B1	7	1	B2	0.0020	12250.4027	0.0004
7	3	A1	6	3	A2	0.0020	12252.5139	-0.0001
7	3	B1	6	3	B2	0.0020	12252.6019	-0.0005
8	0	B1	7	0	B2	0.0020	12343.9429	0.0000
8	0	E2+1	7	0	E2+1	0.0020	12346.2586	-0.0006
8	0	E1+1	7	0	E1+1	0.0020	12346.5222	-0.0004
8	0	A1	7	0	A2	0.0020	12346.6563	0.0003
8	1	B1	7	0	B2	0.0020	12371.6030	-0.0009
7	1	E1-1	6	1	E1-1	0.0020	12373.8415	-0.0019
7	1	E2+1	6	1	E2+1	0.0020	12373.9194	-0.0013
7	1	A1	6	1	A2	0.0020	12373.9642	-0.0039
7	1	B1	6	1	B2	0.0020	12374.1253	-0.0045
8	1	E2-1	7	0	E2+1	0.0040	12427.6198	0.0000
7	3	E2-1	7	1	E2+1	0.0040	12547.5998	0.0015
7	3	A2	7	1	A1	0.0040	12560.1120	-0.0011
7	3	B2	7	1	B1	0.0040	12560.2704	0.0014
8	1	A1	7	0	A2	0.0040	12606.7889	-0.0013
3	2	A2	2	0	A1	0.0100	12701.2039	0.0137

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
3	2	E2-1	2	0	E2+1	0.0100	12707.0156	0.0006
7	2	E1+1	6	2	E1+1	0.0020	12716.5030	-0.0002
7	2	E2-1	6	2	E2-1	0.0020	12716.5312	-0.0012
7	2	B2	6	2	B1	0.0020	12716.7044	0.0010
7	2	A2	6	2	A1	0.0020	12716.7665	-0.0013
6	3	E2-1	6	1	E2+1	0.0040	12855.4340	0.0036
6	3	A1	6	1	A2	0.0040	12878.7355	-0.0001
6	3	B1	6	1	B2	0.0100	12878.9199	0.0026
5	3	A2	5	1	A1	0.0100	13285.4844	-0.0067
8	2	B2	7	2	B1	0.0020	13317.8830	0.0014
8	2	E2+1	7	2	E2+1	0.0020	13317.9810	-0.0016
8	2	A2	7	2	A1	0.0020	13318.1070	-0.0003
8	2	E1-1	7	2	E1-1	0.0020	13318.1310	0.0048
4	2	A1	3	1	A2	0.0100	13416.9299	0.0038
11	1	A1	11	1	A2	0.0100	13586.2594	0.0051
11	1	E2+1	11	1	E2-1	0.0100	13586.6790	0.0065
4	2	E2-1	3	1	E2-1	0.0100	13598.5843	0.0078
9	0	E2+1	8	1	E2-1	0.0020	13691.0150	0.0014
9	1	B2	8	1	B1	0.0020	13707.8828	-0.0001
9	1	E1+1	8	1	E1+1	0.0020	13712.9285	0.0016
9	1	A2	8	1	A1	0.0020	13713.0227	0.0007
9	1	E2-1	8	1	E2-1	0.0020	13713.8861	0.0004
4	3	B1	4	1	B2	0.0020	13718.5020	-0.0062
9	1	B2	8	0	B1	0.0020	13735.5450	0.0011
9	0	B2	8	1	B1	0.0020	13750.9080	-0.0002
8	5	A1	7	5	A2	0.0020	13762.1070	0.0004
8	5	B1	7	5	B2	0.0020	13762.2570	0.0006
8	5	E1-1	7	5	E1-1	0.0020	13762.5031	-0.0028
8	5	E2+1	7	5	E2+1	0.0020	13762.5480	0.0000
8	5	E1+1	7	5	E1+1	0.0040	13762.8504	-0.0007
8	5	E2-1	7	5	E2-1	0.0020	13762.9580	-0.0009
6	2	A2	5	1	A1	0.0100	13762.9753	-0.0073
8	5	A2	7	5	A1	0.0020	13763.0870	0.0001
8	5	B2	7	5	B1	0.0020	13763.2360	-0.0002
9	0	E2+1	8	0	E2+1	0.0020	13772.3724	-0.0018
9	0	E1+1	8	0	E1+1	0.0020	13773.3356	-0.0010
9	0	A2	8	0	A1	0.0020	13773.4426	0.0024
8	3	A1	7	3	A2	0.0020	13774.3737	-0.0010
8	3	B1	7	3	B2	0.0020	13774.5334	-0.0011
8	3	E1+1	7	3	E1+1	0.0020	13778.1518	0.0010
9	0	B2	8	0	B1	0.0020	13778.5739	0.0047
8	3	E2-1	7	3	E2-1	0.0020	13779.0637	0.0012

