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Supplementary information: Aromatic embedding wins over classical hydrogen bonding - a multi-spectroscopic approach for the diphenyl ether-methanol complex

Chris Medcraft[1,2], Sabrina Zinn[1,2], Melanie Schnell*[1,2],

Anja Poblotzki[3], Jonas Altnöder[3], Matthias Heger[3], Martin A. Suhm*[3],

Dominic Bernhard[4], Anke Stamm[4], Fabian Dietrich[4], Markus Gerhards*[4]

[1]*Max-Planck-Institut für Struktur und Dynamik der Materie, Luruper Chaussee 149, D-22761 Hamburg, Germany. Email: melanie.schnell@mpsd.mpg.de*

[2]*Center for Free-Electron Laser Science, Luruper Chaussee 149, D-22761 Hamburg, Germany.*

[3]*Institut für Physikalische Chemie, Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany. Email: msuhm@gwdg.de*

[4] *Fachbereich Chemie und Research Center Optimas, TU Kaiserslautern, Erwin-Schrödinger-Str. 52, D-67663 Kaiserslautern, Germany. Email: gerhards@chemie.uni-kl.de*

1 R2PI and IR/R2PI spectroscopy

In case of the resonant-two-photon-ionization (R2PI) spectroscopy, a first UV photon excites the vibrational ground state or a vibrational mode in the electronically excited state. A second UV photon subsequently ionizes the molecule. By doing this, a mass- and isomer-selective vibronic spectrum can be obtained. A distinction is made between the one-color (1+1) R2PI process using two isoenergetic UV photons and the two-color (1+1′) R2PI process using two UV photons with different energies. By using the two-color technique the excess energy transferred to the ion can be reduced in order to prevent photofragmentation.

The IR/R2PI spectroscopy represents a combination of IR spectroscopy with the R2PI process and measures resonant vibrations as a depletion of an ion signal. For this purpose the UV excitation laser is set to a resonance of the R2PI spectrum and the R2PI process (either one- or two-color) generates a constant ion signal of the corresponding species, which represents the baseline of the IR/R2PI spectrum. If now a resonant IR photon arrives prior to the UV excitation laser, the vibrational ground state of the S_0 state is depopulated. Thus, the UV excitation laser excites less molecules than before, less molecules are ionized and the ion signal is finally depleted, i.e., by IR/R2PI spectroscopy an IR spectrum of the S_0 state is obtained. Since the ions of the R2PI process are detected in a time of flight-mass spectrometer, the IR/R2PI spectroscopy is mass-selective. If the UV excitation of the R2PI process is isomer-selective, only the corresponding isomer is excited and ionized so that additionally an isomer-selective IR spectrum is obtained.

2 Figures

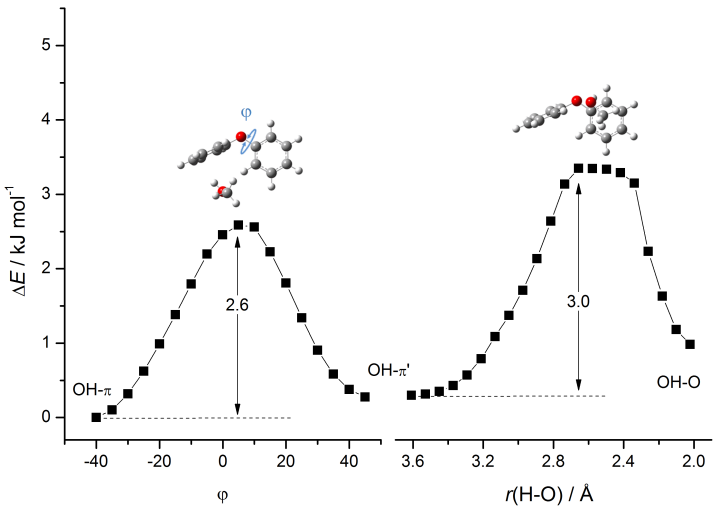

Figure S 1: A sequential low-barrier reaction pathway (obtained by Gaussian 09) from OH-π to OH-O starting with a relaxed scan from OH-π to OH-π' by varying the dihedral φ_2 of diphenyl ether followed by the shortening of the (O)H-O distance from OH-π' to OH-O.

