Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

for

A close competition between O-H···O and O-H···π hydrogen bonding: IR spectroscopy of anisole-methanol complex in helium nanodroplets

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1. NBO analysis of anisole···methanol complexes

The second-order perturbation energy, $E^{(2)}$, for the overlaps between different orbitals of anisole and methanol-d4 units in the experimentally observed structures of anisole…methanol complex are summarized in Table S1.

Table S1: Second order perturbation energy $E^{(2)}$ values for interaction between donar and acceptor NBOs. The calculations were performed at MP2/6-311++G (d,p) level theory. The atomic labels are same as given in the *Section I*.

Conformer	**Interaction**	**Donor (i)**	**Acceptor(j*)**	**$E^{(2)}$ (kJ/mol)**
Structure 1	O-H···O	O_{12} (n_σ)	O_{17}-H_{18} (σ*)	9.87
		O_{12} (n_p)	O_{17}-H_{18} (σ*)	6.15
Structure 2	O-H···O	O_{12} (n_σ)	O_{17}-H_{18} (σ*)	1.04
		O_{12} (n_p)	O_{17}-H_{18} (σ*)	7.90
	C–H···π	C_1=C_6	C_{19}-H_{20} (σ*)	0.83
Structure 3	O–H···π	C_2=C_3	O_{17}-H_{18} (σ*)	2.67
	C-H··· O	O_{17} (n_σ)	C_{13}-H_{16}(σ*)	0.37
		O_{17} (n_p)	C_{13}-H_{16}(σ*)	1.25
Structure 4	O–H···π	C_1=C_6	O_{17}-H_{18} (σ*)	2.17
		C_4=C_5	O_{17}-H_{18} (σ*)	0.79

2. Pickup curves of water at the observed bands:

The experimental bands observed at 2659.1, 2663.5**,** 2678.4**,** 2689.2, and 2690.8 cm^{-1} are assigned to anisole···methanol complexes. To examine if there is any contribution from water molecules at at these ovserbed bands, we recorded the change in intensity of the depletion signal as a function water partial pressure, as shown in the Figure S1. For this, we added anisole in the first chamber, and methanol and water in the second pickup chamber. The pressure of anisole and methanol fixed at ~2×10^{-6} mbar and ~15×10^{-6} mbar and partial pressure of water was varied.

