

Supporting Information

The Effect of Dispersion on the Structure of Diphenyl Ether Aggregates

Fabian Dietrich⁺, Dominic Bernhard⁺, Mariyam Fatima⁺, Cristóbal Pérez, Melanie Schnell,^{} and Markus Gerhards^{*}*

anie_201801842_sm_miscellaneous_information.pdf

Supporting Information

Table of contents

- Computational and Experimental Section..... 2
 - Computational Methods.....2
 - Rotational Spectroscopy..... 2
 - IR/UV Spectroscopy..... 3

- Theoretical Results..... 3
 - DFT-D, SCS-CC2 and LMP2 (*Figure S1 and Tables S1–S5*)..... 3
 - DID Plots (*Figures S2–S5*)..... 5
 - SAPT calculations (*Table S6*)..... 6

- Experimental Results..... 7
 - R2PI Spectroscopy (*Figure S6*)..... 7
 - CP-FTMW Spectroscopy..... 8
 - DPE–H₂O (*Figure S7 and Tables S7–S11*)..... 8
 - DPE–AdOH (*Figure S8 and Table S12*)..... 10
 - Line lists (*Tables S13–S32*)..... 11

Computational and Experimental Section

Computational Methods

Calculations are performed using the B3LYP functional with dispersion corrections and Becke-Johnson damping (D3BJ)^[1] and the def2-TZVP basis set. Furthermore, SCS-CC2^[2] calculations with the def2-TZVP basis set as well as the auxiliary basis set def2-TZVP-cbas^[3] are performed using the ricc2 module of Turbomole 7.0^[4]. The minimum structures are tested by frequency calculations yielding no imaginary modes at both levels of theory. Basis set superposition errors (BSSE) are considered by application of Counterpoise Corrections. Dispersion percentages are obtained from LMP2/aug-cc-pVQZ calculations with MOLPRO 2099.9^[5] using a localization method to partition the interacting molecules and calculating the dispersion interaction density (DID)^[6]. SAPT(0) calculations were performed using the Psi4 package.

Rotational Spectroscopy

The rotational spectra of diphenyl ether-(H₂O) and diphenyl ether-adamantanol were recorded with the CP-FTMW spectrometer COMPACT in Hamburg operating between 2–8 GHz. Experimental details are given elsewhere^[7]. To observe the diphenyl ether (DPE)-H₂O clusters, DPE (stated purity ≥ 99%) was purchased from Sigma-Aldrich and used without further purification. The molecules were seeded into a supersonic expansion using a pulse nozzle (Parker General Valve, Series 9, 0.9 mm orifice) equipped with a heatable reservoir in front of the solenoid, close to the valve orifice. In this arrangement, DPE was placed in this small sample reservoir and heated to 90 °C. Water was placed in a reservoir on a separate section of tubing outside of the vacuum chamber. The carrier gas neon (3 bar backing pressure) was allowed to flow over the water and mixed with DPE to create a supersonic expansion in the chamber. For observing the DPE-adamantanol complex, DPE and adamantanol (AdOH) were premixed, placed into the small sample reservoir in front of the solenoid, close to the valve orifice, and heated to 80 °C. AdOH was purchased from Sigma-Aldrich (stated purity ≥ 99%). A neon carrier gas backing pressure of 3.5 bar was used.

For each gas pulse, the ensemble of molecules was polarized with a series of eight microwave chirps of 4 μs duration spanning 2 → 8 GHz. The chirps were generated with an arbitrary waveform generator (AWG), amplified to 300 W with a travelling wave tube amplifier, and transmitted into the vacuum chamber with a horn antenna. We used the fast-frame approach, including 8 frames. Following each excitation, 40 μs of the free induction decay (FID) of the macroscopic ensemble of polarized molecules were recorded, yielding a frequency resolution of 25 kHz. For both experiments, a total of 5 million FIDs were co-added and Fourier transformed with a Kaiser window function to give the broadband rotational spectrum in the frequency domain. All of the spectra were first fit using the JB95 program^[8] and further refined with the AABS program suite^[9].

For the OH-π isomer of DPE-H₂O, the signal-to-noise (S/N) ratio was sufficient to assign all the singly substituted ¹³C isotopologues. Kraitchman's equations, implemented in the KRA program,^[10] were used to determine the coordinates of each carbon atom from this isotopic information with respect to the molecular center of mass in the principal axis system. Since with this analysis we can only determine the magnitudes of the atomic positions, the signs of the coordinates were inferred from quantum-chemical calculation. To determine the position of the water oxygen atoms, an isotopically enriched sample of water with 50% H₂¹⁸O was used. This provided us with the positions of the H₂¹⁸O-oxygen atoms for both isomers. A comparison between the Kraitchman structure and the structure calculated at the B3LYP-D3(BJ)/def2-TZVP level is shown in Figure 2 for both OH-π and OH-O isomers. The results of the fitted rotational constants for ¹³C and ¹⁸O isotopologues, the line lists for the parent ¹²C and the ¹³C and ¹⁸O isotopologues, and the results of the Kraitchman analysis for the OH-π isomer are given in Tables S7–S10 and S13–S29. For the OH-O isomer of DPE–water, the results of the fitted rotational constants for ¹⁸O isotopologues and line lists for the parent ¹²C and the ¹³C and ¹⁸O isotopologues are given in Tables S11 and S30–S31.

The experimental and calculated rotational parameters for DPE-AdOH are summarized in Table S12, while the corresponding line list is given in Table S32.

IR/UV spectroscopy

For the IR/UV experiments, the chosen experimental setup including different laser systems and a molecular beam apparatus is described in detail elsewhere^[11], thus only a brief description is given here. All experiments were carried out in a molecular beam apparatus consisting of a differentially pumped linear time-of-flight (TOF) mass spectrometer with a pulsed valve (General Valve Iota One, 500 μm orifice) for skimmed jet expansion. The DPE sample was purchased from Fluka ($\geq 99.9\%$) and used without further purification. Water was supplied *via* a cooled reservoir and co-expanded with DPE (room temperature) in neon at 2.5–3.0 bar.

For the one-color R2PI and IR/R2PI experiments, two tunable nanosecond laser systems were necessary: one UV and one IR laser system. The UV laser radiation is obtained *via* second harmonic generation in a BBO crystal using the output of a dye laser (Sirah, Cobra-Stretch), which is pumped by the second harmonic (532 nm) of a Nd:YAG laser (Innolas, SpitLight 600). The IR radiation in the region of 3250–3750 cm^{-1} is produced by difference frequency mixing (DFM) in a LiNbO₃ crystal using the fundamental (1064 nm) of a seeded Nd:YAG laser (Spectra-Physics, Quanta-Ray Pro-230) and the output of a dye laser (Sirah, PrecisionScan), which is pumped by the second harmonic (532 nm) of the same Nd:YAG laser. The resulting IR radiation is amplified by an optical parametric amplification (OPA) process in a further LiNbO₃ crystal using the DFM output and again the fundamental (1064 nm) of the Nd:YAG laser. In order to record the IR/R2PI spectra, the IR laser was fired 50 ns prior to the UV laser.