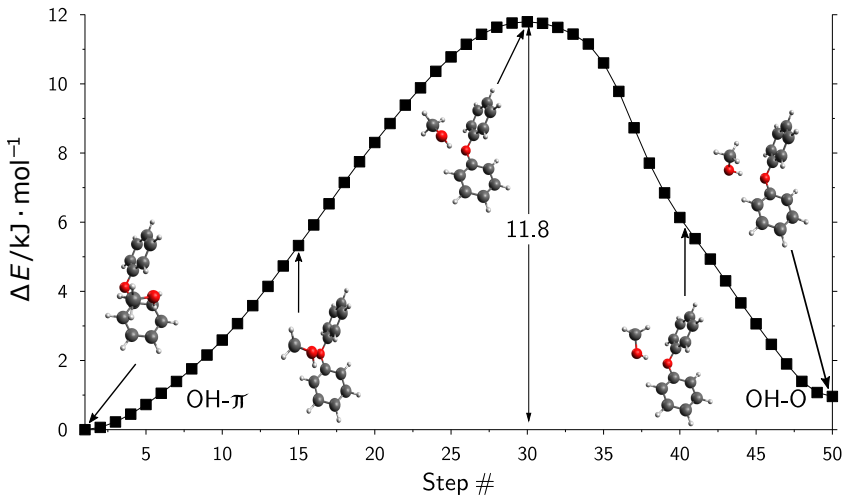

Figure S 2: Calculation of a direct reaction pathway between the OH-π and the OH-O conformers using woelfling (implemented in Turbomole 7.0). Comparing the barrier height with the relaxed scan in Fig. S1 leads to the conclusion that the woelfling path is far from the lowest path.

3 Tables

Table S 1: Selected DPE-MeOH geometry parameters (length s of O-H bond, angle ∢ C-O-H of methanol) and harmonic OH-stretching vibrational wavenumbers $\tilde{\nu}_s$ for different structures and computational levels. Calculations on the most relevant OH-O and OH-π motifs are marked bold. Corresponding parameters for isolated methanol are also given. aVTZ stands for aug-cc-pVTZ.

structure	method	s(O-H)/Å	∢(COH)/°	$\tilde{\nu}_s$(O-H)/cm^{-1}
OH-O	**B3LYP-D3(BJ)/def2-TZVP**	**0.966**	**107.8**	**3741.2**
OH-O′	B3LYP-D3(BJ)/def2-TZVP	0.967	107.8	3730.5
OH-π	**B3LYP-D3(BJ)/def2-TZVP**	**0.965**	**108.8**	**3772.9**
OH-π'	B3LYP-D3(BJ)/def2-TZVP	0.965	108.8	3771.5
OH-πp	B3LYP-D3(BJ)/def2-TZVP	0.965	108.8	3776.5
OH-O	B3LYP/def2-TZVP	0.967	108.9	3737.5
OH-π	B3LYP/def2-TZVP	0.965	109.0	3774.1
OH-O	**B3LYP-D3(BJ)/aVTZ**	**0.965**	**107.8**	**3746.7**
OH-π	**B3LYP-D3(BJ)/aVTZ**	**0.963**	**108.8**	**3784.8**
MeOH	B3LYP-D3(BJ)/def2-TZVP	0.962	108.7	3810.3
MeOH	B3LYP/def2-TZVP	0.962	108.7	3810.4
MeOH	B3LYP-D3(BJ)/aVTZ	0.961	109.0	3828.6
For comparison: data for anisole-MeOH taken from [1]				
OH-O	B3LYP-D3(BJ)/def2-TZVP			3710.7
OH-π	B3LYP-D3(BJ)/def2-TZVP			3760.5
OH-O	B3LYP-D3(BJ)/aVTZ			3711.5
OH-π	B3LYP-D3(BJ)/aVTZ			3766.7

Table S 2: Comparison of different levels of calculation for the DPE-MeOH cluster. The energies of the most stable OH-O conformer are given relative to the most stable OH-π conformer on the same level. The ΔCCSD(T) correction is performed with the 6-311+G*-basis set. The qualitative predictions, that OH-π wins and that it further benefits from zero point energy, are uniform across all listed methods. aVTZ stands for aug-cc-pVTZ.

