The low barrier methyl internal rotation in the rotational spectrum of 3-methylphenylacetylene

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Abstract

The rotational spectrum of 3-methylphenylacetylene has been recorded in the 2-8 GHz region using a broadband chirped-pulse microwave spectrometer. Torsion-rotation transition splittings are observed from a tunneling motion along the methyl internal rotation axis. The XIAM program was used to characterize the splitting, yielding an internal rotation barrier, V_3 , of 11.21745 ± 0.00002 cm⁻¹. While this barrier is considered low, fits of *A*-state only transitions yield a quality, rigid-rotor fit and are compared to the combined *A/E* fits. Computationally predicted barriers are estimated between 14.4 and 28.9 cm⁻¹.

Keywords: Low barrier, internal rotation, rotational spectroscopy, 3mp, 3-methylphenylacetylene, 3-ethynyltoluene, CAS 766-82-5

1. Introduction

The handling of low barrier methyl internal rotation in high-resolution spectroscopy remains a challenging aspect to spectroscopic research. As was outlined recently by Eibl et al.,[1] the research challenges of low barrier ($V_3 > 30$ 5 cm⁻¹) internal rotation are a combination of experimental and computational shortcomings. Computationally, low barriers are difficult to predict to a level of confidence that is useful to experimentalists, which increases the difficulty of

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assigning observed spectra based on these predictions. Even with more accurate predictions, the large splittings from low barriers still present a challenge in assignment for experimentalists, and splittings can be on the order of hundreds of MHz or even GHz. Additionally, the fitting procedure is often complicated by the need for large amounts of tunneling parameters, and there is not a well established procedure for determining which tunneling parameters will be important in the fitting process. Often, the initial values of the tunneling parameters are difficult to predict. Unlike centrifugal distortion constants, the physical meaning of the torsional tunneling parameters is not as clear.

Despite the difficulties associated with their assignment in rotational spectroscopy, internal rotation barriers are chemically useful as they can serve as a probe for local and long-range interactions in a molecule. When following a specific chemical motif, the internal rotation barrier can be used as a benchmark data set for computational methods. An example is seen in the change of the potential barrier of toluene for various levels of halogenation around the benzyl ring. In toluene, the V_6 barrier is reported as $4.837920599(11) \text{ cm}^{-1}$, [2] and increases for *p*-chlorotoluene ($4.872(14) \text{ cm}^{-1}$) [3], 3,5-difluorotoluene ($7.156(84) \text{ cm}^{-1}$) [4] and 2,4-difluorotoluene ($12.432(20) \text{ cm}^{-1}$), [4] but decreases slightly for *p*-fluorotoluene ($4.8298(64) \text{ cm}^{-1}$) [5]. In a more recent study, an investigation of *p*-halotoluenes found a *p*-chlorotoluene V_6 barrier of $4.836(29) \text{ cm}^{-1}$, which was also found to be a good barrier to describe the tunneling motion in *p*-bromotoluene and *p*-iodotoluene. [6] These studies provide a good data set for the interplay of local steric interactions and ring induction effects as measured by the change in internal rotation barrier.

An example of the change in internal rotation barrier in van der Waals complexes can also be seen, again with toluene as the subject. In a rotational spectroscopy study of the toluene complex with SO_2 , the potential barrier was increased to $V_3 = 83.236(2) \text{ cm}^{-1}$. [7] Comparing this to a non-polar binding partner, the potential barrier in the $\text{Ar} \cdots \text{toluene}$ complex was determined to

be $20 \pm 1 \text{ cm}^{-1}$ in an 2D laser induced fluorescence experiment.[8] In both
 40 cases, the interaction of the binding partner is with the π cloud of the ring, and
 changes in the barrier are likely a combination of intermolecular forces and steric
 effects. It should be noted that from a change of symmetry, the barriers are
 now 3-fold in the van der Waals complexes, instead of the 6-fold in the toluene
 and *p*-toluene molecules.

45 In a similar fashion to the toluene studies, 3-methylphenylacetylene (3mp,
 Figure 1) can be used as a basic structural motif to measure changes in the
 methyl group internal rotation barrier due to changes in the local chemical en-
 vironment. Unlike with toluene, van der Waals complexes involving 3mp can
 50 also have interactions with the carbon-carbon triple bond, instead of the π cloud
 of the ring. This will remove some of the steric interactions on the internal ro-
 tation barrier that are caused directly by forming a gas-phase complex, instead
 allowing for changes in barrier height from dispersion interactions and from ring
 induction induced by dispersion interactions to be observed. To begin this se-
 55 ries, this study focuses on the internal rotation of the low barrier internal methyl
 rotation of the 3mp monomer.