Remark on comparability: We have already shown in our previous investigations on DPE–alcohol aggregates^[12,13] that the sources in the IR/UV and CP-FTMW experiments yield comparable results. The pulse valves and operating conditions are similar in both experiments, so the cluster production is assumed to be similar as well.

Theoretical Results

DFT-D3, SCS-CC2 and LMP2 results

Remark: Both motifs of DPE-water (OH-O and OH- π) have the same amount of equivalent structures. For OH-O and OH- π , both phenyl rings can be rotated by 180°, yielding the same structure. The same is true for the water molecule. In the OH- π structure, the water molecule can interact also with the other phenyl ring, while in the OH-O structure the water molecule can also interact with the second lone pair of the ether oxygen atom. This yields $2^4 = 16$ structures for OH-O as well as for OH- π .

Table S1 Comparison of relative energies E_{rel} and zero-point corrected energies $E_{0,\text{rel}}$ (including BSSE corrections) of the aggregate of diphenyl ether with water, as well as unscaled and scaled values of the OH-stretching frequencies, scaling factors = 0.9600 (B3LYP-D3(BJ)/def2-TZVP) and 0.9635 (SCS-CC2/def2-TZVP).

Method	Isomer	E_{rel} /kJ/mol	$E_{0,\text{rel}}$ /kJ/mol	$\tilde{\nu}_{1,\text{unscaled}}/\text{cm}^{-1}$	$\tilde{\nu}_{1,\text{scaled}}/\text{cm}^{-1}$	$\tilde{\nu}_{2,\text{unscaled}}/\text{cm}^{-1}$	$\tilde{\nu}_{2,\text{scaled}}/\text{cm}^{-1}$
B3LYP-D3(BJ)/	OH-O	0.8	2.3	3730	3581	3852	3698
def2-TZVP	OH- π	0.0	0.0	3768	3617	3852	3698
SCS-CC2/	OH-O	0.9	2.8	3745	3609	3858	3717
def2-TZVP	OH- π	0.0	0.0	3750	3614	3682	3721

Table S2 Calculated adiabatic excitation wavenumber $\tilde{\nu}_{\text{adiabatic}}$, using SCS-CC2/def2-TZVP.

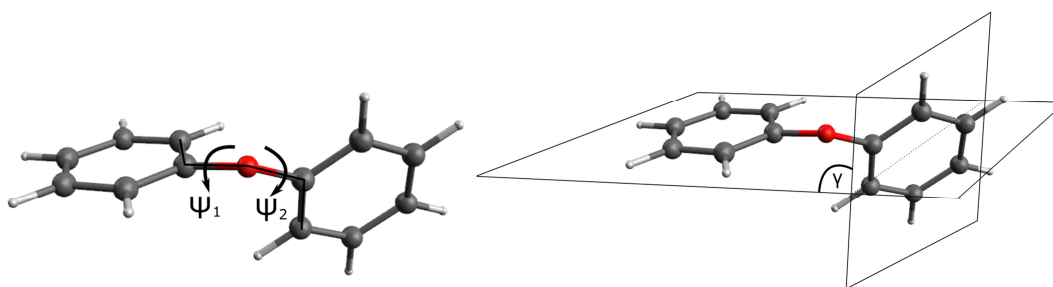
Isomer	$\tilde{\nu}_{\text{adiabatic}}/\text{cm}^{-1}$
OH-O	37846
OH- π	37194

Table S3 Relative zero-point corrected (including BSSE corrections) energies of the OH-O and OH- π isomer of different aggregates of diphenyl ether with polar solvent molecules, values given in kJ/mol.

Method	Isomer	DPE-H ₂ O	DPE-MeOH	DPE-tBuOH	DPE-AdOH
B3LYP-D3(BJ)/ def2-TZVP	OH-O	2.3	1.7	0.0	0.0
	OH- π	0.0	0.0	0.0	2.3
SCS-CC2/ def2-TZVP	OH-O	2.8	1.9	0.7	0.0
	OH- π	0.0	0.0	0.0	2.6

Table S4 Dihedral angles (Ψ_1 and Ψ_2) of diphenyl ether in the aggregates with different alcohols, the interphenyl angle γ (angle between the phenyl ring planes) and the energy relative to the pure DPE. The experimental values for the DPE-H₂O OH- π cluster are given in square brackets. For the experimental determination, the position of the oxygen atom was taken from the theoretical structure due to the lack of ¹⁸O isotopic data (0.2% natural abundance).

Cluster	Isomer	$\Psi_1/^\circ$	$\Psi_2/^\circ$	$\gamma/^\circ$	$E_{\text{twist}}/\text{kJ/mol}$	$\Delta E_{\text{twist}}/\text{kJ/mol}$
DPE-H ₂ O	OH-O	11.7	75.0	80.4	1.05	0.65
	OH- π	52.2 [52.72(88)]	30.7 [27.10(83)]	70.5 [65.61(73)]	0.40	
DPE-MeOH	OH-O	25.9	56.4	71.6	0.56	0.18
	OH- π	33.9	44.6	66.3	0.38	
DPE-tBuOH	OH-O	37.5	43.3	68.7	0.33	-0.45
	OH- π	23.1	51.8	64.8	0.78	
DPE-AdOH	OH-O	34.6	47.0	69.7	0.46	-0.92
	OH- π	62.0	11.8	66.9	1.38	
DPE		37.0	37.0	76.3		

**Figure S1** Definition of dihedral angles (Ψ_1 and Ψ_2) and the interphenyl angle γ as given in Table S4.**Table S5** Total amount of dispersion energy, obtained from the LMP2/aug-cc-pVQZ single-point calculations on the B3LYP-D3(BJ)/def2-TZVP optimized structures, values given in kJ/mol.

Isomer	DPE-H ₂ O	DPE-MeOH	DPE-tBuOH	DPE-AdOH
OH-O	-9.3	-14.8	-21.4	-27.8
OH- π	-11.4	-16.6	-22.0	-26.0
difference	2.1	1.8	0.6	-1.8

Dispersion Interaction Density (DID)-Plots

LMP2/AVQZ calculations are performed on the optimized structures on the B3LYP-D3(BJ)/def2-TZVP level. For this approach^[6], the orbitals are localized on the DPE and the solvent molecule, respectively. The color scale indicates the strengths of the intermolecular interaction, plotted on an isosurface representing the total electron density.

Color scale: 

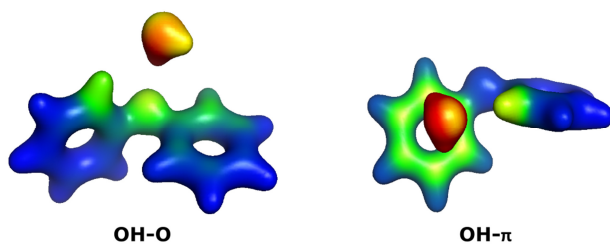


Figure S2 DID plot of the isomers of the diphenyl ether – water aggregate.