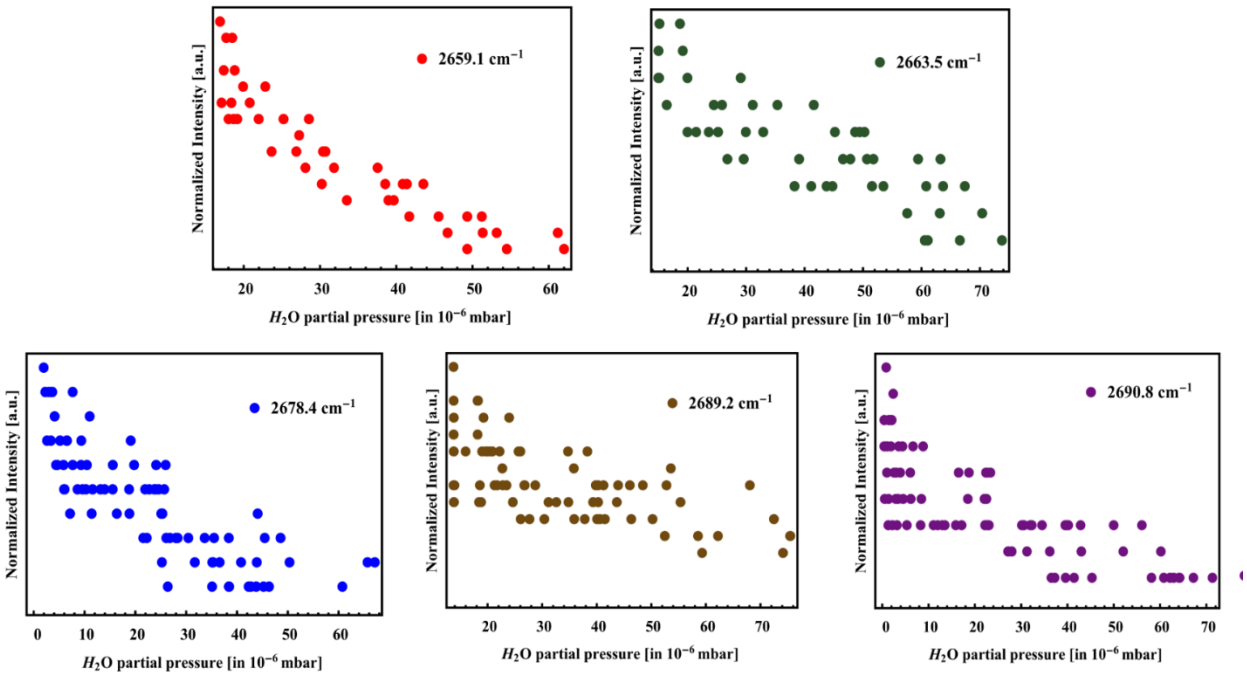


Figure S1: Pickup curves of water at distinct observed IR bands, measured at m/z ≥ 22. The anisole partial pressure kept fixed at ~2×10^{-6} mbar while methanol partial pressure fixed at ~ 15×10^{-6} mbar.

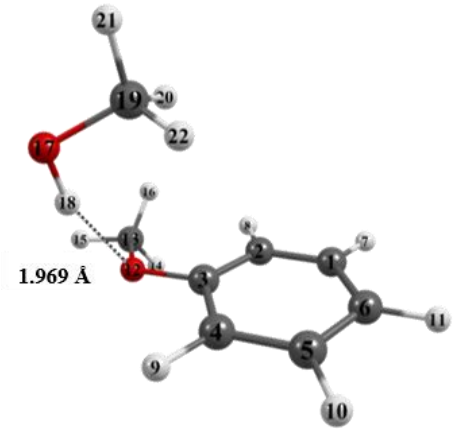
The intensities of all the observed bands in this study was found to decrease with water pressure. This confirms that none of the observed bands depend on water and are from anisole···methanol cluster.

3. Cartesian coordinates for the optimized molecular geometries

a. The cartesian cooridnates for the the five optimized structures anisole···methanol complex and (methanol-d_4)-dimer are given below. The geometry optimization was performed at MP2/6-311++G(d,p) level of theory.

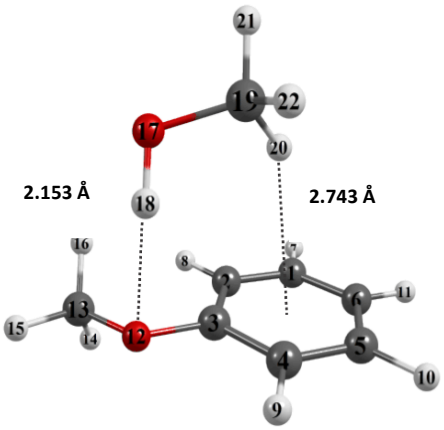
Structure 1

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-1.83896	-0.33153	1.22884
2	C	-0.61677	-0.93106	0.88570
3	C	-0.10226	-0.75705	-0.40909
4	C	-0.81980	0.00257	-1.34884
5	C	-2.03616	0.58772	-0.99608
6	C	-2.55062	0.43181	0.29978
7	H	-2.22743	-0.46779	2.23475
8	H	-0.08015	-1.50938	1.62919
9	H	-0.40495	0.11540	-2.34659
10	H	-2.57978	1.17323	-1.73288
11	H	-3.49462	0.89196	0.57593
12	O	1.08484	-1.26354	-0.84473
13	C	1.92987	-1.84538	0.14484
14	H	1.47618	-2.74681	0.57145
15	H	2.84602	-2.11800	-0.37823
16	H	2.15311	-1.12079	0.93455
17	O	1.50548	1.55477	1.04961
18	H	0.58591	1.27937	0.98046
19	C	1.87317	2.08809	-0.21767
20	H	1.24375	2.93952	-0.50103
21	H	2.90389	2.43398	-0.12612
22	H	1.82448	1.32819	-1.00586



