Next level achievement of the XIAM code in modeling the microwave spectrum of m-methylanisole

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Next level achievement of the *XIAM* code in modeling the microwave spectrum of *m*-methylanisole

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Abstract

The *XIAM* code is one of the most frequently used programs to treat the microwave spectra of molecules with up to three methyl internal rotors. *XIAM* is user-friendly and fast, but often shows difficulties in dealing with low torsional barriers. An example is the case of *m*-methylanisole where the methyl group attached at the meta-position of the ring undergoes internal rotation with a barrier height of about 56 cm^{-1} for the *cis* conformer and 37 cm^{-1} for the *trans* conformer. The standard deviation obtained with *XIAM* is much larger than the measurement accuracy for both conformers. Recently, the code has been modified, and three higher order effective parameters connected to the potential term $\cos(3\alpha)$ were implemented, which reduced the standard deviations of the fits to almost measurement accuracy.

The molecular jet Fourier transform microwave spectra of two conformers of *m*-methylanisole (MMA) have been measured in the frequency range from 2 to 26.5 GHz [1]. Large splittings arising from the internal rotation of the methyl group at the meta-position of the ring were observed, leading to the determination of low V_3 potential barriers of 55.7693(90) and 36.6342(84) cm^{-1} for the *cis*- and the *trans*-conformer, respectively. These torsional splittings were analyzed with the program *XIAM* [2], which works in a combined axis system. For each methyl rotor, the Hamiltonian for the internal rotation is set up in the rho axis system, and then rotated into the principal axis system. *XIAM* is one of the codes most frequently used in the microwave spectroscopic community for fitting spectra of molecules with methyl internal rotations, because it is user-friendly and fast. However, the fitting results for MMA were not satisfactory. While the line frequencies could be determined with a measurement accuracy of about 4 kHz, the standard deviation of the fit was 27.0 kHz for the *cis* conformer and 32.1 kHz for the *trans* conformer [1]. This might be traced back to (i) the limited number of high order parameters available in *XIAM* and (ii) the fact that interactions between different v_t states are not considered explicitly and some matrix elements are neglected. The second assumption has been tested in Ref. [1] by the program *aixPAM*, which works exclusively in the principal axis system (PAM) and does not neglect any matrix elements except for the truncation of the matrix (k_{max}). Fitting the same data set using the same set of parameters, *aixPAM* provided a slightly better standard deviation of 23.0 kHz for *cis*-MMA and 28.3 kHz for *trans*-MMA. The fits are presented as Fit I (*XIAM*) and Fit II (*aixPAM*) in Table II of Ref. [1]. The *XIAM* fits are also given in Table I.

By adding more effective parameters in the *aixPAM* fits, the standard deviations were reduced to measurement accuracy [1]. This indicated that high order effective terms are needed to model the microwave spectra of MMA, and we believed that adding more effective parameters to *XIAM* would yield fits with satisfactory deviations. However, it was not

possible at that time to test this assumption because higher order terms cannot be easily implemented in the *XIAM* code.

Recently, we succeeded to modify the *XIAM* code to deal with the chirped pulse microwave spectrum of 4-methylacetophenone [3]. Two effective higher order parameters D_{3cK} and D_{3c-}, multiplying the potential terms $\cos(3\alpha)\,P_a^2$ and $\cos(3\alpha)\,(P_b^2 - P_c^2)$, respectively, have been implemented in addition to the already available D_{3cJ} parameter which is connected with the $\cos(3\alpha)\,P^2$ term. They are often the most decisive parameters which reduce the standard deviation significantly, especially when the internal rotor axis does not lie along a principal axis. Not only in programs working in the principal axis system such as *aixPAM* [1] or *PAM-C_{2v}-2tops* [4], or in the "quasi-PAM" system such as the two-top programs written by Ohashi et al. [5] or *BELGI-C_s-2Tops* [6], these three terms or their comparable versions have also provided their efficiency in treating internal rotation problems in programs working in the rho axis system like *BELGI-C_s* [7], *BELGI-C_1* [8], and *RAM36* [9]. By using only one of those parameters, D_{3cK}, the root-mean-square (rms) deviation of the 4-methylacetophenone *XIAM* fit has been reduced from 99 kHz to 29 kHz, close to the measurement accuracy of about 25 kHz [3]. The modified *XIAM* code has been checked again the program *ntop* [10], which is an extended version of *aixPAM*, using comparable data and parameter set. The difference in rms deviations is 29 kHz (*XIAM*) versus 26 kHz (*ntop*). This is essentially the same difference between Fit I (*XIAM*) and Fit II (*aixPAM*) in Table II of Ref. [1].