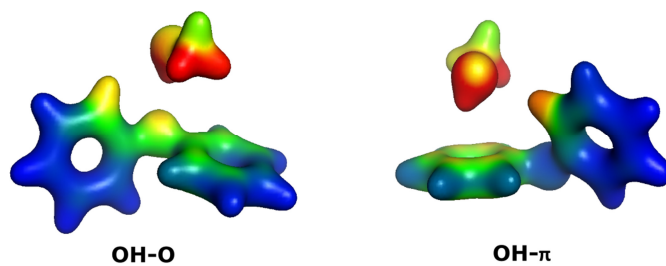


Figure S3 DID plot of the isomers of the diphenyl ether – methanol aggregate.

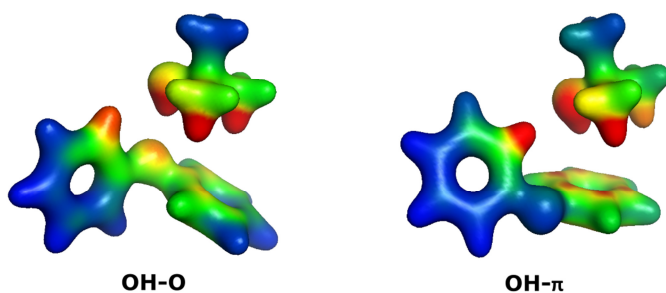


Figure S4 DID plot of the isomers of the diphenyl ether – *tert*-butanol aggregate.

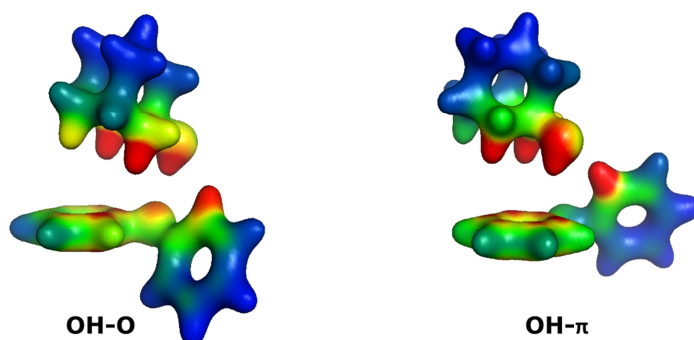


Figure S5 DID plot of the isomers of the diphenyl ether – adamantanol aggregate.

SAPT calculations

Table S6 Energy decompositions (kJ/mol) from a SAPT(0)/jun-cc-pVDZ analysis for the structures calculated at the B3LYP-D3(BJ)/def2-TZVP level.

species	isomer	E_{tot}	$E_{\text{el}}^{(1)}$	$E_{\text{exch}}^{(1)}$	$E_{\text{ind}}^{\text{tot}}$	$E_{\text{disp}}^{\text{tot}}$
DPE-H ₂ O	OH-O	-19.9	-29.8	30.2	-7.6	-12.6
	OH- π	-17.8	-25.2	28.2	-5.9	-14.8
DPE-MeOH	OH-O	-23.9	-30.5	34.5	-8.0	-19.8
	OH- π	-22.8	-25.9	32.4	-7.3	-22.0
DPE- <i>t</i> -BuOH	OH-O	-29.4	-34.1	44.7	-9.5	-30.5
	OH- π	-26.9	-29.4	41.9	-8.3	-31.1
DPE-AdOH	OH-O	-34.7	-33.9	48.5	-8.9	-40.4
	OH- π	-30.9	-31.2	47.8	-9.0	-38.5

Table S6 summarizes the decompositions of the interaction energies for the four different DPE complexes, each separated into the OH-O and the OH- π isomer, as determined using SAPT(0) calculations employing the Psi4 program package. The dispersion energies, and in particular the differences between the isomers, are very similar to the values presented in Table S5, obtained using LMP2/aug-cc/pVTZ calculations. As previously described, electrostatic interactions dominate over dispersion interactions for the DPE-MeOH complex, and a slight preference of the OH-O isomer is observed. The situation is different for the isomers of the DPE-*t*BuOH complex, where electrostatic and dispersion interactions are of the same order of magnitude. Here, the experiments revealed a preference of the OH-O isomer. These two examples already indicate that the total interaction energy provided by these zero order SAPT(0) calculations might often not fully agree with the energy differences calculated using quantum-chemical structure optimizations using decent size basis sets. However, the breakdown into different energy contributions can nevertheless be useful for interpreting the experimental results. Especially relative values, like differences between comparable molecular species such as isomers, are more reliable than absolute values, as is the case for many approaches. A comparison with more sophisticated DFT-SAPT/aug-cc-pVTZ calculations^[13] indicated an overestimation of the stability of the OH-O isomer because of the underestimation of the first order exchange contribution E_{exch} . However, the dispersion energy and electrostatics contributions provide reliable results.

For DPE-AdOH, contributions due to dispersion interactions dominate over electrostatic interactions. For the two isomers, however, there are overall stronger interactions observed for the OH-O isomer than the OH- π isomer, resulting in an overall preference for the OH-O isomer, in agreement with the other quantum-chemical calculations reported above.

However, for the DPE-water complex, both the electrostatic energy and the dispersion contribution prefer the OH-O isomer over the OH- π isomer. This is opposite to what we observe in the experiment and what is predicted using quantum-chemical calculations, where we observe a preference for the OH- π isomer.

Experimental Results

R2PI Spectroscopy

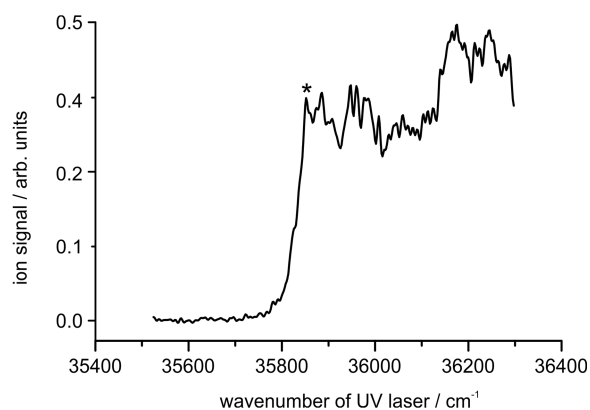


Figure S6 One-color R2PI spectrum of DPE–H₂O in the range of 35520–36300 cm⁻¹ using the carrier gas neon; the asterisk (*) indicates the onset of the spectrum (35852 cm⁻¹), yielding the IR/R2PI spectrum of the OH- π isomer.