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
9	1	E2-1	8	0	E2+1	0.0020	13795.2460	-0.0003
8	4	B2	7	4	B1	0.0020	13806.7430	-0.0011
8	4	A2	7	4	A1	0.0020	13806.8879	-0.0006
8	4	E2+1	7	4	E2+1	0.0020	13818.6918	0.0009
8	4	E1-1	7	4	E1-1	0.0020	13819.1150	0.0004
6	2	E1-1	5	1	E1-1	0.0100	13820.3269	-0.0124
8	4	E1+1	7	4	E1+1	0.0020	13824.0086	-0.0004
8	4	E2-1	7	4	E2-1	0.0020	13824.2924	-0.0003
8	4	B1	7	4	B2	0.0020	13836.0416	-0.0008
8	4	A1	7	4	A2	0.0020	13836.1757	-0.0011
8	1	E1-1	7	1	E1-1	0.0020	13937.9102	-0.0033
8	1	E2+1	7	1	E2+1	0.0020	13938.0191	-0.0014
8	1	A2	7	1	A1	0.0020	13938.0996	-0.0027
8	1	B2	7	1	B1	0.0020	13938.3218	-0.0014
6	2	E2+1	5	1	E2+1	0.0100	13940.4994	-0.0142
6	2	B2	5	1	B1	0.0100	14002.6858	-0.0090
8	3	E2+1	7	3	E2+1	0.0020	14134.8001	-0.0010
8	3	E1-1	7	3	E1-1	0.0020	14135.5964	0.0040
8	3	A2	7	3	A1	0.0020	14139.1105	0.0005
8	3	B2	7	3	B1	0.0020	14139.1858	-0.0016
3	3	B2	2	2	B1	0.0020	14270.6144	0.0000
3	3	B1	2	2	B2	0.0020	14298.9193	0.0022
3	3	E2-1	2	2	E2+1	0.0040	14322.0574	-0.0037
3	3	E2+1	2	2	E2-1	0.0040	14361.8413	-0.0004
3	3	E1+1	2	2	E1-1	0.0100	14451.3165	0.0011
3	3	E1-1	2	2	E1+1	0.0100	14473.0498	0.0035
3	3	A2	2	2	A1	0.0040	14510.7472	-0.0008
3	3	A1	2	2	A2	0.0020	14539.0470	0.0004
8	2	E2-1	7	2	E2-1	0.0020	14573.7715	-0.0006
8	2	E1+1	7	2	E1+1	0.0020	14573.7863	0.0008
8	2	B1	7	2	B2	0.0020	14573.8502	-0.0007
8	2	A1	7	2	A2	0.0020	14573.9371	-0.0014
4	2	B1	3	0	B2	0.0040	14738.9745	0.0044
4	2	A1	3	0	A2	0.0040	14739.0290	0.0137
4	2	E2-1	3	0	E2+1	0.0100	14139.7467	0.0049
4	2	E1+1	3	0	E1+1	0.0100	14740.4235	0.0050
9	2	B1	8	2	B2	0.0020	14883.6763	-0.0014
9	2	E2+1	8	2	E2+1	0.0020	14883.6891	0.0006
9	2	E1-1	8	2	E1-1	0.0020	14883.8378	-0.0015
9	2	A1	8	2	A2	0.0020	14883.9486	-0.0003
10	1	B1	9	0	B2	0.0020	15129.1240	0.0001
10	1	E2-1	9	1	E2-1	0.0020	15168.3317	0.0028