We then applied the modified *XIAM* code to fit the microwave spectra of MMA by adding the D_{3cJ}, D_{3cK}, and D_{3c-} parameters to the *XIAM* fit given in Table I. The respective standard deviation was reduced to 6.0 kHz for *cis*-MMA and 4.3 kHz for *trans*-MMA. Fitting the comparable parameters V_J, V_K, and V_-, multiplying the operators $(1-\cos(3\alpha))P^2$, $(1-\cos(3\alpha))P_a^2$, and $(1-\cos(3\alpha))(P_b^2 - P_c^2)$, respectively, with *aixPAM* yielded the respective

standard deviation of 5.3 kHz and 4.0 kHz. The fits are presented as *XIAM*$_{mod}$ and *aixPAM* in Table 1. A list of all fitted frequencies along with their residues is available in Table S1 and S2 of the Supplementary Material for *cis*-MMA and *trans*-MMA, respectively.

The fit obtained with the modified version of *XIAM* for the *trans* conformer of MMA is quite satisfactory with a standard deviation close to measurement accuracy, proving that effective parameters associating with the cos(3α) term of the Hamiltonian also work efficiently in the combined axis system. We emphasize that in different coordinate systems, the parameters are not equivalent and have to be transformed to become comparable. For this reason, the fitted V_3 barriers from the original version of *XIAM* and *aixPAM* agree with each other better than with the modified version of *XIAM*, showing that the fitted barrier depends on the choice of effective constants. Figure 1 and 2 visualize the satisfaction of the fitting improvement for *trans*-MMA. For *cis*-MMA, the deviation is still slightly higher than the measurement accuracy, but has been significantly reduced compared to that of the fit obtained with the original version of *XIAM* [1]. It is possible that the implementation and use of other higher order effective parameters would succeed to reduce the current standard deviation for *cis*-MMA and improve the *XIAM* code.

With the results presented here, our assumption given in Ref. [1] that "additional effective parameters in *XIAM* would allow fits with standard deviations close to those obtained with *aixPAM*" is definitely confirmed. We note that the present work on MMA represents an application on a one-top problem, but the modified *XIAM* code can also be applied for a two-top and three-top problem as the original version of *XIAM*. The modified version of *XIAM* will be available at the PROSPE website [11]. The *XIAM* and *aixPAM* inputs and outputs are available as separate files in the supplementary material.

Acknowledgments

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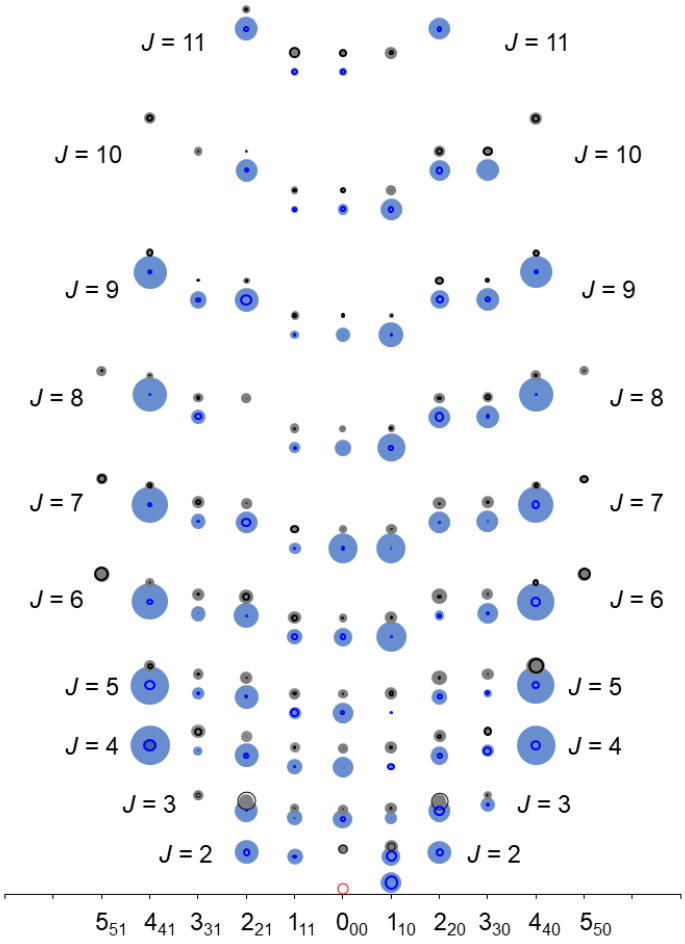