The R2PI spectrum of the DPE–H₂O complex (for the spectrum of the DPE monomer, cf. Ref. ^[14]) exhibits partly overlapping resonances of OH-O and OH- π isomers:

The origin of the spectrum at 35852 cm⁻¹ marked with an asterisk (*) is a transition, which exclusively belongs to the OH- π isomer. Consequently, the IR/R2PI spectrum recorded *via* this resonance is isomer-selective for the OH- π structure, exhibiting two OH stretching vibrations. However, other transitions above 35950 cm⁻¹ appearing in the R2PI spectrum are not selective for one single isomer; resonances of the two isomers (OH- π or OH-O) overlap. Therefore, the corresponding IR/R2PI spectra contain altogether four OH stretching transitions from the OH- π *and* the OH-O isomer. By considering the isomer selective IR/R2PI spectrum *via* the transition at 35852 cm⁻¹ the two remaining transitions in the other IR/R2PI spectra can be assigned to the OH-O structure. The relative shifts of the vibrational transitions are excellently predicted by theory (cf. Communication) Furthermore the relative excitations energies ($S_{1\leftarrow}S_0$ transitions) of the OH- π and OH-O isomers are correctly predicted (cf. Table S2) with the origin of the OH- π isomer being red-shifted compared to the origin of the OH-O isomer.

Results from CP-FTMW spectroscopy

DPE-H₂O

Table S7 Molecular parameters of the DPE monomer and DPE-H₂O complexes: Comparison of experimental and calculated rotational constants A , B , and C , the centrifugal distortion constants Δ_J , Δ_{JK} , δ_J and δ_K , and the standard deviation σ of the fit. The DPE monomer shows a splitting of each transition into three lines due to internal motion of the two phenyl rings with respect to each other, and the experimental rotational constants reported here include only the middle transition from each triplet.

	DPE monomer		OH- π		OH-O			
	Experiment	State 0-	State 0+	B3LYP-D3(BJ)/def2-TZVP	SCS-CC2/def2-TZVP	B3LYP-D3(BJ)/def2-TZVP	SCS-CC2/def2-TZVP	
A /MHz	2362.06937(76)	1359.68029(42)	1362.4557(11)	1416.46	1386.24	1062.1032(17)	1165.99	1190.48
B /MHz	437.98841(17)	409.24121(14)	409.12297(45)	407.09	408.32	434.29784(37)	427.99	426.60
C /MHz	412.44302(17)	365.31297(13)	365.43020(43)	367.38	370.24	343.60921(39)	354.46	364.85
Δ_J /kHz	0.02641(62)	0.02233(85)	0.0235(24)			0.0103(27)		
Δ_{JK} /kHz	0.9963(69)	0.2683(48)	0.263(21)			1.087(41)		
δ_J /kHz	-0.00208(11)	-	-			-		
δ_K /kHz	0.559(33)	-	-			-		
σ /kHz	4.7	5.6	6.6			8.7		
N_{Lines}	52(0/52/0)	95(71/0/24)	78(57/0/21)			30(0/30/0)		
$\mu_a/\mu_b/\mu_c$				0.7/1.1/0.9	0.7/1.0/0.8		0.2/3.0/0.5	0.1/3.0/0.2

The comparison between experimental and quantum-chemical results clearly indicate that the overall geometry of the cluster is not affected by the level of calculation, the relative orientation of the water monomer with respect to DPE experiences noticeable changes. Calculations at the MP2 level for the OH- π isomer of the DPE-water complex show (Table S8) that the b-component of the dipole moment dramatically changes and goes to nearly zero when this level of theory is applied. This shows how the water monomer orientation can undergo very subtle changes that are difficult to capture. Therefore, we believe that the water hydrogen orientation is mainly responsible for the non-observation of b-type transitions. In fact, the observation of water tunneling, resembled by the O⁺ and O⁻ states, further indicates that internal dynamics are taking place, which can lead to an average structure with a vanishing μ_b dipole moment component and thus non-observable b-type transitions.

Table S8 Comparison of the calculated rotational constants A , B , C and the dipole moment at B3LYP-D3(BJ) and MP2 level of theory for the DPE-water OH- π isomer.

	B3LYP-D3(BJ)/ def2-TZVP	MP2/6-311g++(d,p)
A /MHz	1416.46	1377.04
B /MHz	407.09	413.82
C /MHz	367.38	370.50
$\mu_a/\mu_b/\mu_c$	0.7/1.1/0.9	1.5/0.13/0.15

DPE–water: OH- π isomer

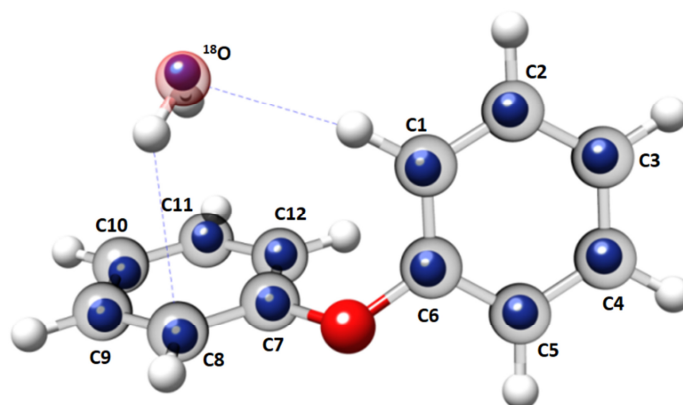


Figure S7 Kraitchman structure and atom labeling for the OH- π isomer of the DPE-water complex, overlaid with the optimized structure at the B3LYP-D3(BJ)/def2-TZVP level of theory.

Table S9 Experimental rotational parameters for the assigned ^{13}C isotopologues for the DPE-water OH- π isomer.

	A/MHz	B/MHz	C/MHz	Δ_J/kHz	Δ_{JK}/kHz	N_{lines}^a	σ/kHz
N	1359.68029(42)	409.24121(14)	365.31297(13)	0.02233(85)	0.2683(48)	95	5.6
C1	1356.512(45)	408.48864(29)	364.54138(28)	<i>b</i>	<i>b</i>	19	4.3
C2	1352.080(48)	406.83915(36)	362.86755(33)	<i>b</i>	<i>b</i>	18	5.9
C3	1357.716(29)	404.49947(19)	361.47781(20)	<i>b</i>	<i>b</i>	20	3.7
C4	1357.103(65)	404.83099(45)	361.67368(37)	<i>b</i>	<i>b</i>	21	7.8
C5	1353.230(43)	407.28133(34)	363.28099(32)	<i>b</i>	<i>b</i>	21	5.5
C6	1358.174(33)	408.59357(21)	364.77737(19)	<i>b</i>	<i>b</i>	19	3.7
C7	1357.401(31)	408.91430(23)	364.91141(21)	<i>b</i>	<i>b</i>	21	4.1
C8	1352.838(51)	407.40667(36)	363.92993(33)	<i>b</i>	<i>b</i>	23	6.4
C9	1357.456(47)	405.42459(31)	362.25247(33)	<i>b</i>	<i>b</i>	23	6.6
C10	1357.097(37)	405.02620(23)	362.10193(24)	<i>b</i>	<i>b</i>	23	4.6
C11	1350.699(60)	406.58629(46)	363.84780(46)	<i>b</i>	<i>b</i>	23	7.7
C12	1355.171(38)	408.46607(34)	364.96755(29)	<i>b</i>	<i>b</i>	18	5.1

^a The number of fitted lines.