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
10	1	E1+1	9	1	E1+1	0.0020	15171.1365	-0.0007
10	1	A1	9	1	A2	0.0020	15171.2500	0.0016
10	1	B1	9	1	B2	0.0020	15172.1485	-0.0007
10	0	E2+1	9	1	E2-1	0.0020	15186.4796	-0.0008
10	1	E2-1	9	0	E2+1	0.0020	15191.2017	0.0008
10	0	B1	9	0	B2	0.0020	15205.7246	-0.0001
10	0	E1+1	9	0	E1+1	0.0020	15206.5483	0.0014
10	0	A1	9	0	A2	0.0020	15206.6332	0.0005
10	0	E2+1	9	0	E2+1	0.0020	15209.3535	0.0011
10	0	B1	9	1	B2	0.0020	15248.7522	0.0023
9	1	E1-1	8	1	E1-1	0.0020	15426.7770	0.0007
9	1	A1	8	1	A2	0.0020	15427.0200	-0.0042
9	1	B1	8	1	B2	0.0020	15427.3100	-0.0024
9	7	A2	8	7	A1	0.0100	15443.3605	0.0020
9	7	A1	8	7	A2	0.0100	15443.3605	0.0010
9	7	E1-1	8	7	E1-1	0.0100	15443.3605	-0.0018
9	7	E2+1	8	7	E2+1	0.0100	15443.4168	-0.0034
9	7	E1+1	8	7	E1+1	0.0100	15443.5155	-0.0023
9	7	B2	8	7	B1	0.0100	15443.5346	0.0017
9	7	B1	8	7	B2	0.0100	15443.5346	0.0008
9	7	E2-1	8	7	E2-1	0.0100	15443.6293	-0.0054
9	6	E2-1	8	6	E2-1	0.0020	15468.5650	-0.0004
9	6	E1+1	8	6	E1+1	0.0020	15468.6160	-0.0019
9	6	A1	8	6	A2	0.0020	15468.7430	-0.0030
9	6	E2+1	8	6	E2+1	0.0020	15468.8400	0.0038
9	6	E1-1	8	6	E1-1	0.0020	15468.9540	-0.0005
9	3	A2	8	3	A1	0.0020	15477.2160	-0.0007
9	3	B2	8	3	B1	0.0020	15477.4040	-0.0005
9	3	E1+1	8	3	E1+1	0.0020	15478.8510	0.0003
9	3	E2-1	8	3	E2-1	0.0020	15479.3140	0.0009
12	2	E2+1	12	0	E2+1	0.0040	15537.8183	0.0039
12	2	A2	12	0	A1	0.0040	15541.9590	-0.0001
9	4	B1	8	4	B2	0.0020	15563.3370	-0.0007
9	4	A1	8	4	A2	0.0020	15563.4970	0.0000
9	4	E2+1	8	4	E2+1	0.0020	15580.9220	0.0006
9	4	E1-1	8	4	E1-1	0.0020	15582.3490	0.0022
9	4	E1+1	8	4	E1+1	0.0020	15612.8020	0.0002
9	4	E2-1	8	4	E2-1	0.0020	15614.0780	-0.0004
9	4	B2	8	4	B1	0.0020	15631.4170	0.0052
9	4	A2	8	4	A1	0.0020	15631.5470	-0.0014
4	3	B1	3	2	B2	0.0040	15918.5493	-0.0003
4	3	B2	3	2	B1	0.0040	16061.6128	0.0024

