Microwave Spectroscopic and Computational Analyses of the Phenylacetylene⋯Methanol Complex: Insights into Intermolecular Interactions

Surabhi Gupta[a], Charlotte N. Cummings[b], Nicholas R. Walker[b] and Elangannan Arunan[a]*

[a]Department of Inorganic and Physical Chemistry, Indian Institute of Science Bangalore, 560012, India

[b]Chemistry-School of Natural and Environmental Sciences, Newcastle University, Bedson Building, Newcastle-upon-Tyne NE1 7RU, United Kingdom

Email: arunan@iisc.ac.in

Supplementary Information:

Table S1: Experimentally observed rotational transition and their assignments for the $C_6H_5CCH\cdots CH_3OH$ complex.

Transitions	A-State		E-State	
	ν_{obs}	$\nu_{obs-cal}$	ν_{obs}	$\nu_{obs-cal}$
2 1 2 → 1 1 1	2674.841	0.007	--	--
1 1 0 → 0 0 0	2751.909	0.005	2752.338	-0.007
2 0 2 → 1 0 1	2827.838	0.000	2826.037	0.005
4 2 3 → 4 1 3	2916.086	0.014	2916.819	-0.011
2 1 1 → 1 1 0	3015.822	0.002	3015.006	0.001
4 2 2 → 4 1 3	3166.729	-0.005	--	--
3 0 3 → 2 1 2	3193.478	-0.003	--	--
3 2 2 → 3 1 2	3232.010	0.007	3230.366	-0.003
2 2 1 → 2 1 1	3476.099	0.007	3467.847	-0.005
2 2 0 → 2 1 1	3493.570	0.013	--	--
9 2 7 → 9 2 8	3503.176	0.001	--	--
4 0 4 → 3 1 2	3695.687	0.012	--	--
2 1 2 → 1 0 1	3833.575	0.000	3834.746	-0.005
3 1 3 → 2 1 2	4001.784	0.002	4003.048	0.000
2 2 0 → 2 1 2	4005.049	0.008	--	--
3 0 3 → 2 0 2	4199.220	0.002	4195.706	0.002
3 2 2 → 3 1 3	4253.832	0.008	4249.064	-0.007
3 2 2 → 2 2 1	4268.033	0.003	4273.546	0.003
5 1 4 → 4 2 2	4283.618	0.013	4278.869	-0.050
3 2 1 → 2 2 0	4336.692	-0.006	4329.521	0.000
3 2 1 → 3 1 3	4339.962	0.006	4340.359	-0.016
2 1 1 → 1 0 1	4345.061	0.002	4345.467	-0.007
5 0 5 → 4 1 3	4510.777	-0.002	--	--
3 1 2 → 2 1 1	4512.123	0.004	4511.031	0.005
4 0 4 → 3 1 3	4717.498	0.002	--	--

4 2 2 → 4 1 4	4863.771	0.003	--	--
3 1 3 → 2 0 2	5007.522	0.003	5011.761	-0.006
7 3 5 → 7 2 5	5043.567	0.000	5042.878	-0.011
4 1 4 → 3 1 3	5317.678	0.003	5321.644	0.001
6 3 4 → 6 2 4	5480.410	0.004	5476.219	0.010
4 0 4 → 3 0 3	5525.800	0.003	5518.885	-0.001
5 2 3 → 5 1 5	5621.210	0.006	--	--
4 2 3 → 3 2 2	5676.961	0.003	5677.705	0.003
4 3 2 → 3 3 1	5722.617	-0.002	5724.548	0.026
4 3 1 → 3 3 0	5729.323	0.000	5725.029	-0.019
6 1 5 → 5 2 3	5780.008	0.028	--	--
5 3 3 → 5 2 3	5808.497	0.006	5797.215	0.008
4 2 2 → 3 2 1	5841.485	-0.001	5838.612	0.004
4 1 3 → 3 1 2	5992.891	0.003	5991.252	0.011
4 3 2 → 4 2 2	6024.618	-0.004	6005.570	-0.003
3 1 2 → 2 0 2	6029.343	0.003	--	--
3 3 1 → 3 2 1	6143.491	0.002	--	--
3 3 0 → 3 2 1	6144.614	0.000	--	--
3 3 0 → 3 2 2	6230.757	0.010	--	--
4 3 1 → 4 2 3	6283.095	-0.017	--	--
5 3 2 → 5 2 4	6394.379	-0.020	--	--
2 2 1 → 1 1 0	6491.915	0.002	--	--
2 2 0 → 1 1 0	6509.379	0.002	6482.864	0.007
5 1 5 → 4 1 4	6621.112	0.001	6631.209	-0.006
2 2 1 → 1 1 1	6662.414	0.004	6653.836	-0.001
2 2 0 → 1 1 1	6679.885	0.011	--	--
5 0 5 → 4 0 4	6807.994	0.002	6794.241	-0.003
5 2 4 → 4 2 3	7074.246	0.004	7073.758	0.015
5 3 3 → 4 3 2	7162.420	0.003	7168.254	0.037
5 3 2 → 4 3 1	7185.525	-0.004	7176.774	-0.017
5 1 5 → 4 0 4	7221.290	0.000	--	--
5 2 3 → 4 2 2	7378.557	0.009	7376.599	0.016