^b Kept fixed at the value for the normal species.

^N Normal species.

Table S10 Experimental rotational parameters for the assigned ^{18}O isotopologue for the DPE-water OH- π isomer.

	A/MHz	B/MHz	C/MHz	Δ_J/kHz	Δ_{JK}/kHz	N_{lines}^a	σ/kHz
0-	1308.03538(39)	407.44023(15)	360.39120(16)	0.0222(25)	0.323	89	6.4
0+	1310.59583(52)	407.31658(16)	360.50059(18)	0.0232(13)	0.2493(72)	65	6.4

^a The number of fitted lines.

DPE–water: OH-O isomer

Table S11 Experimental rotational parameters for the assigned ^{18}O isotopologue for the OH-O isomer.

	A/MHz	B/MHz	C/MHz	Δ_J /kHz	Δ_{JK} /kHz	N_{lines}^a	σ /kHz
N	1062.1032(17)	434.29784(37)	343.60921(39)	0.0103(27)	1.087(41)	30	8.7
^{18}O	1007.23262(83)	434.22768(32)	337.66869(31)	0.0104(20)	1.065(13)	29	6.9

^a The number of fitted lines.

^N Normal species.

DPE–AdOH: OH-O isomer

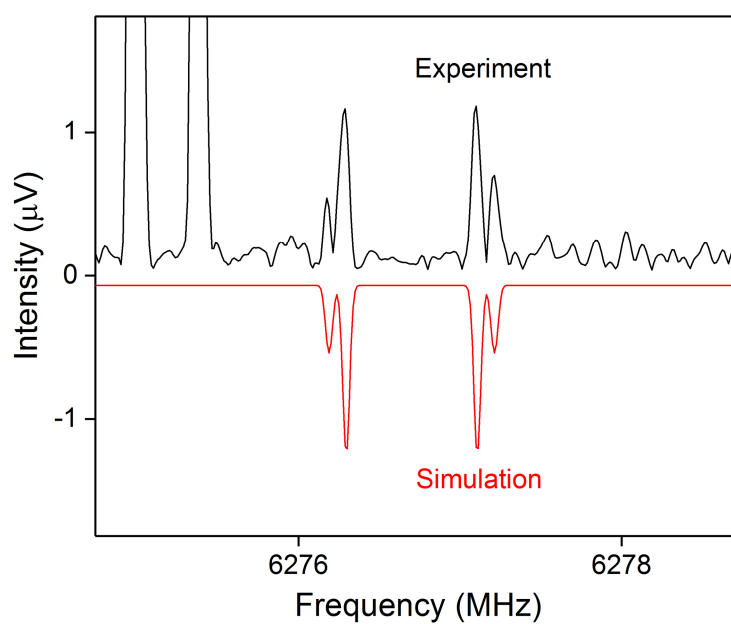


Figure S8 A section of the measured 2-8 GHz spectrum of DPE–AdOH (3 million acquisitions). The upper experimental trace in black is compared with simulations based on fitted parameters. Comparison with the results from quantum-chemical calculations allows us to clearly assign the observed complex to the OH-O isomer (Table S12).

Table S12 Molecular parameters of DPE–AdOH complexes: Comparison of experimental and calculated rotational constants A , B , and C , the centrifugal distortion constants Δ_J , and the standard deviation σ of the fit as well as calculated dipole-moment components.

	OH-O			OH- π	
	Experiment	B3LYP-D3(BJ)/def2-TZVP	SCS-CC2/def2-TZVP	B3LYP-D3(BJ)/def2-TZVP	SCS-CC2/def2-TZVP
A /MHz	350.53783(12)	352.81	351.09	380.46	379.9063
B /MHz	174.71795(22)	178.77	178.91	161.13	160.9968
C /MHz	137.28843(29)	139.99	140.32	132.96	133.0061
Δ_J /kHz	0.02202(38)				
σ /kHz	10.14				
N_{Lines}	91(0/47/66)				
$\mu_a/\mu_b/\mu_c$ (D)		1.0/1.7/2.1	1.0/1.7/2.2	0.2/0.8/0.2	0.2/0.8/0.2

Line lists

Table S13 Line list for the DPE-water OH- π isomer (0^+ state).

J'	K_a'	K_c'	J''	K_a''	K_c''	V_{obs}	$V_{\text{obs}}-V_{\text{calc}}$										
3	1	3	←	2	1	2	2257.2138	0.0000	7	3	4	←	6	3	3	5435.9861	0.0006
3	2	2	←	2	2	1	2323.6553	0.0046	7	1	6	←	6	1	5	5553.5112	-0.0032
3	2	1	←	2	2	0	2329.5256	0.0151	4	2	2	←	3	1	2	5914.3482	0.0039
3	1	2	←	2	1	1	2388.2597	-0.0016	8	1	8	←	7	1	7	5995.9246	-0.0032
2	1	1	←	1	0	1	2589.8251	0.0028	8	0	8	←	7	0	7	6084.9403	0.0088
5	0	5	←	4	1	3	2632.3099	0.0011	4	2	3	←	3	1	3	6154.5704	0.0052
4	1	4	←	3	1	3	3007.9774	0.0034	8	2	7	←	7	2	6	6178.4880	-0.0005
4	0	4	←	3	0	3	3083.6297	0.0010	8	5	3	←	7	5	2	6203.4591	0.0054
4	2	3	←	3	2	2	3097.0473	-0.0091	8	4	5	←	7	4	4	6206.5425	-0.0027
4	2	2	←	3	2	1	3111.6294	-0.0044	8	3	6	←	7	3	5	6210.2802	0.0155
4	1	3	←	3	1	2	3182.5608	0.0006	8	3	5	←	7	3	4	6217.8977	-0.0075
6	0	6	←	5	1	4	3254.7443	0.0028	8	2	6	←	7	2	5	6289.7535	-0.0041
3	1	2	←	2	0	2	3430.4488	0.0029	8	1	7	←	7	1	6	6337.8300	0.0024
5	1	5	←	4	1	4	3757.4176	0.0032	5	2	3	←	4	1	3	6630.1402	0.0128
5	0	5	←	4	0	4	3843.8857	-0.0031	9	1	9	←	8	1	8	6738.5324	-0.0069
5	2	4	←	4	2	3	3869.4503	-0.0320	9	0	9	←	8	0	8	6819.6955	0.0023
5	3	3	←	4	3	2	3877.4603	0.0013	9	4	6	←	8	4	5	6984.7429	-0.0069
5	3	2	←	4	3	1	3878.1110	0.0060	9	4	5	←	8	4	4	6985.1697	-0.0024
5	2	3	←	4	2	2	3898.3406	-0.0027	9	3	7	←	8	3	6	6988.7158	-0.0008
5	1	4	←	4	1	3	3975.2301	-0.0020	9	3	6	←	8	3	5	7002.5714	-0.0053
4	1	3	←	3	0	3	4295.2108	0.0020	5	2	4	←	4	1	4	7016.0741	0.0006
2	2	0	←	1	1	0	4454.2639	0.0052	7	1	6	←	6	0	6	7064.5387	0.0141
2	2	1	←	1	1	1	4496.4914	0.0077	9	2	7	←	8	2	6	7095.4250	-0.0083
6	1	6	←	5	1	5	4505.3145	0.0013	9	1	8	←	8	1	7	7117.9059	-0.0021
6	0	6	←	5	0	5	4597.6659	0.0010	3	3	0	←	2	2	0	7198.9891	-0.0071
6	4	3	←	5	4	2	4652.2361	0.0037	3	3	1	←	2	2	1	7200.4234	-0.0097
6	3	4	←	5	3	3	4654.5038	0.0005	6	2	4	←	5	1	4	7345.1959	-0.0004
6	3	3	←	5	3	2	4656.2188	-0.0024	10	1	10	←	9	1	9	7479.3911	-0.0033
6	2	4	←	5	2	3	4690.2966	-0.0044	10	0	10	←	9	0	9	7550.2824	0.0015
6	1	5	←	5	1	4	4765.7460	-0.0055	10	2	9	←	9	2	8	7708.6949	0.0118
5	1	4	←	4	0	4	5186.8116	-0.0005	10	4	7	←	9	4	6	7763.7282	0.0001
3	2	1	←	2	1	1	5190.9811	0.0093	10	4	6	←	9	4	5	7764.6454	0.0065
7	1	7	←	6	1	6	5251.5159	0.0025	10	3	8	←	9	3	7	7767.2615	-0.0004
3	2	2	←	2	1	2	5314.7255	0.0029	10	3	7	←	9	3	6	7790.6683	0.0027
7	0	7	←	6	0	6	5344.5860	0.0077	10	1	9	←	9	1	8	7892.8988	-0.0030
7	2	6	←	6	2	5	5410.4269	-0.0049	6	2	5	←	5	1	5	7899.3434	-0.0023
7	5	2	←	6	5	1	5426.9583	-0.0011	10	2	8	←	9	2	7	7902.9259	-0.0026
7	4	4	←	6	4	3	5429.0615	-0.0009	4	3	1	←	3	2	1	7970.6978	-0.0056
7	3	5	←	6	3	4	5432.1378	0.0000	4	3	2	←	3	2	2	7977.8067	-0.0084
																RMS	6.6 kHz