geometry optimization	energy calculation	zero point correction	ΔE_{el}/kJ·mol^{-1}	ΔE_0/kJ·mol^{-1}
B97D/TZVP	B97D/TZVP	B97D/TZVP	2.5	4.2
B3LYP-D3(BJ)/def2-TZVP	B3LYP-D3(BJ)/def2-TZVP	B3LYP-D3(BJ)/def2-TZVP	0.9	1.8
B3LYP-D3(BJ)/def2-TZVP	MP2/aVTZ	B3LYP-D3(BJ)/def2-TZVP	2.2	3.1
B3LYP-D3(BJ)/def2-TZVP	MP2/aVTZ+ ΔCCSD(T)	B3LYP-D3(BJ)/def2-TZVP	1.1	2.0
B2PLYP-D3(BJ)/def2-TZVP	B2PLYP-D3(BJ)/def2-TZVP	B3LYP-D3(BJ)/def2-TZVP	1.0	1.9
B3LYP-D3(BJ)/aVTZ	B3LYP-D3(BJ)/aVTZ	B3LYP-D3(BJ)/aVTZ	0.6	1.4
MP2/aVTZ	MP2/aVTZ	B3LYP-D3(BJ)/def2-TZVP	2.6	3.5
MP2/aVTZ	MP2/aVTZ+ ΔCCSD(T)	B3LYP-D3(BJ)/def2-TZVP	1.5	2.4

Table S 3: Comparison of various methods and basis sets to the experimental microwave data for the DPE-MeOH complex (OH-π conformer). φ_1 and φ_2 are the dihedral angles about the C-O bonds in the diphenyl ether molecule as illustrated in Figure 1 of the main text. λ_a, λ_b and λ_c are the direction cosines between the methyl rotor and the inertial axis (as defined in the main text and also given in Table 2 of the main text).

Method	Basis Set	A_e (MHz)	B_e (MHz)	C_e (MHz)	φ_1	φ_2	$\sphericalangle_{COC}$	λ_a	λ_b	λ_c
B3LYP-D3(BJ)	def2-TZVP	1019.7	382.7	333.0	138.1	150.1	120.8	0.035	-0.253	0.973
B2PLYP-D3(BJ)	def2-SVP	989.6	388.0	338.7	122.6	163.9	120.1	-0.011	-0.377	0.925
B2PLYP-D3	def2-TZVP	1019.2	382.4	330.3	138.1	149.3	119.5	0.235	-0.260	0.942
B2PLYP-D3	def2-QZV	973.6	383.7	334.6	124.1	164.3	119.5	-0.076	-0.366	0.967
MP2	cc-pVDZ	999.0	387.5	341.5	123.9	162.8	117.2	-0.007	-0.342	0.946
MP2	def2-SVP	1022.9	386.3	343.0	127.8	161.6	118.7	-0.034	-0.308	0.949
M062X	cc-pvtz	1077.4	387.2	344.8	141.0	149.5	120.1	-0.104	-0.187	0.977
M062X	def2-TZV	1072.4	386.9	343.7	140.9	149.5	120.1	-0.105	-0.185	0.977
MP2	def2-TZVP	1041.6	387.0	340.3	137.4	151.1	117.8	0.038	-0.244	0.974
MP2	def2-QZV	961.2	385.0	335.0	121.7	170.8	117.1	-0.100	-0.377	0.968
Experiment										
DPE-MeOH, Fit 2		**997.98324(101)**	**380.73236(28)**	**326.79163(26)**				0.0626(8)	0.1695(73)	0.7679(78)

4 Further calculations applying SAPT

The contributing forces of the intermolecular interactions can be quantified using Symmetry Adapted Perturbation Theory (SAPT)[2]. This method calculates the interaction energy as a sum of contributions with defined physical meaning, which allows for an interpretation of the nature of the intermolecular interaction. We used the SAPT(0)/jun-cc-pVDZ level of theory as implemented in the Psi4 program package with the optimized geometries for each of the five lowest energy conformers from B3LYP-D3(BJ)/def2-TZVP calculations (Figure 2 of the main text). The results are summarized in Table S4. The two lowest energy conformers (OH-π and OH-π') have virtually identical interaction energies. The electrostatic interactions are significantly higher (>4 kJ/mol) in the two OH-O conformers indicating that the polar contribution in the hydrogen bond to the ether oxygen is stronger than in the OH-π interaction. Note, however, that the SAPT method fails in qualitatively predicting the OH-π preference over the OH-O preference robustly documented in Tab. S2 and our experiment.

Table S 4: Results from a zeroth order symmetry adapted perturbation theory calculation showing the various contributions to the intermolecular bonding for the DPE-MeOH conformers in kJ/mol. For comparison, the relative non-ZPE corrected energies are also given, calculated on the B3LYP-D3(BJ)/def2-TZVP level of theory.