Transitions	A-State ν_{obs}	A-State $\nu_{obs-cal}$	E-State ν_{obs}	E-State $\nu_{obs-cal}$
$5_{14} \to 4_{13}$	7450.348	0.010	7447.968	0.009
$6_{16} \to 5_{15}$	7912.137	-0.008	7933.091	-0.009
$4_{22} \to 3_{12}$	9159.610	-0.012	9160.259	-0.022
$7_{17} \to 6_{16}$	9192.020	-0.019	9224.673	-0.003
$7_{07} \to 6_{06}$	9295.237	-0.014	--	--
$8_{18} \to 7_{17}$	10462.766	-0.023	10499.712	0.006
$8_{08} \to 7_{07}$	10529.847	-0.028	10486.925	-0.009
$7_{25} \to 6_{24}$	10478.934	0.011	10476.565	0.003
$7_{16} \to 6_{25}$	8134.095	0.000	8123.680	0.004
$6_{16} \to 5_{05}$	8325.425	-0.018	--	--
$8_{17} \to 7_{16}$	11587.576	0.025	11579.838	0.011
$6_{06} \to 5_{05}$	8058.715	-0.011	8033.366	-0.002
$6_{15} \to 5_{14}$	8874.930	0.007	8871.543	-0.002
$6_{24} \to 5_{23}$	8931.475	-0.011	8929.484	-0.003
$7_{07} \to 6_{16}$	9028.527	-0.006	--	--

Table S2: Experimentally observed rotational transition and their assignments for the $C_6H_5CCH\cdots CH_3OD$ complex.

Transitions	A-State		E-State	
	ν_{obs}	$\nu_{obs-cal}$	ν_{obs}	$\nu_{obs-cal}$
$1_{11} \to 0_{00}$	2582.175	0.012	--	--
$2_{12} \to 1_{11}$	2644.110	-0.035	--	--
$1_{10} \to 0_{00}$	2748.775	-0.007	2749.012	0.003
$2_{02} \to 1_{01}$	2794.261	-0.006	2793.176	-0.010
$2_{11} \to 1_{10}$	2977.379	0.004	2976.878	0.013
$2_{12} \to 1_{01}$	3820.910	-0.016	3821.489	-0.005
$3_{13} \to 2_{12}$	3956.335	0.003	3956.824	0.001
$3_{03} \to 2_{02}$	4151.204	-0.004	4149.152	-0.002
$3_{22} \to 2_{21}$	4216.191	0.013	4219.458	0.017
$3_{21} \to 2_{20}$	4281.025	0.016	4276.589	0.030
$2_{11} \to 1_{01}$	4320.778	0.002	4320.977	0.007

Transitions	ν_{obs}	$\nu_{obs-cal}$	ν_{obs}	$\nu_{obs-cal}$
$3_{12} \rightarrow 2_{11}$	4455.117	-0.015	4454.413	-0.010
$3_{13} \rightarrow 2_{02}$	4983.000	0.010	4985.130	0.000
$4_{14} \rightarrow 3_{13}$	5258.032	0.002	5259.890	0.001
$4_{04} \rightarrow 3_{03}$	5465.460	0.003	5461.531	0.002
$6_{34} \rightarrow 6_{24}$	5592.913	0.000	--	--
$4_{23} \rightarrow 3_{22}$	5608.600	-0.007	5608.753	-0.008
$4_{32} \rightarrow 3_{31}$	5651.775	0.015	--	--
$4_{31} \rightarrow 3_{30}$	5657.863	0.001	5654.315	-0.009
$4_{22} \rightarrow 3_{21}$	5764.340	-0.018	5762.665	-0.006
$4_{13} \rightarrow 3_{12}$	5918.318	-0.002	5917.271	0.001
$3_{12} \rightarrow 2_{02}$	5981.639	-0.002	5982.201	-0.006
$4_{14} \rightarrow 3_{03}$	6089.814	0.001	--	--
$5_{05} \rightarrow 4_{14}$	6112.264	0.002	--	--
$5_{15} \rightarrow 4_{14}$	6547.833	-0.003	6552.975	0.001
$5_{05} \rightarrow 4_{04}$	6736.621	0.002	6728.896	0.000
$5_{24} \rightarrow 4_{23}$	6990.037	-0.013	6989.497	-0.002
$5_{33} \rightarrow 4_{32}$	7073.534	0.004	7078.131	0.005
$5_{32} \rightarrow 4_{31}$	7094.590	0.001	7087.912	-0.015
$5_{23} \rightarrow 4_{22}$	7279.388	0.000	7278.132	-0.003
$5_{14} \rightarrow 4_{13}$	7359.715	0.017	7358.216	0.008

Table S3: Experimentally observed rotational transition and their assignments for the $C_6H_5CCD\cdots CH_3OH$ complex.