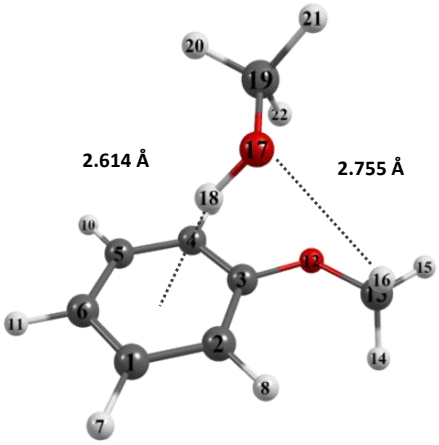
Structure 2

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	1.79825	-0.28667	-1.29343
2	C	0.53290	-0.81037	-0.98841
3	C	0.06725	-0.74835	0.33173
4	C	0.85992	-0.16554	1.33291
5	C	2.11502	0.35316	1.01481
6	C	2.58885	0.30355	-0.30437
7	H	2.15533	-0.33625	-2.31878
8	H	-0.06840	-1.24673	-1.77752
9	H	0.47637	-0.13986	2.34933
10	H	2.72183	0.80066	1.79747
11	H	3.56593	0.70751	-0.55248
12	O	-1.16977	-1.17629	0.73786
13	C	-1.94569	-1.88545	-0.22643
14	H	-1.40472	-2.76700	-0.58627
15	H	-2.84902	-2.19681	0.29700
16	H	-2.21403	-1.23484	-1.06489
17	O	-2.20086	1.47103	-0.17657
18	H	-1.94553	0.81590	0.48115
19	C	-1.15225	2.43088	-0.24635
20	H	-0.20358	1.97817	-0.55664
21	H	-1.45108	3.16900	-0.99235
22	H	-1.00385	2.94492	0.71073



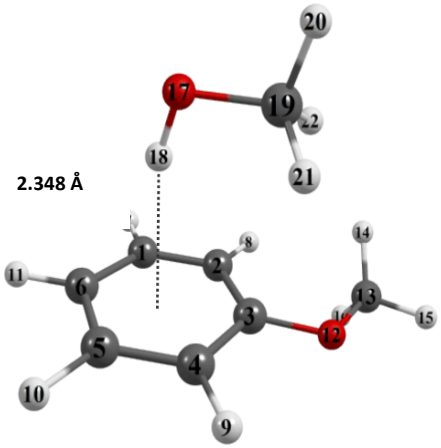
Structure 3

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-1.83896	-0.33153	1.22884
2	C	-0.61677	-0.93106	0.88579
3	C	-0.10226	-0.75705	-0.40910
4	C	-0.81980	0.00257	-1.34885
5	C	-2.03616	0.58772	-0.99608
6	C	-2.55062	0.43181	0.29978
7	H	-2.22743	-0.46779	2.23475
8	H	-0.08015	-1.50938	1.62919
9	H	-0.40495	0.11540	-2.34659
10	H	-2.57978	1.17323	-1.73288
11	H	-3.49462	0.89196	0.57593
12	O	1.08484	-1.26354	-0.84474
13	C	1.92987	-1.84538	0.14484
14	H	1.47618	-2.74681	0.57145
15	H	2.84602	-2.11800	-0.37824
16	H	2.15311	-1.12079	0.93455
17	O	1.50548	1.55477	1.04961
18	H	0.58591	1.27937	0.98046
19	C	1.87317	2.08809	-0.21768
20	H	1.24375	2.93952	-0.50104
21	H	2.90389	2.43398	-0.12613
22	H	1.82448	1.32819	-1.00586