2. Experimental Methods

The broadband rotational spectrum from 2-8 GHz was collected on the
 60 COMPACT spectrometer at the Deutsches Elektronen-Synchrotron in Ham-
 burg, Germany. The details of the setup are described elsewhere,[9, 10] and
 is based on the chirp-pulsed broadband microwave (CP-FTMW) spectrometer
 design of Pate and co-workers.[11] A sample of 3mp was obtained from Sigma-
 Aldrich (97%) and used without further purification. With a boiling point of
 65 $170 - 175^\circ\text{C}$, a sufficient vapor pressure was achieved at room temperature. The
 vapor of 3mp was seeded in 4 bar (absolute pressure) of 5.0 neon and expanded
 through a General Valve Series 9 nozzle with an orifice of 1.1 mm at a repetition

rate of eight Hz. For each gas pulse, eight direct excitation pulses of 2-8 GHz were used. The free-induction decay of the induced polarization was directly
70 detected via a microwave horn antenna, resulting in an effective experimental repetition rate of 64 Hz. A total of one million free-induction decay signals were collected and converted to the frequency domain using a fast-Fourier transformation. Fitting procedures utilized the SPFIT/SPCAT software of Pickett[12] for initial fits. The two tunneling states, A and E , produced by the coupling of
75 the methyl rotor angular momentum to the rotational angular momentum, were predicted using the XIAM program[13]. While there are cases of SPFIT/SPCAT being used to predict and fit the A/E tunneling states and torsional splittings of a methyl rotor, XIAM presents a more straightforward approach to the handling of the torsional splitting. XIAM uses the inertial axis method to treat internal
80 rotation, and examples of its use are numerous. The graphical interface program AABS[14] was used to aid in pattern matching from predictions to assignments. Links to all programs used can be found on the PROSPE website,[15] which includes examples and references their respective uses.

3. Computational Methods

85 All calculations were completed using the ORCA computational chemistry software version 4.1.0[16] on the Maxwell Cluster at Deutsches Elektronen-Synchrotron. Optimizations of 3mp were completed using three different combinations of methods and basis sets. First, the single hybrid DFT, B3LYP,[17] with a def2-SVDP[18] basis set was employed. A double hybrid DFT level of
90 theory was also used, the B2PLYP[19] method with a def2-TZVPP[20] basis set. Both density functional methods were applied using Grimme’s dispersion correction, D3(BJ).[21, 22] Finally, an MP2[23] calculation with the aug-cc-pVDZ[24, 25] basis set was employed. Once the structure of 3mp was optimized for each method, that structure was used in a relaxed scan calculation of the
95 methyl groups, to predict the V_3 potential barrier, at increments of 10° from 0° to 120° . The optimized equilibrium state rotational constants and predicted V_3

Figure 1: Optimized structure of 3mp from the B2PLYP/def2-TZVPP D3(BJ) calculation.

barriers can be found in Table 1, and the optimized structure from the B2PLYP calculation is shown in Figure 1. The predicted value of δ , the angle between the methyl internal rotation axis and the principal a -axis, can also be found in

100 Table 1.

4. Results and Discussion

Rotational patterns belonging to the a -type transitions of 3mp were easily identified from predicted rotational constants, consistent with the approximately 1 D μ_a -dipole component predicted from the optimized structures in

105 Table 1. Initial fits of the A -state were completed using SPFIT/SPCAT. The A -symmetry torsional sub-level of the methyl tunneling states can often be described by a rigid-rotor Hamiltonian, which is why it was fit before the E -symmetry sub-level. In specific cases, the E -state transitions can also be fit separate of the A -state[26, 27] but this has only been carried out for systems

110 with an internal rotation barrier above 400 cm^{-1} . [26, 27, 28] While there is a small μ_b dipole moment component predicted for 3mp, only a -type transitions

Table 1: Predicted spectroscopic constants for 3mp.

		B3LYP	B2PLYP	MP2
		def2-SVPD	def2-TZVPP	aug-cc-pVDZ
A	MHz	3280	3313	3243
B	MHz	1186	1197	1171
C	MHz	876	884	865
V_3	cm^{-1}	28.9	14.4	14.7
V_3	kJ/mol	0.346	0.172	0.176
δ^{a}	deg	43.0	43.1	43.2
μ_a	D	1.01	1.00	0.94
μ_b	D	-0.07	-0.07	-0.10
μ_c^{b}	D	0	0	0

^a δ is the angle between the methyl rotor and the a -axis.