Figure 1.

Schematic illustration of the residuals of almost all the A species rotational transitions of *trans*-MMA. The residuals are plotted in columns labeled by a given K_a, ranging from 0 to 5. The J value in each column increases from $J = K_a$ to $J = 11$. For pairs of columns with the same K_a but different K_c, the column with $K_a + K_c = J$ is plotted to the right of the central $K_a = 0$ position, while the column with $K_a + K_c = J + 1$ is plotted to the left. All J and K values refer to the upper level of a $J''_{K_a'' K_c''} \leftarrow J'_{K_a' K_c'}$ transition. Open circles refer to the *XIAMmod* fit, while filled circles are residuals obtained from the original version of *XIAM*. The red open circle gives the position of the hypothetic $J'' = 0$ for orientation. The blue circles are *b*-type transitions, and the grey/black ones are *a*-type. The circle size and the residual are linear propotional. To avoid clutter, 27 A species residuals are not plotted in this figure. It can be seen that the *XIAMmod* fit provides much smaller residuals for *b*-type transitions than the fit obtained using the original version of *XIAM*.

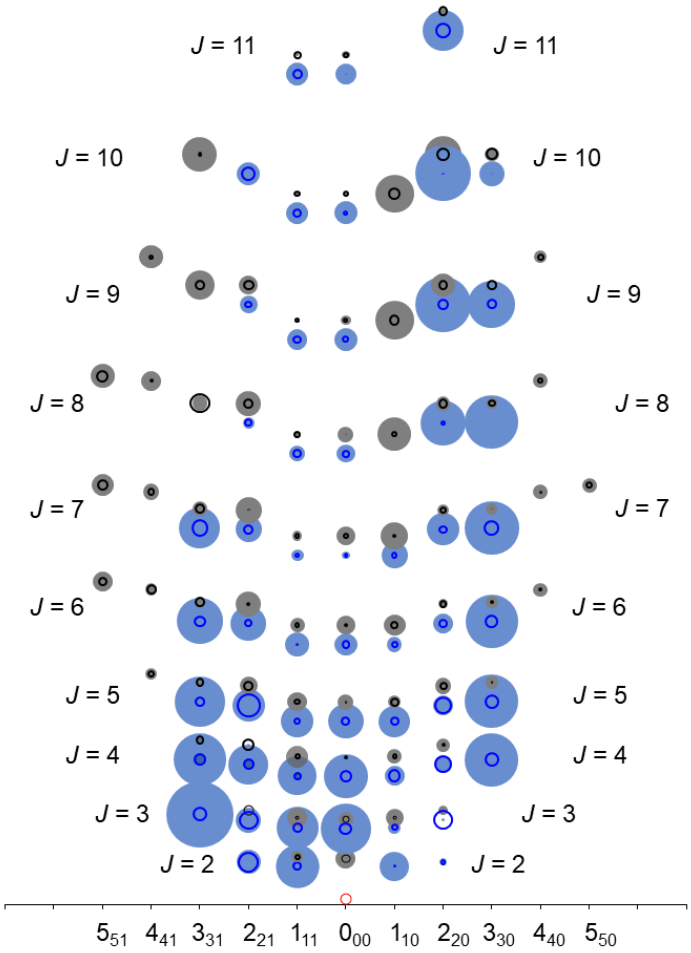

Figure 2.