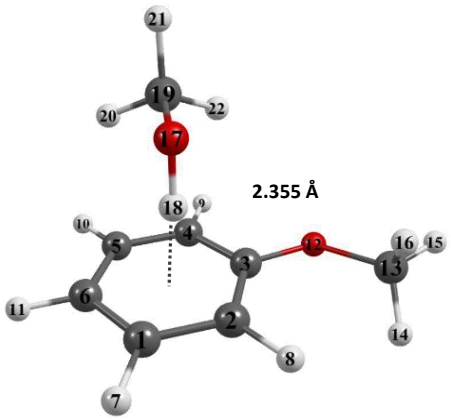
Structure 4

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	1.08157	-1.15963	1.28755
2	C	-0.26173	-0.84570	1.02456
3	C	-0.67070	-0.62068	-0.29864
4	C	0.26269	-0.71535	-1.34502
5	C	1.59419	-1.02714	-1.07027
6	C	2.01396	-1.25142	0.25081
7	H	1.39123	-1.32969	2.31521
8	H	-0.96118	-0.77856	1.85004
9	H	-0.07998	-0.53946	-2.36077
10	H	2.30641	-1.09387	-1.88813
11	H	3.05079	-1.49228	0.46498
12	O	-1.94153	-0.29730	-0.67378
13	C	-2.91261	-0.22556	0.36129
14	H	-2.65932	0.55227	1.09052
15	H	-3.85001	0.02989	-0.13149
16	H	-3.01750	-1.18921	0.87217
17	O	1.41684	2.22933	0.30455
18	H	1.42577	1.26785	0.27391
19	C	0.10915	2.64420	-0.05715
20	H	0.11531	3.73537	-0.07093
21	H	-0.18070	2.27999	-1.04983
22	H	-0.64255	2.30906	0.66911



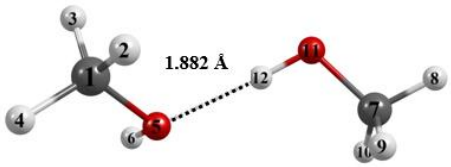
Structure 5

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-0.75040	0.98301	1.40848
2	C	0.46773	0.33963	1.14215
3	C	1.03648	0.43950	-0.13744
4	C	0.38628	1.18820	-1.13406
5	C	-0.82461	1.82437	-0.85502
6	C	-1.40382	1.72272	0.41930
7	H	-1.18398	0.90004	2.40184
8	H	0.95146	-0.23033	1.92738
9	H	0.84543	1.24796	-2.11660
10	H	-1.31869	2.39593	-1.63615
11	H	-2.34615	2.21719	0.63579
12	O	2.20985	-0.14365	-0.50922
13	C	2.72618	-1.13953	0.36610
14	H	1.97942	-1.91994	0.54873
15	H	3.58646	-1.56603	-0.14850
16	H	3.05317	-0.70508	1.31727
17	O	-1.34137	-1.79337	-0.91098
18	H	-1.02874	-0.88618	-0.83994
19	C	-2.28323	-1.98794	0.13307
20	H	-2.66471	-3.00520	0.03096
21	H	-1.82344	-1.88250	1.12329
22	H	-3.12584	-1.28968	0.06181