^b The dipole projection on the c -axis is zero by definition as the molecule has a plane of symmetry in the ab -plane.

were observed for the A -state. The initial fits using A -state rotational constants and the barrier and methyl rotation angle parameter δ from the B2PLYP optimized structure were used to predict transitions belonging to the E -state. Finally, a total of 19 A -state transitions and 35 E -state transitions were observed. A region of the recorded spectrum showing the A/E torsional splittings is shown in Figure 2. Searches for the singly substituted ^{13}C isotopologues in natural abundances were unsuccessful. A few possible candidates were identified for some of the stronger a -type transitions, but not enough were found to make a fit of the isotopic species.

A fit of A -state transitions with only $K_a = 0, 1$ yields a satisfactory rigid-rotor fit with an rms value of 8.8 kHz, a typical rms for a molecule with no large amplitude motions when using the Hamburg COMPACT spectrometer. Inclusion of higher K_a transitions from the A -state, up to $K_a = 3$, does not significantly increase the uncertainty of the fit, now 15.0 kHz. This has the most prominent effect on the A constant, changing by hundreds of kHz with the addition of higher K_a transitions. However, the inclusion of centrifugal distortion constants does not significantly affect the quality of the fit. Various combinations of the five quartic centrifugal distortion constants showed that only D_{JK} made any significant contribution, and D_J often had the incorrect sign when it was included (D_J must be positive). With these dubious values, it was assumed that the contributions of the distortion constants were compensating for the tunneling parameters in the A -state only fit, and therefore only the rigid-rotor constants are presented in Table 2.

Using the XIAM program, and the A -state fit as a starting point, the E -state lines were predicted and fit. The value of $V_3 = 14.4 \text{ cm}^{-1}$ was taken from the B2PLYP calculation as an initial value for the prediction, although starting from either the B3LYP (28.9 cm^{-1}) or MP2 (14.7 cm^{-1}) calculation yields the same result. As seen in Table 1, the internal rotation structural parameter δ , the angle between the internal rotation axis and a -axis, did not vary between the

three computational methods. The other structural internal rotation parameter, ϵ , was fixed to zero. This parameter is the angle between the projection of the methyl axis onto the bc -plane and the b -axis, but as the molecule is heavy-atom planar with the methyl internal rotation axis and the b -axis coplanar, ϵ is zero.

Inclusion of the tunneling parameters from XIAM was essential to producing the fit found in Table 2. The choice of parameters to include in the A/E state fits with XIAM required careful consideration of parameter values and correlations between these parameters. Due to the low number of E -state transitions, V_3 and F could not be fit simultaneously, and F was fixed at the values of 158.3 GHz. F is the angular momentum term for the methyl top, and it is common that it correlates to V_3 during the fitting process. Often it is chosen to be fixed in favor of the V_3 term. The internal rotation-molecular rotation distortion tunneling parameters, D_{c3J} , $D_{\pi2J}$, $D_{\pi2K}$, and $D_{\pi2-}$, were included, although the D_{c3J} parameter was the most significant in reducing the error of the fit and in including the b -, c -, and x -type selection rule transitions of the E -state. The c -type transitions would be dipole forbidden if the molecule did not have methyl torsional coupling, but the large angular momentum coupling from the methyl torsion in the E -state allows for the observation of the c -type and x -type transitions. At various points in the fitting procedure, the inclusion of the centrifugal distortion constants did little for the quality of the fit, and they were highly correlated to each other and to other parameters, so that they were again excluded from the fit. Attempts were made to fit a V_6 potential, and a value of about 2 cm^{-1} was determined, but this was highly correlated to the V_3 value. No matter which combination of tunneling parameters were used, the potential barrier V_3 was consistently around 11.2 cm^{-1} , imparting credibility to the value of $11.21745(2) \text{ cm}^{-1}$ in Table 2. In the fit chosen for Table 2, there is still high correlation between the D_{c3J} and $D_{\pi2J}$.

An improved fit uncertainty can be achieved by removing certain E -state transitions from the fit. However, this keeps the V_3 close to the $11.21745(2)$

Figure 2: Observed spectrum of 3mp from 5200 MHz to 7100 MHz. Red labeled transitions show the A/E symmetry state splittings for selected a -type transitions. A/E splittings vary depending on transition, from a few MHz to almost a GHz. In green, an x -type transition belonging to the E -state. Many of the weaker transitions between 5250-5750 are c -type and x -type transitions. Not seen in this frequency region are the observed b -type transitions.