Tables S15-S28 : Line list for all singly substituted ^{13}C isotopologues (indicated by the labelling of the respective C atom, cf. Figure S8) and the H_2^{18}O isotopologue of the OH- π isomer:

Table S15 C1

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	1	3	←	2	1	2	2252.2361	-0.0114
3	0	3	←	2	0	2	2313.1310	0.0029
3	1	2	←	2	1	1	2384.0601	0.0025
4	0	4	←	3	0	3	3077.2904	0.0007
4	1	3	←	3	1	2	3176.9239	-0.0001
5	0	5	←	4	0	4	3835.7939	0.0023
5	2	3	←	4	2	2	3891.1517	-0.0025
5	1	4	←	4	1	3	3968.1306	-0.0034
6	1	6	←	5	1	5	4495.2331	-0.0016
6	0	6	←	5	0	5	4587.7200	0.0031
6	2	5	←	5	2	4	4631.4441	0.0080
6	2	4	←	5	2	3	4681.8534	-0.0064
6	1	5	←	5	1	4	4757.1499	-0.0014
7	1	7	←	6	1	6	5239.6884	0.0031
7	2	6	←	6	2	5	5399.5801	0.0029
8	1	8	←	7	1	7	5982.3271	-0.0007
8	0	8	←	7	0	7	6071.0708	-0.0048
8	3	5	←	7	3	4	6206.1395	0.0045
8	1	7	←	7	1	6	6326.0474	-0.0013
							RMS	4.3 kHz

Table S16 C2

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	0	3	←	2	0	2	2303.1342	-0.0002
4	1	4	←	3	1	3	2987.9655	-0.0063
4	0	4	←	3	0	3	3063.9392	0.0011
4	2	3	←	3	2	2	3077.6424	-0.0041
4	1	3	←	3	1	2	3163.6618	-0.0050
5	0	5	←	4	0	4	3819.0642	0.0024
5	2	4	←	4	2	3	3845.1716	-0.0099
5	1	4	←	4	1	3	3951.5506	0.0007
6	0	6	←	5	0	5	4567.5935	0.0052
6	1	5	←	5	1	4	4737.2255	-0.0048
7	1	7	←	6	1	6	5216.2710	-0.0018
7	2	5	←	6	2	4	5454.9483	-0.0113
8	0	8	←	7	0	7	6044.1137	0.0023
8	1	7	←	7	1	6	6299.4127	0.0019
9	1	9	←	8	1	8	6693.0011	-0.0040
9	0	9	←	8	0	8	6773.4717	-0.0003
9	2	7	←	8	2	6	7053.8676	0.0139
10	1	10	←	9	1	9	7428.6892	0.0062
							RMS	5.9 kHz

Table S17 C3

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	0	3	←	2	0	2	2292.2510	0.0057
4	1	4	←	3	1	3	2975.0954	-0.0017
4	0	4	←	3	0	3	3049.7604	0.0000
4	2	2	←	3	2	1	3076.9256	-0.0043
4	1	3	←	3	1	2	3147.0050	-0.0020
5	1	5	←	4	1	4	3716.3922	0.0000
5	0	5	←	4	0	4	3801.8628	-0.0001
5	2	3	←	4	2	2	3854.7053	-0.0041
5	1	4	←	4	1	3	3930.8810	-0.0020
6	2	5	←	5	2	4	4589.4370	0.0069
6	3	4	←	5	3	3	4602.8439	0.0009
6	1	5	←	5	1	4	4712.6768	0.0010
7	2	5	←	6	2	4	5425.7564	0.0029
7	1	6	←	6	1	5	5491.8023	-0.0004
8	1	8	←	7	1	7	5930.7190	-0.0097
8	0	8	←	7	0	7	6019.3843	0.0021
8	1	7	←	7	1	6	6267.5962	0.0004
9	1	9	←	8	1	8	6665.3709	0.0054
9	2	7	←	8	2	6	7015.0883	0.0006
9	1	8	←	8	1	7	7039.2976	-0.0025
							RMS	3.7 kHz

Table S18 C4

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	0	3	←	2	0	2	2293.7904	0.0038
3	1	2	←	2	1	1	2363.3391	0.0046
4	1	4	←	3	1	3	2976.9136	-0.0021
4	0	4	←	3	0	3	3051.7716	0.0031
4	1	3	←	3	1	2	3149.3531	-0.0132
5	1	5	←	4	1	4	3718.6512	0.0029
5	0	5	←	4	0	4	3804.3039	0.0026
5	2	3	←	4	2	2	3857.5190	-0.0030
6	1	6	←	5	1	5	4458.8859	0.0140
6	2	5	←	5	2	4	4592.5511	0.0028
7	1	7	←	6	1	6	5197.4226	-0.0085
7	0	7	←	6	0	6	5289.9264	0.0022
7	2	6	←	6	2	5	5354.3663	0.0107
7	2	5	←	6	2	4	5429.8608	-0.0112
7	1	6	←	6	1	5	5495.8005	-0.0123
8	1	8	←	7	1	7	5934.2274	-0.0110
8	0	8	←	7	0	7	6022.8898	-0.0071
8	1	7	←	7	1	6	6272.1210	0.0118
9	1	9	←	8	1	8	6669.2785	0.0043
9	2	7	←	8	2	6	7020.5618	0.0060
10	1	10	←	9	1	9	7402.5814	0.0000
							RMS	7.8 kHz