Transitions	E-State			
	ν_{obs}	$\nu_{obs-cal}$	ν_{obs}	$\nu_{obs-cal}$
$2_{12} \rightarrow 1_{11}$	2635.172	-0.002	2635.666	-0.018
$2_{02} \rightarrow 1_{01}$	2790.078	0.002	2788.263	0.010
$2_{11} \rightarrow 1_{10}$	2983.027	0.000	2982.196	-0.002
$3_{22} \rightarrow 3_{12}$	3057.972	-0.003	3056.206	0.002
$3_{03} \rightarrow 2_{12}$	3191.811	0.007	3185.137	-0.005

Transitions	ν_{obs}	$\nu_{obs-cal}$	ν_{obs}	$\nu_{obs-cal}$
$2_{1\,2} \to 1_{0\,1}$	3737.278	0.001	3738.490	-0.001
$3_{1\,3} \to 2_{1\,2}$	3941.414	0.000	3942.873	0.007
$3_{0\,3} \to 2_{0\,2}$	4139.01	0.005	4135.382	0.002
$3_{2\,2} \to 2_{2\,1}$	4213.658	-0.020	4219.575	0.005
$2_{1\,1} \to 1_{0\,1}$	4259.056	-0.004	4259.475	-0.011
$3_{1\,2} \to 2_{1\,1}$	4461.871	0.001	4460.776	0.000
$3_{1\,3} \to 2_{0\,2}$	4888.625	0.010	4893.103	-0.002
$4_{1\,4} \to 3_{1\,3}$	5235.776	-0.002	5240.274	0.001
$4_{0\,4} \to 3_{0\,3}$	5440.198	0.000	5432.862	0.001
$4_{2\,3} \to 3_{2\,2}$	5603.285	-0.012	5604.167	0.002
$4_{3\,1} \to 3_{3\,0}$	5660.493	0.003	5655.775	-0.015
$4_{2\,2} \to 3_{2\,1}$	5780.984	0.005	5778.073	0.006
$4_{1\,3} \to 3_{1\,2}$	5923.645	-0.009	5921.996	0.000
$3_{1\,2} \to 2_{0\,2}$	5930.859	0.005	5932.014	0.005
$4_{1\,4} \to 3_{0\,3}$	5985.38	-0.007	5998.002	0.005
$2_{2\,0} \to 1_{1\,0}$	6308.194	-0.005	6317.367	-0.001
$7_{3\,4} \to 7_{2\,6}$	6742.715	-0.002	--	--
$5_{2\,4} \to 4_{2\,3}$	6980.282	0.000	6979.908	0.004
$11_{3\,9} \to 10_{4\,7}$	6982.021	-0.001	--	--
$5_{3\,3} \to 4_{3\,2}$	7075.431	0.013	7304.185	0.002
$5_{2\,3} \to 4_{2\,2}$	7306.128	-0.003	--	--
$3_{2\,1} \to 2_{1\,1}$	7613.412	0.011	--	--
$6_{1\,6} \to 5_{1\,5}$	7785.148	0.008	7808.210	-0.003
$6_{0\,6} \to 5_{0\,5}$	7921.241	-0.007	--	--

Table S4: Experimentally observed rotational transition and their assignments for the $C_6H_5CCH \cdots {}^{13}CH_3OH$ complex.

Transitions	A-State		E-State	
	ν_{obs}	$\nu_{obs-cal}$	ν_{obs}	$\nu_{obs-cal}$
$1_{1\,0} \to 0_{0\,0}$	2975.255	-0.003	2721.880	-0.001