	Conformer	ΔE_{elst}[a]	ΔE_{exch}[b]	ΔE_{ind}[c]	ΔE_{disp}[d]	ΔE_{tot}	non-ZPC Energy
(c)	OH-π	-25.9	32.4	-7.3	-22.0	-22.8	0
(d)	OH-π'	-25.0	33.1	-7.3	-22.9	-22.2	0.2
(a)	OH-O	-30.5	34.5	-8.0	-19.8	-23.9	0.9
(b)	OH-O′	-32.2	33.5	-8.8	-15.8	-23.3	2.9
(e)	OH-πp	-16.1	24.1	-5.0	-20.6	-17.7	6.0

[a] ΔE_{elst} is the electrostatic or Coulombic exchange. [b] ΔE_{exch} represents the repulsion due to quantum-mechanical exchange. [c] ΔE_{ind} corresponds to the induction and charge-transfer interactions. [d] ΔE_{disp} accounts for the dispersive interactions. [e] ΔE_{tot} is the total binding energy obtained from the SAPT calculations of the respective complexes.

5 Coordinates

Optimized structures at the B3LYP-D3(BJ)/def2-TZVP level shown in Figure 2.

OH-O

O -0.0771651 0.2844111 -0.8752452

C 1.0719781 -0.2943234 -0.3710503

C 2.2166647 -0.1625184 -1.1477973

C 1.1218082 -0.9101880 0.8740030

C 3.4242718 -0.6543233 -0.6716211

H 2.1464081 0.3283302 -2.1093820

C 2.3368945 -1.4039623 1.3345070

H 0.2277001 -0.9969574 1.4747035

C 3.4903295 -1.2798243 0.5691015

H 4.3161752 -0.5500773 -1.2761579

H 2.3787589 -1.8823181 2.3048612

H 4.4322753 -1.6650193 0.9363978

C -1.3199644 -0.1620515 -0.4505697

C -2.2164377 0.7796746 0.0328714

C -1.6759120 -1.4994922 -0.5744454

C -3.4936039 0.3696068 0.4006323

H -1.9116809 1.8155049 0.1082289

C -2.9512653 -1.8968170 -0.1953953

H -0.9601961 -2.2129265 -0.9603570

C -3.8630324 -0.9657782 0.2930034

H -4.1986736 1.1000916 0.7761183

H -3.2354506 -2.9370838 -0.2903217

H -4.8568484 -1.2803863 0.5834375

O 0.3027902 3.1503275 -0.3397929

H 0.2021940 2.2832738 -0.7541516

C 0.9741209 2.9648684 0.8968567

H 1.0779605 3.9468680 1.3581817

H 0.4084406 2.3195616 1.5797342

H 1.9720593 2.5333286 0.7630479

OH-O′

O -0.0430383 0.5249184 -0.0017350

C 1.0114069 -0.3724426 0.0211420

C 2.1386808 -0.0425611 -0.7191466

C 0.9786065 -1.5172437 0.8087470

C 3.2490155 -0.8769248 -0.6695666

H 2.1373761 0.8632093 -1.3110712

C 2.0926611 -2.3463644 0.8409395

H 0.0942063 -1.7531397 1.3843938

C 3.2297157 -2.0318024 0.1041171

H 4.1302783 -0.6222380 -1.2442820

H 2.0720840 -3.2391482 1.4529643

H 4.0947849 -2.6810227 0.1356930

C -1.3478647 0.0695969 -0.0440726

C -2.2929591 0.8115173 0.6513018

C -1.7208157 -1.0343644 -0.8019584

C -3.6303249 0.4405169 0.5891190

H -1.9714976 1.6696046 1.2264790

C -3.0604578 -1.3993554 -0.8484499

H -0.9735909 -1.5959402 -1.3452244

C -4.0188423 -0.6673121 -0.1557015

H -4.3688576 1.0187847 1.1293974

H -3.3554702 -2.2577785 -1.4384487

H -5.0605427 -0.9565543 -0.1990399

O 0.9514853 3.1874839 -0.6218027

H 0.4553688 2.3692040 -0.4840226

C 1.6743613 3.4624677 0.5663210

H 2.2576285 4.3663510 0.3899749

H 1.0112663 3.6420097 1.4210808

H 2.3639351 2.6505276 0.8268511

<u>OH-π</u>

O -0.4311667 1.0537093 -1.0486539

C -1.5725452 0.5489459 -0.4511092

C -2.7274791 1.3115771 -0.5587497

C -1.5898715 -0.6993046 0.1630886