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
9	3	E2+1	8	3	E2+1	0.0020	16071.4630	-0.0007
9	3	E1-1	8	3	E1-1	0.0020	16071.7970	-0.0001
9	3	A1	8	3	A2	0.0020	16073.1390	0.0011
9	3	B1	8	3	B2	0.0020	16073.2030	-0.0001
5	2	A2	4	1	A1	0.0100	16086.5265	0.0106
4	3	A1	3	2	A2	0.0020	16158.5572	-0.0001
5	2	E2-1	4	1	E2-1	0.0100	16266.4568	0.0115
4	3	A2	3	2	A1	0.0040	16301.6051	0.0059
9	2	E2-1	8	2	E2-1	0.0020	16377.8770	-0.0007
9	2	E1+1	8	2	E1+1	0.0020	16377.9220	-0.0005
9	2	A2	8	2	A1	0.0020	16378.0830	0.0000
10	2	E2+1	9	2	E2+1	0.0020	16423.1850	0.0013
10	2	B2	9	2	B1	0.0020	16423.2390	0.0002
10	2	E1-1	9	2	E1-1	0.0020	16423.3500	-0.0011
10	2	A2	9	2	A1	0.0020	16423.5640	-0.0008
11	1	E2-1	10	0	E2+1	0.0020	16607.4134	0.0014
11	1	E1+1	10	1	E1+1	0.0020	16624.6970	0.0021
11	1	A2	10	1	A1	0.0020	16624.8070	0.0011
11	1	B2	10	1	B1	0.0020	16625.0230	0.0037
11	1	E2-1	10	1	E2-1	0.0020	16625.5630	-0.0005
11	0	E2+1	10	0	E2+1	0.0020	16643.9480	0.0017
11	0	B2	10	0	B1	0.0020	16644.6823	0.0001
11	0	E1+1	10	0	E1+1	0.0020	16644.8205	0.0037
11	0	A2	10	0	A1	0.0020	16644.9025	0.0021
11	0	E2+1	10	1	E2-1	0.0020	16662.0971	-0.0006
10	1	E1-1	9	1	E1-1	0.0020	16858.1570	0.0002
10	1	E2+1	9	1	E2+1	0.0020	16858.3290	0.0003
10	1	A2	9	1	A1	0.0020	16858.4310	0.0024
10	1	B2	9	1	B1	0.0020	16858.7870	-0.0013
5	2	E2-1	4	0	E2+1	0.0100	17095.6569	0.0066
5	2	E1+1	4	0	E1+1	0.0100	17095.9258	0.0042
5	2	A2	4	0	A1	0.0100	17096.3233	0.0091
5	2	B2	4	0	B1	0.0100	17096.3586	0.0084
10	3	A1	9	3	A2	0.0020	17158.0680	0.0011
10	3	B1	9	3	B2	0.0020	17158.2880	0.0004
10	3	E1+1	9	3	E1+1	0.0020	17158.8240	0.0015
10	3	E2-1	9	3	E2-1	0.0020	17159.1050	-0.0009
10	5	A1	9	5	A2	0.0020	17267.3330	-0.0001
10	5	B1	9	5	B2	0.0020	17267.5110	0.0015
10	5	E1+1	9	5	E1+1	0.0020	17271.9050	-0.0019
10	5	E2-1	9	5	E2-1	0.0020	17272.0730	0.0001
10	5	A2	9	5	A1	0.0020	17275.9800	0.0005