$2_{02} \rightarrow 1_{01}$	2791.584	0.005	2789.806	-0.001
$2_{11} \rightarrow 1_{10}$	2975.255	0.002	2974.473	-0.001
$3_{22} \rightarrow 3_{12}$	3212.272	-0.004	3210.961	0.006
$2_{21} \rightarrow 2_{11}$	3451.221	-0.002	3443.889	-0.003
$2_{20} \rightarrow 2_{11}$	3468.075	-0.001	3476.825	-0.002
$4_{04} \rightarrow 3_{12}$	3651.260	0.004	3640.049	0.007
$2_{12} \rightarrow 1_{01}$	3792.125	0.007	3793.274	-0.004
$3_{13} \rightarrow 2_{12}$	3952.390	0.004	3953.580	-0.002
$2_{20} \rightarrow 2_{12}$	3968.472	0.009	3976.447	-0.004
$3_{03} \rightarrow 2_{02}$	4146.289	0.004	4142.857	-0.001
$3_{22} \rightarrow 3_{13}$	4211.972	0.013	4207.605	0.001
$3_{22} \rightarrow 2_{21}$	4212.732	-0.002	4217.673	0.003
$3_{21} \rightarrow 2_{20}$	4279.031	0.004	4272.432	-0.005
$2_{11} \rightarrow 1_{01}$	4292.506	0.001	4292.899	-0.003
$3_{21} \rightarrow 3_{13}$	4295.099	-0.005	4295.301	-0.004
$9_{27} \rightarrow 9_{18}$	4332.372	-0.002	4450.605	-0.002
$3_{12} \rightarrow 2_{11}$	4451.682	0.001	4440.807	-0.008
$5_{05} \rightarrow 4_{13}$	4463.654	0.005	--	--
$4_{23} \rightarrow 4_{14}$	4563.263	0.004	--	--
$4_{22} \rightarrow 4_{14}$	4805.410	0.002	4799.166	0.008
$3_{13} \rightarrow 2_{02}$	4952.922	-0.002	4957.094	0.040
$4_{14} \rightarrow 3_{13}$	5252.411	0.001	5256.188	-0.004
$4_{04} \rightarrow 3_{03}$	5457.579	0.001	5450.886	0.000
$4_{23} \rightarrow 3_{22}$	5603.708	-0.002	5604.249	-0.007
$4_{32} \rightarrow 3_{31}$	5647.826	0.000	5649.597	0.021
$4_{31} \rightarrow 3_{30}$	5654.205	-0.001	5650.072	-0.031
$4_{22} \rightarrow 3_{21}$	5762.721	0.007	5760.047	0.002
$5_{33} \rightarrow 5_{23}$	5771.138	-0.009	--	--
$4_{13} \rightarrow 3_{12}$	5913.154	0.002	5911.526	-0.003
$3_{12} \rightarrow 2_{02}$	5952.606	-0.001	5953.695	-0.007
$4_{14} \rightarrow 3_{03}$	6059.039	-0.011	6070.375	-0.013
$3_{31} \rightarrow 3_{21}$	6095.394	0.007	--	--

Transitions				
$2_{20} \rightarrow 1_{10}$	6443.333	0.004	6451.296	-0.004
$5_{15} \rightarrow 4_{14}$	6540.351	0.000	--	--
$2_{21} \rightarrow 1_{11}$	6593.271	-0.003	--	--
$5_{05} \rightarrow 4_{04}$	6725.546	0.001	6712.304	0.002
$5_{24} \rightarrow 4_{23}$	6983.439	-0.008	--	--
$5_{33} \rightarrow 4_{32}$	7068.684	-0.001	7074.050	0.020
$5_{23} \rightarrow 4_{22}$	7278.044	0.006	7276.145	0.002
$5_{14} \rightarrow 4_{13}$	7352.188	-0.004	--	--
$4_{13} \rightarrow 3_{03}$	7719.463	-0.011	7722.370	-0.004
$3_{21} \rightarrow 2_{11}$	7747.101	-0.002	7749.264	0.000
$6_{16} \rightarrow 5_{15}$	7816.217	0.000	--	--

Table S5: Experimentally observed rotational transition and their assignments for the $C_6H_5CCH \cdots CD_3OD$ complex.

Transitions	A-State	
	ν_{obs}	$\nu_{obs-cal}$
$3_{22} \rightarrow 3_{12}$	3147.106	-0.009
$3_{13} \rightarrow 2_{12}$	3798.181	0.013
$3_{03} \rightarrow 2_{02}$	3980.725	0.013
$3_{22} \rightarrow 2_{21}$	4039.832	-0.017
$9_{27} \rightarrow 9_{18}$	4076.803	0.002
$2_{11} \rightarrow 1_{01}$	4126.719	-0.014
$3_{12} \rightarrow 2_{11}$	4262.502	-0.008
$4_{14} \rightarrow 3_{13}$	5048.690	0.008
$4_{23} \rightarrow 3_{22}$	5374.702	0.000
$6_{15} \rightarrow 5_{23}$	5405.121	-0.019
$4_{22} \rightarrow 3_{21}$	5516.688	0.022
$4_{13} \rightarrow 3_{12}$	5663.543	-0.004
$5_{32} \rightarrow 5_{23}$	5672.107	0.000
$3_{12} \rightarrow 2_{02}$	5711.068	0.016

