Supporting Information

Characterization of Large Amplitude Motions and Hydrogen Bonding Interactions in the Thiophene–Water Complex by Rotational Spectroscopy

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Appendix 1: Cartesian coordinates for the conformers of thiophene–w

Appendix 2: Assigned transitions and residuals for the observed conformer of thiophene–w

Appendix 3: Full set of calculated spectroscopic parameters for conformer I of thiophene–w

Appendix 1: Cartesian coordinates for the conformers of thiophene–w

Table S1. Cartesian coordinates of conformer I obtained at the B2PLYP-D3(BJ)/def2-TZVP level

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.925293	0.411849	-1.084408
C	-0.316248	1.463377	-0.454135
C	0.065843	1.150140	0.878095
C	-0.260564	-0.134116	1.228478
S	-1.035542	-0.958938	-0.059518
H	-1.313903	0.372027	-2.088390
H	-0.145611	2.420477	-0.923510
H	0.557753	1.841239	1.546273
H	-0.089015	-0.632086	2.168257
O	2.910053	-0.448003	-0.283490
H	2.682679	-0.763899	-1.162251
H	2.076111	-0.132049	0.083516

Table S2. Cartesian coordinates of conformer II obtained at the B2PLYP-D3(BJ)/def2-TZVP level

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-1.994018	-0.389195	0.000016
C	-1.916196	0.977448	0.000012
C	-0.574728	1.445202	-0.000008
C	0.341110	0.427520	-0.000020
S	-0.434202	-1.102586	-0.000007
H	-2.876908	-1.006386	0.000029
H	-2.783162	1.621488	0.000024
H	-0.298096	2.489151	-0.000014
H	1.418347	0.484990	-0.000036
O	3.724794	0.140015	0.000009
H	4.269497	-0.067794	0.764643
H	4.269586	-0.067750	-0.764574

Table S3. Cartesian coordinates of conformer III obtained at the B2PLYP-D3(BJ)/def2-TZVP level

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.140701	0.814034	0.313083
C	1.067768	-1.399349	0.050345
C	2.080545	-0.451279	-0.257618
C	1.619660	0.836813	-0.223995
S	-0.044997	0.894796	0.187812
H	-1.081336	-1.275449	0.562898
H	1.226382	-2.467236	0.075633
H	3.102277	-0.710559	-0.492354
H	2.167485	1.745196	-0.411602
O	-3.280322	-0.264850	-0.201134
H	-4.162486	0.113503	-0.147055
H	-2.859895	0.175440	-0.946294

Table S4. Cartesian coordinates of conformer IV obtained at the B2PLYP-D3(BJ)/def2-TZVP level

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	1.473007	-1.120028	-0.000018
C	0.116685	-1.305486	0.000017
C	-0.605758	-0.081816	0.000045
C	0.223056	1.007661	0.000031
S	1.876102	0.546924	-0.000017
H	2.249125	-1.867114	-0.000044
H	-0.348245	-2.280279	0.000024
H	-1.684165	-0.011317	0.000075
H	-0.049155	2.050005	0.000045
O	-4.078833	0.142123	-0.000018
H	-4.661116	0.179419	0.764232
H	-4.660949	0.179469	-0.764393

Appendix 2: Assigned transitions and residuals for the observed conformer of thiophene–w

Table S5. Assigned transitions and residuals for the parent species the observed conformer

J'	K_a'	K_c'	v'	J''	K_a''	K_c''	v''	ν_{obs} /MHz	$\nu_{obs - calc}$
2	1	2	0	1	1	1	0	7727.9358	0.0022
2	1	2	1	1	1	1	1	7748.7076	0.0003
2	0	2	0	1	0	1	0	7912.5292	0.0000
2	0	2	1	1	0	1	1	7933.6215	-0.0005
2	1	1	0	1	1	0	0	8146.5282	0.0002
2	1	1	1	1	1	0	1	8166.4924	-0.0001
3	1	3	0	2	1	2	0	11576.8750	-0.0014
3	1	3	1	2	1	2	1	11608.4783	-0.0003
3	0	3	0	2	0	2	0	11808.5114	-0.0003
3	0	3	1	2	0	2	1	11841.8562	0.0004
3	2	2	0	2	2	1	0	11904.7201	0.0013
3	2	2	1	2	2	1	1	11935.4044	0.0000
3	2	1	0	2	2	0	0	12001.9472	-0.0006
3	2	1	1	2	2	0	1	12029.8164	-0.0001
3	1	2	0	2	1	1	0	12202.7501	-0.0006
3	1	2	1	2	1	1	1	12233.2612	0.0003
4	1	4	0	3	1	3	0	15410.2640	-0.0009
4	1	4	1	3	1	3	1	15453.0865	0.0000
4	0	4	0	3	0	3	0	15643.6069	0.0005
4	0	4	1	3	0	3	1	15690.3906	0.0000
4	2	3	0	3	2	2	0	15852.8011	-0.0006
4	2	2	0	3	2	1	0	16082.7275	0.0000
4	2	2	1	3	2	1	1	16118.2466	0.0000
4	1	3	0	3	1	2	0	16235.8842	0.0005
4	1	3	1	3	1	2	1	16277.7696	-0.0001
5	1	5	0	4	1	4	0	19226.5890	0.0009
5	1	5	1	4	1	4	1	19280.9584	0.0000
5	0	5	0	4	0	4	0	19423.5126	-0.0004
5	0	5	1	4	0	4	1	19483.7760	-0.0001

Table S6. Assigned transitions and residuals for the ^{18}O isotopic species of the observed conformer

J'	K_a'	K_c'	v'	J''	K_a''	K_c''	v''	ν_{obs} /MHz	$\nu_{obs - calc}$
2	1	2	0	1	1	1	0	7282.2081	0.0078
2	0	2	0	1	0	1	0	7451.3914	-0.0018
2	0	2	1	1	0	1	1	7470.8678	0.0065
2	1	1	0	1	1	0	0	7657.0922	-0.0060
2	1	1	1	1	1	0	1	7675.9726	-0.0065
3	1	3	0	2	1	2	0	10912.0412	-0.0011
3	1	3	1	2	1	2	1	10941.0749	-0.0011
3	0	3	0	2	0	2	0	11131.8727	-0.0043
3	0	3	1	2	0	2	1	11162.1952	-0.0021
3	2	2	0	2	2	1	0	11203.3950	0.0009
3	2	1	0	2	2	0	0	11275.9299	-0.0035
3	1	2	0	2	1	1	0	11473.1051	0.0080
3	1	2	1	2	1	1	1	11501.7856	0.0032

Appendix 3: Full set of calculated spectroscopic parameters for conformer I of thiophene–w

Table S7. Calculated rotational and centrifugal distortion constants for conformer I of thiophene–w obtained at the B2PLYP-D3(BJ)/def2-TVZP level of theory.

Parameter	AMA-I-w-I
A/MHz	3461
B/MHz	1983
C/MHz	1788
D_J/kHz	8.612
D_{JK}/kHz	5.282
D_K/kHz	1.214
d_1/kHz	-0.425
d_2/kHz	-0.090