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
10	5	B2	9	5	B1	0.0020	17276.1510	-0.0012
10	4	B2	9	4	B1	0.0020	17322.0330	-0.0003
10	4	A2	9	4	A1	0.0020	17322.2090	0.0002
10	4	E2+1	9	4	E2+1	0.0020	17336.7670	-0.0003
10	4	E1-1	9	4	E1-1	0.0020	17339.0800	-0.0001
10	4	E1+1	9	4	E1+1	0.0020	17446.0870	-0.0022
10	4	E2-1	9	4	E2-1	0.0020	17448.2510	0.0030
10	4	B1	9	4	B2	0.0020	17462.6670	0.0008
10	4	A1	9	4	A2	0.0020	17462.7960	-0.0004
5	3	A2	4	2	A1	0.0040	17707.6526	-0.0026
11	2	E2+1	10	2	E2+1	0.0020	17938.9940	-0.0002
11	2	B1	10	2	B2	0.0020	17939.1080	-0.0005
11	2	E1-1	10	2	E1-1	0.0020	17939.1850	0.0001
11	2	A1	10	2	A2	0.0020	17939.5150	0.0005
10	3	E2+1	9	3	E2+1	0.0020	18031.6350	-0.0005
10	3	E1-1	9	3	E1-1	0.0020	18031.7760	0.0006
10	3	A2	9	3	A1	0.0020	18032.2490	0.0017
10	3	B2	9	3	B1	0.0020	18032.3060	-0.0027
12	1	E1+1	11	1	E1+1	0.0020	18075.3480	0.0005
12	1	A1	11	1	A2	0.0020	18075.4530	0.0020
12	1	E2-1	11	1	E2-1	0.0020	18075.5110	-0.0011
12	1	B1	11	1	B2	0.0020	18075.5270	0.0022
12	0	E2+1	11	0	E2+1	0.0020	18086.3479	0.0018
12	0	E1+1	11	0	E1+1	0.0020	18086.5128	0.0008
12	0	B1	11	0	B2	0.0020	18086.5281	0.0040
12	0	A1	11	0	A2	0.0020	18086.6003	-0.0007
10	2	E2-1	9	2	E2-1	0.0020	18115.3530	-0.0010
10	2	E1+1	9	2	E1+1	0.0020	18115.4320	0.0024
10	2	B1	9	2	B2	0.0020	18115.4940	-0.0002
10	2	A1	9	2	A2	0.0020	18115.6640	-0.0010
5	3	A1	4	2	A2	0.0100	18136.3054	0.0074
11	1	E1-1	10	1	E1-1	0.0020	18259.4810	0.0001
11	1	E2+1	10	1	E2+1	0.0020	18259.6820	-0.0019
11	1	A1	10	1	A2	0.0020	18259.7160	0.0044
11	1	B1	10	1	B2	0.0020	18260.1580	-0.0001
11	3	A2	10	3	A1	0.0020	18812.3460	0.0002
11	3	B2	10	3	B1	0.0020	18812.6040	-0.0005
11	3	E1+1	10	3	E1+1	0.0020	18812.6970	0.0001
11	3	E2-1	10	3	E2-1	0.0020	18812.9130	-0.0006
13	1	E1+1	12	1	E1+1	0.0020	19524.2677	0.0001
13	1	E2-1	12	1	E2-1	0.0020	19524.3205	0.0008
13	1	A2	12	1	A1	0.0020	19524.3646	0.0001