Transition	Frequency	Obs-Calc
$5_{1\,5} \rightarrow 4_{1\,4}$	6288.302	-0.020
$2_{2\,1} \rightarrow 1_{1\,1}$	6373.161	0.004
$5_{0\,5} \rightarrow 4_{0\,4}$	6467.771	-0.011
$7_{1\,6} \rightarrow 6_{2\,4}$	6692.759	0.017
$5_{2\,4} \rightarrow 4_{2\,3}$	6699.600	0.017
$5_{2\,3} \rightarrow 4_{2\,2}$	6964.019	-0.016
$5_{1\,4} \rightarrow 4_{1\,3}$	7044.882	0.003
$9_{2\,8} \rightarrow 9_{1\,9}$	7244.447	-0.002
$7_{1\,6} \rightarrow 6_{2\,5}$	7588.900	-0.002

Table S6: Cartesian coordinates (Å) for equilibrium geometry of PhAc···CH₃OH complex for (M-P)$_{Ph}$ structure in the abc principal axes system optimised at MP2/aug-cc-pVDZ level of theory.

Atoms	a	b	c
C1	1.387	-0.953	-1.219
C2	2.090	-1.034	-0.001
C3	1.389	-0.946	1.219
C4	-0.006	-0.780	1.225
C5	-0.715	-0.695	0.001
C6	-0.009	-0.787	-1.223
H7	1.927	-1.011	-2.168
H8	3.177	-1.153	-0.002
H9	1.932	-0.998	2.167
H10	-0.555	-0.703	2.167
H11	-0.560	-0.716	-2.165
C12	-2.140	-0.504	0.002
C13	-3.362	-0.312	0.003
H14	-4.426	-0.165	0.003
C15	-0.251	2.563	-0.009
H16	-0.366	3.655	-0.019
H17	-0.754	2.158	0.886

Atoms	a	b	c
H18	-0.740	2.144	-0.906
O19	1.157	2.300	0.003
H20	1.272	1.339	0.018

Table S7: Cartesian coordinates (Å) for equilibrium geometry of PhAc···CH₃OH complex for (M-P)ₐc structure in the abc principal axes system optimised at MP2/aug-cc-pVDZ level of theory.

Atoms	a	b	c
C1	-1.747	-0.282	-1.266
C2	-2.521	-0.322	-0.090
C3	-2.024	0.250	1.097
C4	-0.756	0.855	1.115
C5	0.025	0.889	-0.064
C6	-0.479	0.322	-1.260
H7	-2.129	-0.728	-2.189
H8	-3.506	-0.798	-0.098
H9	-2.623	0.221	2.012
H10	-0.358	1.293	2.035
H11	0.136	0.341	-2.164
C12	1.347	1.459	-0.042
C13	2.511	1.879	-0.014
H14	3.509	2.277	0.002
C15	0.992	-2.230	0.651
H16	1.000	-3.327	0.606
H17	0.001	-1.865	0.334
H18	1.173	-1.920	1.695
O19	2.034	-1.781	-0.226
H20	2.083	-0.816	-0.153

Table S8: Cartesian coordinates (Å) for equilibrium geometry of PhAc···CH₃OH complex for (P-M)$_{OH}$ structure in the abc principal axes system optimised at MP2/aug-cc-pVDZ level of theory.

Atoms	a	b	c
C1	3.099	-1.189	0.218
C2	1.709	-1.225	0.017
C3	0.983	-0.021	-0.153
C4	1.672	1.215	-0.118
C5	3.062	1.242	0.083
C6	3.780	0.043	0.251
H7	3.652	-2.124	0.348
H8	1.174	-2.179	-0.010
H9	1.110	2.143	-0.251
H10	3.587	2.202	0.107
H11	4.863	0.068	0.408
C12	-0.441	-0.054	-0.358
C13	-1.667	-0.084	-0.533
H14	-2.737	-0.109	-0.682
C15	-4.998	0.195	0.942
H16	-5.940	-0.204	1.352
H17	-4.964	1.287	1.090
H18	-4.155	-0.262	1.476
O19	-4.836	-0.159	-0.444
H20	-5.553	0.250	-0.946

Table S9: Cartesian coordinates (Å) for equilibrium geometry of PhAc···CH₃OH complex for (M-P)$_{Ph}$ structure in the abc principal axes system optimised at B3LYP-D3/aug-cc-pVDZ level of theory.