Schematic illustration of the residuals of the E species rotational transitions of *trans*-MMA, using the same general layout as in Figure 1. To avoid clutter, 12 E species residuals are not plotted. The influence of the new parameters in *XIAMmod* is much greater for the E species than it is for the A species.

Table 1. Molecular parameters of *m*-methylanisole deduced using the *XIAM* code in its original and modified versions as well as the program *aixPAM*.

		***cis*-MMA**			***trans*-MMA**		
Par.[a]	Unit	*XIAM*[b]	$XIAM_{mod}$[c]	*aixPAM*[d]	*XIAM*[b]	$XIAM_{mod}$[c]	*aixPAM*[d]
A	MHz	2755.8636(70)	2755.9200(30)	2743.95(22)	3529.454(40)	3529.901(13)	3521.233(84)
B	MHz	1293.7072(25)	1293.7282(11)	1291.768(61)	1122.3350(17)	1122.35133(54)	1120.859(34)
C	MHz	890.60188(47)	890.60156(11)	889.49(21)	861.12564(46)	861.125443(61)	860.993(59)
Δ_J	kHz	0.0421(31)	0.04366(68)	0.05061(56)	0. 0310(33)	0.02453(45)	0.02314(43)
Δ_{JK}	kHz	−0.027(22)	−0.0734(50)	−0.0962(41)	0.071(21)	0.0636(29)	0.0458(28)
Δ_K	kHz	0.601(99)	0.474(23)	0.415(19)	−0.478(94)	0.334(15)	0.953(15)
δ_J	kHz	0.0129(14)	0.01427(31)	0.01795(25)	0.0091(17)	0.00610(23)	0.00566(22)
δ_K	kHz	0.045(16)	0.0427(36)	0.0841(28)	0.119(57)	0.0781(77)	0.0805(74)
D_{pi2J}	MHz	0.09310(87)	0.2058(94)	0.1519(78)	−0.03480(46)	0.0396(21)	0.0284(15)
D_{pi2K}	MHz	−0.2333(43)	0.761(23)	0.655(18)	0.904(22)	1.551(12)	1.2633(87)
D_{pi2-}	MHz	0.06634(84)	0.181(11)	0.1254(86)	−0.02056(48)	0.1465(39)	0.0329(35)
V_3	cm^{-1}	55.784(34)	56.096(16)	55.618(12)	36.548(32)	36.909(11)	36.5983(77)
F_0	GHz	157.074(96)	157.977(47)	156.914(36)	158.10(15)	159.714(49)	158.718(35)
$V_J/-D_{c3J}$[e]	MHz		1.196(96)	1.30(86)		0.675(19)	1.175(27)
$V_K/-D_{c3K}$[e]	MHz		10.20(23)	17.70(35)		7.679(80)	9.60(12)
$V_-/-D_{c3-}$[e]	MHz		1.21(10)	1.21(17)		1.477(33)	0.969(61)
$\angle$(i,a)[f]	°	51.6451(1)	51.6461(1)	51.5677(27)	146.8215(1)	146.8169(1)	146.8446(15)
N_A/N_E[i]		92/131	92/131	92/131	183/137	183/137	183/137
σ[j]	kHz	27.0	6.0	4.7	32.1	4.3	4.0

[a] All parameters refer to the principal axis system. Watson's A reduction and I^r representation were used. Standard errors are in the units of the last digits. [b] Fit with the original version of *XIAM*. [c] Fit with the modified version of *XIAM*. [d] Fit with the program *aixPAM*. [e] V_J, V_K, V_- in *aixPAM* and D_{3cJ}, D_{3cK}, D_{3c-} in $XIAM_{mod}$. [f] $\angle$(i,c) was fixed to 90° in all fits due to symmetry. [i] Number of the A and E species lines. [j] Standard deviation of the fit.