Table S19 C5

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	0	3	←	2	0	2	2305.6966	-0.0013
4	1	4	←	3	1	3	2991.3342	-0.0010
4	0	4	←	3	0	3	3067.3531	0.0008
4	2	3	←	3	2	2	3081.0698	0.0014
4	1	3	←	3	1	2	3167.1440	-0.0010
5	1	5	←	4	1	4	3736.5701	0.0063
5	0	5	←	4	0	4	3823.3332	0.0100
5	2	4	←	4	2	3	3849.4680	0.0102
6	1	6	←	5	1	5	4480.2229	0.0011
6	2	5	←	5	2	4	4616.5973	-0.0020
6	1	5	←	5	1	4	4742.4429	-0.0001
7	1	7	←	6	1	6	5222.1534	0.0019
7	0	7	←	6	0	6	5315.0985	-0.0028
7	2	5	←	6	2	4	5460.9860	-0.0015
7	1	6	←	6	1	5	5526.1597	-0.0062
8	1	8	←	7	1	7	5962.2681	0.0007
8	0	8	←	7	0	7	6050.8911	0.0004
8	2	7	←	7	2	6	6146.1650	-0.0132
8	2	6	←	7	2	5	6259.5527	-0.0021
8	1	7	←	7	1	6	6306.3638	0.0118
9	0	9	←	8	0	8	6781.0777	-0.0048
							RMS	5.5 kHz

Table S20 C6

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	1	3	←	2	1	2	2253.4757	0.0020
3	0	3	←	2	0	2	2314.1919	-0.0033
4	1	4	←	3	1	3	3002.9691	-0.0030
4	0	4	←	3	0	3	3078.7642	0.0009
4	1	3	←	3	1	2	3178.0491	0.0000
5	0	5	←	4	0	4	3837.7106	-0.0006
5	2	4	←	4	2	3	3863.5344	-0.0063
5	1	4	←	4	1	3	3969.5638	-0.0001
6	1	6	←	5	1	5	4497.7519	-0.0006
6	0	6	←	5	0	5	4590.1196	-0.0048
6	1	5	←	5	1	4	4758.8990	-0.0049
7	1	7	←	6	1	6	5242.6529	-0.0015
7	2	6	←	6	2	5	5402.0476	-0.0025
8	1	8	←	7	1	7	5985.7596	0.0009
8	0	8	←	7	0	7	6074.5645	0.0087
8	2	6	←	7	2	5	6281.0570	0.0068
8	1	7	←	7	1	6	6328.5217	-0.0021
9	1	9	←	8	1	8	6727.0485	-0.0006
9	1	8	←	8	1	7	7107.3129	0.0032
							RMS	3.7 kHz

Table S21 C7

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
4	1	4	←	3	1	3	3004.3852	-0.0055
4	0	4	←	3	0	3	3080.4377	-0.0047
4	1	3	←	3	1	2	3180.2101	-0.0015
5	1	5	←	4	1	4	3752.8887	-0.0004
5	0	5	←	4	0	4	3839.7108	-0.0004
5	2	4	←	4	2	3	3865.7841	0.0011
5	2	3	←	4	2	2	3895.1834	-0.0012
5	1	4	←	4	1	3	3972.2381	0.0007
6	1	6	←	5	1	5	4499.8191	-0.0009
6	0	6	←	5	0	5	4592.3890	-0.0023
6	3	4	←	5	3	3	4650.2632	-0.0042
6	1	5	←	5	1	4	4762.0579	-0.0077
7	1	7	←	6	1	6	5245.0203	-0.0056
7	2	5	←	6	2	4	5483.6970	0.0094
7	1	6	←	6	1	5	5549.0832	0.0049
8	1	8	←	7	1	7	5988.4196	-0.0010
8	0	8	←	7	0	7	6077.2322	0.0042
8	1	7	←	7	1	6	6332.5633	-0.0016
9	1	9	←	8	1	8	6729.9941	0.0045
9	0	9	←	8	0	8	6810.7330	-0.0007
10	0	10	←	9	0	9	7540.0978	0.0033
							RMS	4.1 kHz

Table S22 C8

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	1	3	←	2	1	2	2247.8944	0.0045
3	0	3	←	2	0	2	2308.1602	0.0027
3	1	2	←	2	1	1	2378.2878	-0.0013
4	1	4	←	3	1	3	2995.5479	0.0028
4	0	4	←	3	0	3	3070.7861	-0.0014
4	1	3	←	3	1	2	3169.2680	0.0011
5	2	4	←	4	2	3	3853.4122	0.0069
6	1	6	←	5	1	5	4486.6860	0.0024
6	0	6	←	5	0	5	4578.4599	-0.0001
6	2	4	←	5	2	3	4670.9190	-0.0007
6	1	5	←	5	1	4	4745.8257	0.0025
7	1	7	←	6	1	6	5229.7849	-0.0049
7	0	7	←	6	0	6	5322.2194	-0.0027
7	2	6	←	6	2	5	5387.9403	0.0038
7	6	1	←	6	6	0	5403.2822	-0.0130
7	2	5	←	6	2	4	5464.9694	-0.0058
7	1	6	←	6	1	5	5530.2755	0.0027
8	1	8	←	7	1	7	5971.1192	0.0032
8	0	8	←	7	0	7	6059.4685	0.0149
8	2	7	←	7	2	6	6152.7956	0.0072
8	1	7	←	7	1	6	6311.2747	-0.0011
9	1	9	←	8	1	8	6710.6463	0.0011

9	0	9	←	8	0	8	6791.1117	-0.0169
							RMS	6.4 kHz

Table S23 C9

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	1	3	←	2	1	2	2237.3885	0.0020
3	1	2	←	2	1	1	2366.8582	-0.0147
4	1	4	←	3	1	3	2981.5751	0.0019
4	0	4	←	3	0	3	3056.4414	-0.0035
4	1	3	←	3	1	2	3154.0776	-0.0051
5	1	5	←	4	1	4	3724.4668	-0.0011
5	0	5	←	4	0	4	3810.1377	0.0000
5	2	4	←	4	2	3	3835.1814	0.0071
5	1	4	←	4	1	3	3939.6999	-0.0033
6	1	6	←	5	1	5	4465.8434	-0.0089
6	0	6	←	5	0	5	4557.4705	-0.0034
6	2	5	←	5	2	4	4599.5610	-0.0156
6	1	5	←	5	1	4	4723.2146	-0.0075
7	1	7	←	6	1	6	5205.5710	-0.0002
7	0	7	←	6	0	6	5298.0616	-0.0044
7	2	6	←	6	2	5	5362.5582	0.0061
8	0	8	←	7	0	7	6032.1891	0.0025
8	2	7	←	7	2	6	6123.8784	0.0025
8	1	7	←	7	1	6	6281.5111	-0.0041
9	1	9	←	8	1	8	6679.7355	0.0054
9	1	8	←	8	1	7	7054.8565	0.0043
10	1	9	←	9	1	8	7823.2388	0.0098
10	2	8	←	9	2	7	7831.3844	0.0062
							RMS	6.6 kHz