Atoms	a	b	c
C1	1.365	-1.006	-1.214

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C2	2.062	-1.108	-0.003
C3	1.367	-1.012	1.209
C4	-0.016	-0.819	1.214
C5	-0.723	-0.717	0.000
C6	-0.017	-0.813	-1.216
H7	1.902	-1.072	-2.160
H8	3.142	-1.253	-0.004
H9	1.905	-1.082	2.154
H10	-0.557	-0.737	2.156
H11	-0.560	-0.727	-2.156
C12	-2.138	-0.499	0.002
C13	-3.335	-0.299	0.003
H14	-4.392	-0.131	0.004
C15	-0.221	2.665	-0.008
H16	-0.344	3.755	-0.014
H17	-0.729	2.255	0.880
H18	-0.705	2.250	-0.908
O19	1.181	2.410	0.012
H20	1.320	1.455	0.021

Table S10: Cartesian coordinates (Å) for equilibrium geometry of PhAc···CH₃OH complex for (M-P)$_{Ac}$ structure in the abc principal axes system optimised at B3LYP-D3/aug-cc-pVDZ level of theory.

Atoms	a	b	c
C1	-1.488	-1.513	-0.476
C2	-2.699	-1.026	0.026
C3	-2.789	0.3	0.461
C4	-1.676	1.138	0.393
C5	-0.454	0.652	-0.113
C6	-0.368	-0.684	-0.55
H7	-1.414	-2.547	-0.815

Atoms	a	b	c
H8	-3.571	-1.679	0.081
H9	-3.731	0.685	0.854
H10	-1.743	2.172	0.729
H11	0.577	-1.064	-0.934
C12	0.684	1.519	-0.182
C13	1.644	2.264	-0.236
H14	2.477	2.932	-0.289
C15	2.861	-1.225	0.962
H16	3.18	-2.272	1.034
H17	1.821	-1.15	1.322
H18	3.507	-0.615	1.614
O19	2.978	-0.849	-0.408
H20	2.674	0.064	-0.494

Table S11: Cartesian coordinates (Å) for equilibrium geometry of PhAc···CH₃OH complex for (P-M)ₒₕ structure in the abc principal axes system optimised at B3LYP-D3/aug-cc-pVDZ level of theory.

Atoms	a	b	c
C1	3.184	-1.059	0.287
C2	1.806	-1.220	0.145
C3	0.981	-0.105	-0.111
C4	1.573	1.170	-0.221
C5	2.952	1.322	-0.077
C6	3.763	0.210	0.177
H7	3.811	-1.930	0.485
H8	1.354	-2.207	0.231
H9	0.940	2.034	-0.419
H10	3.397	2.314	-0.165
H11	4.841	0.333	0.289
C12	-0.434	-0.267	-0.257
C13	-1.636	-0.405	-0.375

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H14	-2.700	-0.525	-0.484
C15	-5.004	0.670	0.660
H16	-5.979	0.608	1.168
H17	-4.902	1.658	0.183
H18	-4.209	0.561	1.407
O19	-4.827	-0.396	-0.280
H20	-5.495	-0.324	-0.971

Table S12: Normal modes of vibrations for the structures (M-P)$_{Ph}$, (M-P)$_{Ac,}$ and (P-M)$_{OH}$ of the PhAc$\cdots$CH$_3$OH complex calculated at MP2/aug-cc-pVDZ level of theory.

Modes (cm^{-1})	(M-P)$_{Ph}$	(M-P)$_{Ac}$	(P-M)$_{OH}$
1	38.1	32.1	8.4
2	44.4	48.1	17.8
3	53.0	66.9	29.1
4	105.8	102.5	47.9
5	124.1	112.1	73.3
6	137.6	139.8	124.5
7	144.9	145.2	147.9
8	145.9	180.4	164.2
9	321.3	331.5	314.4
10	329.4	392.5	319.8
11	397.6	410.4	397.6
12	459.5	460.1	463.2
13	495.0	494.7	496.8
14	499.5	506.4	506.1
15	562.3	570.9	615.5
16	612.1	612.0	637.5
17	614.7	614.7	689.5
18	660.0	658.0	741.4
19	750.8	745.4	750.9

20	762.2	762.9	762.8
21	844.7	840.3	837.7
22	901.4	899.4	888.6
23	958.1	954.6	932.1
24	958.9	956.9	941.0
25	997.7	997.6	996.5
26	1037.1	1038.3	1035.6
27	1048.4	1046.7	1038.6
28	1080.1	1084.1	1072.8
29	1085.7	1087.8	1085.5
30	1164.9	1166.1	1164.3
31	1165.4	1167.7	1168.7
32	1183.5	1184.3	1183.0
33	1216.1	1214.9	1215.2
34	1306.6	1308.3	1304.9
35	1371.6	1377.0	1361.9
36	1429.4	1432.6	1427.0
37	1459.3	1459.1	1466.4
38	1479.3	1482.5	1477.8
39	1489.5	1490.3	1490.6
40	1490.6	1492.0	1493.3
41	1497.0	1500.3	1505.6
42	1598.5	1602.5	1601.4
43	1627.2	1629.8	1630.5
44	2104.6	2098.8	2093.2
45	3037.6	3041.8	3059.3
46	3114.0	3120.8	3142.5
47	3174.3	3174.3	3190.2
48	3206.8	3203.6	3200.7
49	3212.6	3211.4	3208.3
50	3221.0	3219.9	3217.8
51	3227.8	3227.0	3224.3