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
13	1	B2	12	1	B1	0.0020	19524.3980	0.0035
13	0	E2+1	12	0	E2+1	0.0020	19530.2958	-0.0003
13	0	E1+1	12	0	E1+1	0.0020	19530.3522	0.0032
13	0	B2	12	0	B1	0.0020	19530.4104	-0.0005
13	0	A2	12	0	A1	0.0020	19530.4448	0.0020
12	1	E1-1	11	1	E1-1	0.0020	19654.8517	-0.0035
12	1	A2	11	1	A1	0.0020	19654.9197	-0.0019
12	1	E2+1	11	1	E2+1	0.0020	19655.0937	-0.0015
12	1	B2	11	1	B1	0.0020	19655.5377	-0.0008
14	1	E1+1	13	1	E1+1	0.0020	20972.1970	-0.0013
14	1	E2-1	13	1	E2-1	0.0020	20972.2194	0.0015
14	1	A1	13	1	A2	0.0020	20972.2905	-0.0010
14	1	B1	13	1	B2	0.0020	20972.3086	0.0018
14	0	E2+1	13	0	E2+1	0.0020	20975.4430	-0.0008
14	0	E1+1	13	0	E1+1	0.0020	20975.4662	0.0023
14	0	B1	13	0	B2	0.0020	20975.5419	-0.0016
14	0	A1	13	0	A2	0.0020	20975.5609	0.0009
13	1	A1	12	1	A2	0.0020	21057.0411	-0.0018
13	1	E1-1	12	1	E1-1	0.0020	21057.6043	0.0000
13	1	E2+1	12	1	E2+1	0.0020	21057.9162	-0.0003
13	1	B1	12	1	B2	0.0020	21058.3004	0.0002
15	1	E1+1	14	1	E1+1	0.0020	22419.5846	-0.0018
15	1	E2-1	14	1	E2-1	0.0020	22419.5963	0.0007
15	1	A2	14	1	A1	0.0020	22419.6757	-0.0012
15	1	B2	14	1	B1	0.0020	22419.6893	0.0007
15	0	E2+1	14	0	E2+1	0.0020	22421.3105	-0.0006
15	0	E1+1	14	0	E1+1	0.0020	22421.3214	0.0008
15	0	B2	14	0	B1	0.0020	22421.4038	-0.0019
15	0	A2	14	0	A1	0.0020	22421.4178	0.0008
14	1	A2	13	1	A1	0.0020	22464.5266	0.0007
14	1	E1-1	13	1	E1-1	0.0020	22471.4599	0.0005
14	1	E2+1	13	1	E2+1	0.0020	22472.0193	-0.0006
14	1	B2	13	1	B1	0.0020	22472.3380	0.0001
16	1	E1+1	15	1	E1+1	0.0100	23866.6937	0.0050
16	1	E2-1	15	1	E2-1	0.0100	23866.6937	-0.0010
16	1	A1	15	1	A2	0.0020	23866.7778	-0.0016
16	1	B1	15	1	B2	0.0020	23866.7898	0.0009
16	0	E2+1	15	0	E2+1	0.0040	23867.5936	-0.0021
16	0	E1+1	15	0	E1+1	0.0040	23867.6020	0.0001
16	0	B1	15	0	B2	0.0020	23867.6859	-0.0022
16	0	A1	15	0	A2	0.0020	23867.6984	0.0005
15	1	E1-1	14	1	E1-1	0.0020	23893.9616	-0.0003

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
15	1	E2+1	14	1	E2+1	0.0020	23896.3478	0.0007
15	1	B1	14	1	B2	0.0020	23896.6183	0.0008
15	1	A1	14	1	A2	0.0020	23909.8259	0.0000
14	2	A1	13	2	A2	0.0020	24254.2397	0.0002
14	4	B2	13	4	B1	0.0020	24261.5417	0.0023
14	4	A2	13	4	A1	0.0020	24261.8189	-0.0025
14	4	E2+1	13	4	E2+1	0.0020	24262.4964	0.0000
14	4	E1-1	13	4	E1-1	0.0020	24262.8515	-0.0005
14	6	A2	13	6	A1	0.0040	24267.2482	-0.0017
14	6	E2+1	13	6	E2+1	0.0040	24274.2682	0.0014
14	6	E2-1	13	6	E2-1	0.0040	24274.3463	0.0091
14	6	A1	13	6	A2	0.0020	24281.4148	0.0007
14	5	A1	13	5	A2	0.0020	24367.4990	0.0023
14	5	B1	13	5	B2	0.0020	24367.7229	-0.0002
14	5	E1+1	13	5	E1+1	0.0020	24382.1355	-0.0020
14	5	E2-1	13	5	E2-1	0.0020	24384.6795	-0.0015
14	5	E2+1	13	5	E2+1	0.0040	24528.8397	0.0001
14	5	E1-1	13	5	E1-1	0.0040	24531.1879	-0.0022
14	5	A2	13	5	A1	0.0040	24545.3151	-0.0017
14	5	B2	13	5	B1	0.0040	24545.4736	0.0001
15	3	E1+1	14	3	E1+1	0.0020	25130.5005	0.0016
15	3	A2	14	3	A1	0.0020	25130.6894	0.0004
15	3	E2-1	14	3	E2-1	0.0020	25130.7369	0.0020
15	3	B2	14	3	B1	0.0020	25131.1580	0.0006
14	4	E1+1	13	4	E1+1	0.0040	25255.7991	-0.0040
14	4	E2-1	13	4	E2-1	0.0020	25255.9875	0.0003
14	4	B1	13	4	B2	0.0020	25256.4410	-0.0012
14	4	A1	13	4	A2	0.0020	25256.4952	-0.0018
16	2	E1-1	15	2	E1-1	0.0040	25290.8229	-0.0009
16	2	E2+1	15	2	E2+1	0.0020	25296.7336	-0.0008
16	2	B2	15	2	B1	0.0020	25297.0829	-0.0010
16	2	A2	15	2	A1	0.0020	25298.5029	-0.0003
17	1	E1+1	16	1	E1+1	0.0100	25313.6509	0.0036
17	1	E2-1	16	1	E2-1	0.0100	25313.6509	-0.0014
17	1	A2	16	1	A1	0.0020	25313.7354	-0.0021
17	1	B2	16	1	B1	0.0020	25313.7465	-0.0003
17	0	E2+1	16	0	E2+1	0.0100	25314.1214	0.0013
17	0	E1+1	16	0	E1+1	0.0100	25314.1214	-0.0039
17	0	B2	16	0	B1	0.0020	25314.2088	-0.0024
17	0	A2	16	0	A1	0.0020	25314.2208	0.0001
16	1	A2	15	1	A1	0.0020	25327.1839	0.0002
16	1	E2+1	15	1	E2+1	0.0020	25328.3585	-0.0006