C -3.9204391 0.8191014 -0.0430585

H -2.6780604 2.2756251 -1.0472329

C -2.7885525 -1.1737067 0.6816588

H -0.6840416 -1.2872980 0.2437539

C -3.9550738 -0.4221138 0.5819658

H -4.8226143 1.4116803 -0.1270350

H -2.8072272 -2.1441740 1.1613732

H -4.8840054 -0.8024669 0.9864000

C 0.7797329 0.9567173 -0.4136756

C 1.9028335 0.8271677 -1.2246145

C 0.9143702 1.0311237 0.9705163

C 3.1632712 0.7498752 -0.6474230

H 1.7694728 0.7777921 -2.2969296

C 2.1808330 0.9489759 1.5368494

H 0.0378159 1.1352246 1.5938635

C 3.3097220 0.8006064 0.7357306

H 4.0336165 0.6396081 -1.2816209

H 2.2833775 0.9987302 2.6133567

H 4.2915060 0.7310507 1.1846616

O 1.4580721 -2.2990409 0.5062358

H 1.8809196 -1.4461573 0.6639693

C 1.7814437 -2.7333235 -0.8063439

H 1.3657725 -3.7338688 -0.9231053

H 1.3467124 -2.0806530 -1.5710866

H 2.8638044 -2.7845022 -0.9653847

<u>OH-π'</u>

O 0.4456283 -1.4682768 0.6601669

C 1.5540163 -0.7158419 0.3093616

C 1.5579778 0.6667868 0.4612905

C 2.6809200 -1.3948771 -0.1302979

C 2.7144569 1.3712295 0.1516980

H 0.6728443 1.1754047 0.8235628

C 3.8338705 -0.6769091 -0.4287059

H 2.6430003 -2.4714246 -0.2305317

C 3.8530657 0.7063949 -0.2941522

H 2.7266898 2.4473477 0.2707704

H 4.7162882 -1.2023936 -0.7711712

H 4.7507764 1.2631780 -0.5294157

C -0.7811586 -1.1174298 0.1581530

C -1.8857904 -1.3286708 0.9780380

C -0.9445159 -0.6143702 -1.1301222

C -3.1580620 -1.0260314 0.5071491

H -1.7301948 -1.7174369 1.9752801

C -2.2212575 -0.3149516 -1.5881847

H -0.0796278 -0.4538196 -1.7584664

C -3.3322787 -0.5116287 -0.7747664

H -4.0145373 -1.1831499 1.1502281

H -2.3459867 0.0795830 -2.5886047

H -4.3231274 -0.2707297 -1.1359931

O -1.5255432 2.0794496 1.1041401

H -1.9393714 1.2254733 0.9290715

C -1.5874062 2.8673446 -0.0748737

H -1.2128454 3.8578717 0.1828555

H -0.9649867 2.4530109 -0.8756004

H -2.6123440 2.9677652 -0.4469785

OH-πp

O -0.3934826 -0.2972029 -1.2971665

C 0.7408358 -0.6320165 -0.6029950

C 1.8979332 -0.7861868 -1.3636983

C 0.7812632 -0.7810337 0.7802119

C 3.0962304 -1.0907475 -0.7367316

H 1.8393604 -0.6547668 -2.4357623

C 1.9913887 -1.0882423 1.3954423

H -0.1143268 -0.6502410 1.3697635

C 3.1522463 -1.2445038 0.6474419

H 3.9941674 -1.2008613 -1.3309387

H 2.0226099 -1.1949440 2.4722023

H 4.0896015 -1.4771224 1.1344163

C -1.5995147 -0.2128628 -0.6211862

C -2.0952410 1.0388000 -0.2877612

C -2.3180858 -1.3673625 -0.3414903

C -3.3333549 1.1344728 0.3380058

H -1.5120934 1.9185598 -0.5238614

C -3.5526541 -1.2621720 0.2873369

H -1.9067815 -2.3294297 -0.6172697

C -4.0619387 -0.0133201 0.6290003

H -3.7273904 2.1085622 0.5981054

H -4.1196177 -2.1579780 0.5062212

H -5.0252521 0.0645232 1.1159250

O 2.8635427 2.2084209 0.5730260

H 2.8601406 1.2438738 0.5707192

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H 1.6333064 3.7584125 0.1429522

H 1.3655191 2.3346295 -0.8827967

H 0.7884120 2.3420733 0.7988235

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