Methanol dimer

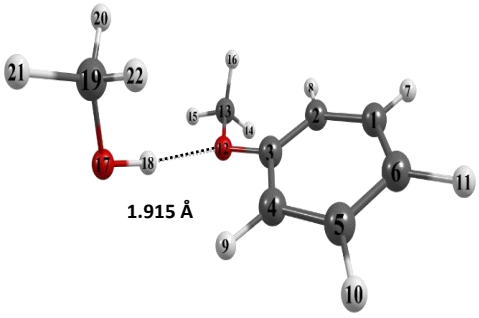
Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-2.16539	-0.38606	-0.24840
2	H	-1.63125	-1.01398	-0.96047
3	H	-2.47473	-1.00212	0.60120
4	H	-3.04778	0.03715	-0.73744
5	O	-1.25240	0.63929	0.15090
6	H	-1.69121	1.18938	0.80464
7	C	2.22812	0.20272	-0.32682
8	H	3.18297	-0.32517	-0.30760
9	H	1.89777	0.28108	-1.37027
10	H	2.38703	1.21540	0.06483
11	O	1.31874	-0.53956	0.46581
12	H	0.47006	-0.07962	0.42262



b. The cartesian cooridnates for the the three optimized structures anisole···methanol complex and (methanol-d_4)-dimer are given below. The geometry optimization was performed at *B3LZP-D3/aug-cc-pVTZ* level of theory.

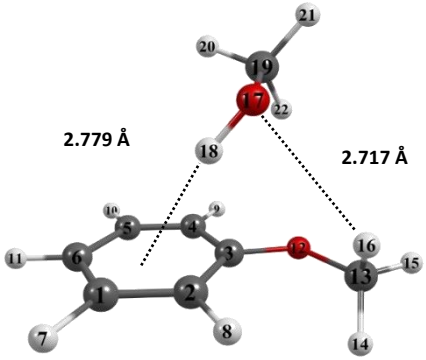
Structure I

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	2.21147	-0.40228	-1.02719
2	C	0.97738	-0.99772	-0.72449
3	C	0.25214	-0.53811	0.38192
4	C	0.75777	0.49779	1.18145
5	C	1.98300	1.08382	0.86442
6	C	2.71746	0.63736	-0.24387
7	H	2.77263	-0.76078	-1.88610
8	H	0.60433	-1.80004	-1.35092
9	H	0.17530	0.82764	2.03738
10	H	2.36681	1.88736	1.48719
11	H	3.67250	1.09251	-0.48868
12	O	-0.98274	-1.01414	0.74995
13	C	-1.46597	-2.15927	0.05260
14	H	-0.76864	-2.99700	0.15491
15	H	-2.41705	-2.40949	0.52107
16	H	-1.62903	-1.93749	-1.00758
17	O	-2.75143	1.19292	0.10923
18	H	-2.23625	0.48620	0.51574
19	C	-1.98235	1.67016	-0.98480
20	H	-1.76718	0.87884	-1.71499
21	H	-2.57428	2.44143	-1.48062
22	H	-1.03125	2.10996	-0.66128



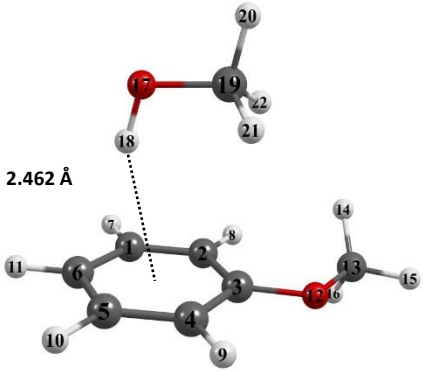
Structure II

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-1.83896	-0.33153	1.22884
2	C	-0.61677	-0.93106	0.88579
3	C	-0.10226	-0.75705	-0.40910
4	C	-0.81980	0.00257	-1.34885
5	C	-2.03616	0.58772	-0.99608
6	C	-2.55062	0.43181	0.29978
7	H	-2.22743	-0.46779	2.23475
8	H	-0.08015	-1.50938	1.62919
9	H	-0.40495	0.11540	-2.34659
10	H	-2.57978	1.173231	-1.73288
11	H	-3.49462	0.89196	0.57593
12	O	1.08484	-1.26354	-0.84474
13	C	1.92987	-1.84538	0.14484
14	H	1.47618	-2.74681	0.57145
15	H	2.84606	-2.11800	-0.37824
16	H	2.15312	-1.12079	0.93455
17	O	1.50548	1.55477	1.04961
18	H	0.58591	1.27937	0.98046
19	C	1.87317	2.08809	-0.21768
20	H	1.24375	2.93952	-0.50104
21	H	2.90389	2.43398	-0.12613
22	H	1.82448	1.32819	-1.00586