Table 2: Results from the spectroscopic fits of SPFIT and XIAM for 3mp

		SPFIT	SPFIT	Xiam
State		<i>A</i> only	<i>A</i> only	<i>A</i> & <i>E</i>
		$K_a = 0$ and $K_a = 1$	all K_a	
<i>A</i>	MHz	3330.32(13) ^a	3330.7009(94)	3294.467(26)
<i>B</i>	MHz	1196.7401(11)	1196.73760(98)	1192.6675(18)
<i>C</i>	MHz	880.35776(72)	880.35771(98)	880.3578(18)
<i>D</i> _{<i>c</i>3<i>J</i>}	MHz	-	-	-2.04(14)
<i>D</i> _{π2<i>J</i>}	MHz	-	-	0.145(12)
<i>D</i> _{π2<i>K</i>}	MHz	-	-	0.7266(14)
<i>D</i> _{π2-}	MHz	-	-	-0.00268(33)
<i>F</i>	GHz	-	-	[158.3] ^b
<i>V</i> ₃	cm ⁻¹	-	-	11.21745(2) ^c
δ^d	deg	-	-	43.06908(14)
<i>N</i> ^e		11	19	54
<i>rms</i> ^f	kHz	8.8	15.0	29.9

^a Values in parenthesis are 1σ uncertainties in the least significant digits.

^b Value was fixed during fitting.

^c For *V*₃, the value in parenthesis is the absolute error in the least significant digit.

^d δ is the angle between the methyl rotor and the *a*-axis.

^e The number of transitions used in the fit.

^f The uncertainty of the fit.

cm^{-1} value of the fit of all transitions. As this does not change the focus pa-
 175 rameter of this study, V_3 , all measured transitions were included in the final
 fit. However, it is clear that there are missing tunneling parameters needed to
 describe the internal rotation in 3mp. XIAM does not contain any additional pa-
 rameters that were not tried in the fitting procedure. Other programs that can
 fit methyl internal rotation were also used, and these programs have additional
 180 tunneling parameters. An attempt was made with Groner’s ERHAM[29, 30] to
 find a more accurate fit, but as is stated in the literature, ”ERHAM requires
 some expertise in choosing the best set of parameters,” [31] and a converged fit
 could not be obtained for 3mp, even with the excellent list of tunneling param-
 eters provided in one of more recent ERHAM publications from the author.[30]
 185 An attempt to fit the observed data set with Ilyushin’s RAM36[2] program pro-
 duced high uncertainties in the fit, but this is likely do to the incorrect choice
 of tunneling parameters. Of the three internal rotation fitting programs tried,
 we were only able to obtain a quality fit with XIAM. Likely this is a mixture of
 faults, first with the limited data set. The majority of the observed transitions
 190 are low J and low K , as the molecule is not heavy with only 9 heavy atoms.
 Likely measurements at higher frequency ranges would be needed to explore the
 use of additional tunneling parameters in ERHAM and RAM36. Even then,
 the choice of tunneling parameters in these programs is not always obvious, and
 careful consideration will be needed in choosing the correct terms.

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Comparison of the observed internal rotation barrier, $V_3 = 11.21745(2)$
 cm^{-1} , to the predicted barriers of the computational methods does shed some in-
 sight onto which methods may perform better at predicting low barrier internal
 rotation problems. Both the double-hybrid B2PLYP and the MP2 calculations
 200 predicted a barrier height to within 3.5 cm^{-1} of the experimental value. The
 B3LYP calculation is significantly less accurate, over-predicting by 17.7 cm^{-1} ,
 an error of 61%. In this case, the more Hartee-Fock included in the calculation,
 the more accurate the resulting barrier. However, this is a comparison of only
 one experimental result with one set of computational methods. A more accu-

205 rate comparison would come from either an experimental data set including the
para and *ortho* equivalent methylphenylacetylene molecules, or a set of van der
Waals complexes to show the effect of the intermolecular forces on the internal
rotation barrier, as was pointed out in the essay of Mata and Suhm.[32]

210 5. Conclusion

With an understanding of the potential barrier, van der Waals complexes
with 3mp can now be studied to observe indirectly the effects of intermolecu-
lar forces. Indeed, some complexes have already been observed that have no
steric interaction with the methyl rotor, but still affect the barrier to internal
215 rotation.[33] It is believed that with an increased mass and lower rotational
constants of the complexes of 3mp compared to the monomer, additional tran-
sitions will allow for a better determination of the tunneling parameters needed
to describe the internal rotation motion in 3mp.

220 6. Supplementary Information

Input and output files for the SPFIT/SPCAT and the XIAM fits presented
in Table 2 are included in the supplementary material.

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