J	Ka	Sym	J'	Ka	'Sym'	Unc(MHz)	Measured(MHz)	o.-c.(MHz)
16	1	B2	15	1	B1	0.0020	25328.6127	-0.0011
16	1	E1-1	15	1	E1-1	0.0020	25334.2623	-0.0028
14	3	E1-1	13	3	E1-1	0.0020	25514.3494	-0.0003
14	3	E2+1	13	3	E2+1	0.0020	25514.4428	0.0008
14	3	A2	13	3	A1	0.0020	25514.5304	0.0048
14	3	B2	13	3	B1	0.0020	25514.7415	0.0004
15	2	E2-1	14	2	E2-1	0.0040	25633.0103	0.0003
15	2	E1+1	14	2	E1+1	0.0040	25633.2752	0.0019
15	2	B2	14	2	B1	0.0040	25633.5497	0.0006
15	2	A2	14	2	A1	0.0040	25634.0974	-0.0006

References

1. Chou Y-C, Hougen JT, J. Chem. Phys 124 (2006) 074319–1-10.
2. Ohashi N, Hougen JT, J. Mol. Spectrosc 121 (1987) 474–501.
3. Ilyushin VV, Alekseev EA, Chou Y-C, Hsu Y-C, Hougen JT, Lovas FJ, Picraux LB, J. Mol. Spectrosc 251 (2008) 56–63.
4. Ilyushin VV, Cloessner EA, Chou Y-C, Picraux LB, Hougen JT, Lavrich R, J. Chem. Phys 133 (2010) 184307–1–184307–9. [PubMed: 21073223]
5. Suenram RD, Grabow JU, Zuban A, Leonov I, Rev. Sci. Instrum 70 (1999) 2127–2135.
6. Ilyushin VV, Alekseev EA, Dyubko SF, Motiyenko RA, Hougen JT, J. Mol. Spectrosc 229 (2005) 170–187.
7. Motiyenko RA, Ilyushin VV, Drouin BJ, Yu S, Margulès L, Astronomy & Astrophysics 563, A137(6pp), 2014.
8. Motiyenko RA, Margulès L, Ilyushin VV, Smirnov IA, Alekseev EA, Halfen DT, Ziurys LM, Astronomy & Astrophysics 587, A152(6pp), 2016.
9. Ohashi N, Tsunekawa S, Takagi K, Hougen JT, J. Mol. Spectrosc 137 (1989) 33–46.
10. Ohashi N, private communication.
11. Taylor BN, Kuyatt CE, NIST Technical Note No. 1297 (1994). This publication may be downloaded from <http://physics.nist.gov/Pubs/guidelines/contents.html>.
12. Ohashi N, Hougen JT, «Cross-contamination of the fitting parameters in multidimensional tunneling treatments», J. Mol. Spectrosc accepted manuscript, 10.1016/j.jms.2017.04.015.