52	3235.7	3233.7	3231.5
53	3479.1	3476.2	3390.1
54	3799.0	3792.1	3837.8

Table S13: Normal modes of vibrations for the structures (M-P)$_{Ph}$, (M-P)$_{Ac,}$ and (P-M)$_{OH}$ of the PhAc···CH$_3$OH complex calculated at B3LYP-D3/aug-cc-pVDZ level of theory. Frequency in cm^{-1}.

Modes (cm^{-1})	(M-P)$_{Ph}$	(M-P)$_{Ac}$	(P-M)$_{OH}$
1	17.1	22.4	7.1
2	34.9	48.9	21.8
3	43.9	75.3	38.4
4	91.0	99.8	51.9
5	116.3	110.1	72.7
6	127.4	118.7	113.5
7	139.0	138.0	154.9
8	152.9	162.2	175.4
9	337.3	345.1	314.8
10	338.8	413.2	347.1
11	408.8	469.7	412.2
12	469.5	496.5	472.2
13	527.1	526.0	526.9
14	534.4	533.0	543.9
15	580.0	570.8	630.1
16	629.3	630.0	704.9
17	656.6	655.8	717.7
18	704.5	709.6	769.0
19	773.1	771.2	772.5
20	778.5	776.4	778.4
21	846.9	856.5	846.3
22	926.3	942.3	927.7
23	980.6	992.0	985.0

24	999.2	1004.3	1004.3
25	1006.1	1009.2	1004.7
26	1043.8	1043.4	1032.4
27	1046.9	1048.0	1045.5
28	1081.1	1084.0	1073.1
29	1098.8	1104.7	1097.7
30	1154.5	1161.9	1157.9
31	1182.5	1182.4	1179.9
32	1198.4	1207.7	1196.7
33	1220.3	1216.0	1218.4
34	1314.4	1319.1	1312.8
35	1347.7	1354.4	1347.0
36	1369.1	1381.6	1355.3
37	1450.1	1449.2	1454.1
38	1459.6	1459.4	1457.9
39	1468.1	1467.0	1468.0
40	1477.1	1481.0	1479.3
41	1508.6	1511.7	1507.6
42	1606.4	1608.0	1606.3
43	1639.9	1641.5	1640.9
44	2208.2	2195.8	2194.7
45	2992.3	2991.6	3004.1
46	3048.1	3046.5	3065.7
47	3114.4	3113.2	3126.1
48	3178.7	3173.6	3170.8
49	3186.7	3183.4	3179.6
50	3196.3	3193.4	3190.8
51	3203.3	3201.0	3198.4
52	3208.1	3204.4	3202.9
53	3478.1	3473.3	3386.8
54	3816.1	3755.2	3829.7

Table S14: Experimental rotational constants (MHz), centrifugal distortion constants (kHz) and second moment obtained from the global fit containing A- and E- state transitions (fit includes transitions obtained from the CP-FTMW spectrometer). F_0 is being fixed in this fit.

Constants	PhAc···CH$_3$OH	PhAc···CH$_3$OD	PhAc-D···CH$_3$OH	PhAc···^{13}CH$_3$OH
A_0	1955.313(3)	1962.814(7)	1891.341(4)	1935.974(5)
B_0	796.553(1)	785.982(2)	789.216(2)	785.488(2)
C_0	625.9945(8)	619.316(2)	615.2275(1)	618.630(1)
D_J	1.140(7)	1.05(2)	1.03(1)	1.15(3)
D_{JK}	-6.10(6)	-5.5(1)	-4.9(1)	-6.3(1)
D_K	17.0(3)	52.4(8)	18.1(8)	19.2(6)
d_1	-0.137(4)	-0.17(2)	-0.10(2)	-0.15(6)
$D_{\pi 2J}$	-258(2)	-219(5)	-265(3)	-268(3)
$D_{\pi 2K}$	823(1)	676(6)	774(2)	780(1)
V_3 (cm^{-1})	200.0(1)	217.8(3)	200.6(1)	200.7(1)
F_0 (cm^{-1})	[5.24][a]	[5.24][a]	[5.24][a]	[5.24][a]
$\angle(i, a)$ (degree)	66.7(2)	67.6(6)	68.4(4)	67.8(4)
$\angle(i, b)$ (degree)	24.2(2)	23.1(6)	22.7(4)	23.0(3)
$\angle(i, c)$ (degree)	96.09(1)	95.6(0)	96.77(1)	95.74(1)
P_{cc} (u Å^2)	42.80	42.22	43.06	43.77
N_A/N_E	72/48	31/25	29/24	44/38
σ (kHz)	22.4	15.5	16.4	25.1