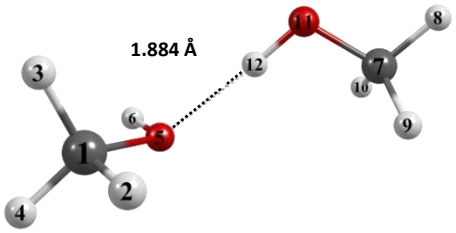
Structure III

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	1.08157	-1.15963	1.28755
2	C	-0.26173	-0.84570	1.02456
3	C	-0.67070	-0.62068	-0.29864
4	C	0.26269	-0.71535	-1.34502
5	C	1.59419	-1.02714	-1.07027
6	C	2.01396	-1.25142	0.25081
7	H	1.39123	-1.32969	2.31521
8	H	-0.96118	-0.77856	1.85004
9	H	-0.07998	-0.53946	-2.36077
10	H	2.30641	-1.09387	-1.88813
11	H	3.05079	-1.49228	0.46498
12	O	-1.94153	-0.29730	-0.67378
13	C	-2.91261	-0.2255	0.361293
14	H	-2.65932	0.55227	1.09052
15	H	-3.85001	0.02989	-0.13149
16	H	-3.01750	-1.18921	0.872178
17	O	1.41684	2.22933	0.304557
18	H	1.42577	1.26785	0.273917
19	C	0.10915	2.64420	-0.05715
20	H	0.11531	3.735371	-0.07093
21	H	-0.18070	2.27999	-1.04983
22	H	-0.64255	2.30906	0.669119



Methanol dimer

Atom label	Atom	x (Å)	y (Å)	z (Å)
1	C	-1.82962	0.56187	0.14985
2	H	-1.06571	1.30581	-0.11442
3	H	-2.71415	0.72211	-0.49440
4	H	-2.12268	0.71461	1.20462
5	O	-1.23109	-0.71362	-0.06689
6	H	-1.87626	-1.38381	0.18451
7	C	1.91826	-0.01405	0.49608
8	H	2.76618	0.68517	0.57454
9	H	1.25399	0.16532	1.36703
10	H	2.32148	-1.04615	0.59515
11	O	1.28234	0.20267	-0.74195
12	H	0.49524	-0.36240	-0.72199



4. Computed vibrational spectra of anisole

Table S2 : Frequency and IR intensity of calculated IR spectra of anisole molecule at MP2/6-311++G (d,p) level theory.

Frequency(cm^{-1})	IR intensity
52.6	4.6
145.7	0.6
204.6	0.5
264.2	0.5
266.9	2.5
361.5	0
445.4	0.8
481.6	5.8
556.6	5.1
618.0	0.3
704.3	106.3
782.3	0.8
797.2	16.7
805.6	1.2
841.1	0.2
856.5	0
1005.6	0.7
1042.5	2.5
1085.8	39.3
1103.4	14.5
1176.9	1.4
1183.5	1.2
1197.6	11.2
1218.7	9.5
1295.3	238.6
1338.2	0.7
1455.1	9.3
1481.8	0
1493.1	22.4
1504.3	7.8
1527.7	114.4
1535.3	0.6
1631.7	18.8
1649.8	69.3
3053.8	47.9
3132.5	33.2
3198.9	19.4
3202.3	0.7
3210.2	8.3
3225.8	12.3
3232.9	8.6
3246.4	3.7