Figure 1. Molecular structure of 5-methyltropone (and 5-MT-OD), a seven membered “aromatic” ring which exhibits two large amplitude motions, internal rotation of the methyl group and a tautomeric proton (deuteron) transfer.

Figure 2.

Representative tunneling splitting patterns of the $6_{06} \leftarrow 5_{05}$ microwave transition of (a) 5-MT-OD and (b) 5-MT-OH, with G_{12} symmetry species labels. All lines consist of Doppler doublets (e.g., the A_1/A_2 line at 9501.524 MHz) because the microwave radiation in the cavity propagates parallel and antiparallel to the unidirectional molecular beam. In addition, each transition has four components because of the interplay of hydrogen-transfer and internal-rotation tunneling splittings in this molecule. Note that in the case of 5-MT-OD the B_1/B_2 and E_2 tunneling components are not fully resolved.

Figure 3.

Schematic illustration of energy level splittings arising from a back-and-forth large amplitude tunneling motion and an internal-rotation large amplitude tunneling motion, according to Eqs. (5) of [1]. The diagram has been drawn with unitless abscissa and ordinate, obtained by dividing both scales by $h_{2v} + h_{3v}$. The detailed description of this type of diagram may be found in Ref. [4]. Markers at the top of the diagram indicate the position along the abscissa appropriate for -OD and -OH isotopologues of 5-MT, as well as positions appropriate for -OD and -OH isotopologues of 2-methylmalonaldehyde [1,3], and for the ground [6] and first excited [9] torsional states of methylamine. Note that the unitless energies in this figure must be multiplied by $h_{2v} + h_{3v}$, and that the values of these two parameters for these examples are either both positive or both negative, so the denominators are never zero. Vertical arrows and their associated integers indicate the number of $\nu E_2 - \nu E_1$ and $\nu B_1 - \nu A_1$ b-type transitions of the -OD isotopologue of 5-MT observed in this work.

Table 1

Molecular parameters^a from our least-squares fit of tunneling-rotational transitions^b in the ground vibrational state of the –OD isotopologue of 5-methyltropolone.

Parameter	5-MT-OD	5-MT-OH [4]	Parameter	5-MT-OD	5-MT-OH [4]
$A - \bar{B}$	1857.30365(37)	1847.451966(30)	h_{2v}	–30.07307(27)	–654.950244(65)
$\bar{B}$	852.069155(16)	865.6481269(64)	h_{2j}	0.0000414(21)	0.00044662(71)
$(B - C)/4$	64.294341(11)	66.2152443(25)	h_{2k}	0.000445(42)	0.0090457(54)
s_1	16.27485(88)	12.396601(28)	f_2	-	–0.00013847(46)
ρ	0.0170663(40)	0.017096909(29)	h_{4v}	0.01630(12)	0.362221(25)
$D_J \times 10^4$	0.15012(70)	0.15669(29)	h_{3v}	–287.756(68)	–295.0732(19)
$D_{JK} \times 10^4$	0.4259(75)	0.4062(13)	h_{3j}	–0.0001118(36)	–0.0001171(15)
$D_K \times 10^4$	4.15(32)	2.353(11)	h_{3k}	-	–0.0001221(93)
$\delta_J \times 10^4$	–0.04280(39)	–0.04437(14)	f_3	–0.0000242(27)	–0.00002720(74)
$\delta_K \times 10^4$	–0.541(13)	–0.5103(36)	r_3	-	0.02555(34)
# of lines ^c	384	1015	rms	0.0028	0.0015

^aNumbers in parentheses denote one standard deviation (type A, $k = 1$) [11] and apply to the last digits of the parameters. All parameters and the root-mean-square deviation (rms) of the fit are in MHz, except for ρ , which is unitless. $\bar{B} \equiv (B + C)/2$.

^bTransition frequencies used in the fit are given in the supplemental material.

^cNumber of transitions included in the fit.