P_{cc} is the second moment given by:
$$P_{cc} = \frac{I_b - I_a - I_c}{2}$$

[a]The corresponding F values for PhAc···CH$_3$OH, PhAc···CH$_3$OD, PhAc-D···CH$_3$OH, and PhAc···^{13}CH$_3$OH are 5.27 cm^{-1}, while the ρ value is approximately 0.004.

Table S15: Calculated harmonic and experimentally obtained vibrational frequencies (cm^{-1}) in the O-H stretch region of H_2O and CH_3OH and their complexes with PhAc reported in references 1 and 2.

Method	PhAc···CH$_3$OH	PhAc···H$_2$O	3-methylphenylacetylene···CH$_3$OH
IR/UV double resonance spectroscopic results[1]			
Experiment	3615	3629[a], 3724[b]	----
Monomer	3681	3657[a], 3756[b]	----
Theory (Ac bound)	3633	3587[a], 3735[b]	----
Theory (Ph bound)	3637	3621[a], 3744[b]	----
FTIR spectroscopic results[2]			
Experiment	3622	3613[a]	3639, 3620 (2685, 2671)[c]
Monomer	3686	3657[a]	3686 (2718)[c]
Theory (Ac bound)	3613	3603[a]	3610 (2661)
Theory (Ph bound)	3637	3621[a]	3659 (2697)

[a]The vibrational frequencies for hydrogen-bonded O-H. [b]The vibrational frequencies for free O-H. [c]The values in the parentheses correspond to the 3-methylphenylacetylene···CH$_3$OD complex.

Table S16: SAPT'2+3' interaction energy decomposition (kJ/mol) for PhAc···H$_2$O and PhAc···H$_2$S complexes calculated at MP2/aug-cc-pVDZ level of theory.

Method	Complex	E^{Electrostatics}	E^{Induction}	E^{Dispersion}	E^{Exchange}	E^{Interaction}
SAPT'2+3' MP2/aug-cc-pVDZ	PhAc···H$_2$O	-24.9	-8.8	-15.2	33.5	-15.5
	PhAc···H$_2$S	-16.3	-5.0	-25.4	33.6	-13.2

References:

1 P. C. Singh and G. N. Patwari, IR-UV double resonance spectroscopic investigation of phenylacetylene- alcohol complexes. Alkyl group induced hydrogen bond switching, *Journal of Physical Chemistry A*, 2008, **112**, 5121–5125.

2 G. Karir, N. O. B. Lüttschwager and M. A. Suhm, Phenylacetylene as a gas phase sliding balance for solvating alcohols, *Physical Chemistry Chemical Physics*, 2019, **21**, 7831–7840.

Table S17: *Rotational constants (MHz), electric dipole moment (Debye), second moments, the binding energies (ΔE), and BSSE corrected binding energies (ΔE$_{BSSE}$) (kJ/mol) calculated at B3LYP-D3(BJ)/aug-cc-pVDZ level of theory.*

Parameters	B3LYP-D3(BJ)/aug-cc-pVDZ		
	$(M-P)_{Ph}$	$(M-P)_{Ac}$	$(P-M)_{OH}$
A_e	1408.6188	2029.7403	4290.2839
B_e	1111.3795	797.7908	367.0376
C_e	800.0728	621.3542	346.3381
μ_a	1.0	-1.6	-1.4
μ_b	-1.5	0.6	1.2
μ_c	0.0	1.2	0.1
P_{cc} (u Å^2)	90.9	34.6	17.8
ΔE	20.9	23.4	15.4
ΔE_{BSSE}	17.7	20.9	13.5

P_{cc} is the second moment given by: $$P_{cc} = \frac{I_b - I_a - I_c}{2}$$

Table S18: *Experimental rotational Constants (MHz), centrifugal distortion constants (kHz) and second moment of A-state for PhAc⋯CH₃OH complex fitted using the ASFIT program (fit includes transitions obtained from the CP-FTMW spectrometer only).*

Constants	ASFIT
A_0	1955.3331(8)
B_0	796.5836(4)

C_0	626.0858(4)
D_J	1.13(8)
D_{JK}	-6.00(2)
D_K	17.53(8)
d_1	-0.144(1)
P_{cc} (u Å^2)	42.85
N_A	58
σ (kHz)	5.4

P_{cc} is the second moment given by: $P_{cc} = \dfrac{I_b - I_a - I_c}{2}$