Table S24 C10

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	1	3	←	2	1	2	2236.1131	-0.0082
3	0	3	←	2	0	2	2295.7203	0.0037
3	1	2	←	2	1	1	2364.8633	-0.0014
4	1	4	←	3	1	3	2979.9030	-0.0012
4	0	4	←	3	0	3	3054.4099	-0.0002
4	1	3	←	3	1	2	3151.4318	0.0064
5	1	5	←	4	1	4	3722.4084	-0.0005
5	0	5	←	4	0	4	3807.7101	0.0014
5	2	4	←	4	2	3	3832.4652	-0.0005
5	1	4	←	4	1	3	3936.4142	-0.0014
6	1	6	←	5	1	5	4463.4143	-0.0048
6	0	6	←	5	0	5	4554.7207	0.0061
6	2	5	←	5	2	4	4596.3503	-0.0059
6	1	5	←	5	1	4	4719.3270	-0.0029
7	1	7	←	6	1	6	5202.7804	0.0004
7	0	7	←	6	0	6	5295.0418	0.0069

7	2	6	←	6	2	5	5358.8328	-0.0029
7	2	5	←	6	2	4	5433.6057	-0.0013
7	1	6	←	6	1	5	5499.5851	-0.0025
8	1	8	←	7	1	7	5940.4054	0.0015
8	1	7	←	7	1	6	6276.5134	-0.0099
9	2	7	←	8	2	6	7025.0912	0.0073
9	1	8	←	8	1	7	7049.3900	0.0050
							RMS	4.6 kHz

Table S25 C11

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	1	3	←	2	1	2	2246.3232	0.0049
3	0	3	←	2	0	2	2305.6377	0.0010
3	2	2	←	2	2	1	2311.3041	0.0106
3	2	1	←	2	2	0	2316.9430	-0.0136
4	1	4	←	3	1	3	2993.5023	0.0012
4	0	4	←	3	0	3	3067.6386	-0.0014
4	2	2	←	3	2	1	3094.7008	-0.0079
4	1	3	←	3	1	2	3164.2809	0.0023
5	2	4	←	4	2	3	3849.0057	0.0088
6	1	6	←	5	1	5	4483.8324	0.0131
6	0	6	←	5	0	5	4574.5751	-0.0054
6	2	4	←	5	2	3	4664.1924	0.0113
6	1	5	←	5	1	4	4738.6133	0.0037
7	1	7	←	6	1	6	5226.5875	0.0024
7	0	7	←	6	0	6	5318.2407	0.0026
7	2	5	←	6	2	4	5456.6740	-0.0173
7	1	6	←	6	1	5	5522.0863	0.0069
8	1	8	←	7	1	7	5967.6192	0.0020
8	0	8	←	7	0	7	6055.4872	-0.0035
8	2	6	←	7	2	5	6253.9027	-0.0040
8	1	7	←	7	1	6	6302.2297	0.0046
9	0	9	←	8	0	8	6787.2377	-0.0113
9	3	7	←	8	3	6	6951.1166	-0.0022
							RMS	7.7 kHz

Table S26 C12

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
3	1	3	←	2	1	2	2254.1465	-0.0020
4	1	4	←	3	1	3	3003.8893	-0.0011
4	0	4	←	3	0	3	3079.1775	-0.0028
4	1	3	←	3	1	2	3177.6989	-0.0007
5	0	5	←	4	0	4	3838.3507	-0.0008
5	2	3	←	4	2	2	3892.6974	0.0047
5	1	4	←	4	1	3	3969.1642	0.0022

6	1	6	←	5	1	5	4499.2056	0.0023
6	0	6	←	5	0	5	4591.0462	-0.0093
7	2	6	←	6	2	5	5402.6232	0.0039
8	1	8	←	7	1	7	5987.8084	-0.0021
8	0	8	←	7	0	7	6076.2599	0.0107
8	2	7	←	7	2	6	6169.5814	0.0111
8	2	6	←	7	2	5	6280.5640	-0.0033
9	1	9	←	8	1	8	6729.4217	-0.0053
9	0	9	←	8	0	8	6810.0177	-0.0006
10	0	10	←	9	0	9	7539.6435	-0.0007
10	1	9	←	9	1	8	7880.8467	-0.0061
							RMS	5.1 kHz

Table S27 ^{18}O (0^- state)

J'	K_a'	K_c'		J''	K_a''	K_c''	V_{obs}	$V_{\text{obs}}-V_{\text{calc}}$										
9	1	8	←	9	1	9	2068.8609	-0.0107	3	2	2	←	2	1	2	5153.7189	-0.0054	
3	1	3	←	2	1	2	2232.1367	0.0010	7	1	7	←	6	1	6	5190.0890	0.0056	
6	1	5	←	5	2	3	2234.1797	-0.0149	7	0	7	←	6	0	6	5282.7843	0.0025	
3	1	2	←	2	1	1	2372.5410	-0.0005	7	2	6	←	6	2	5	5360.9231	0.0047	
2	1	1	←	1	0	1	2532.5612	0.0179	7	3	5	←	6	3	4	5386.8665	0.0025	
9	2	7	←	8	3	5	2649.7228	0.0032	7	3	4	←	6	3	3	5392.0923	0.0008	
2	2	1	←	2	1	1	2709.8301	-0.0032	7	2	5	←	6	2	4	5452.7192	-0.0070	
4	1	4	←	3	1	3	2974.1989	-0.0065	7	1	6	←	6	1	5	5512.5635	-0.0033	
4	0	4	←	3	0	3	3053.6818	-0.0023	8	1	8	←	7	1	7	5924.7431	0.0110	
4	3	2	←	3	3	1	3074.6669	-0.0012	4	2	3	←	3	1	3	5991.4647	0.0008	
4	3	1	←	3	3	0	3074.9123	-0.0075	8	0	8	←	7	0	7	6011.0457	0.0023	
4	2	2	←	3	2	1	3087.4542	0.0011	6	1	5	←	5	0	5	6057.8679	-0.0037	
11	0	11	←	10	2	8	3097.7195	-0.0137	8	2	7	←	7	2	6	6120.9122	0.0059	
4	1	3	←	3	1	2	3161.2109	-0.0067	8	7	2	←	7	7	1	6147.8165	0.0024	
6	0	6	←	5	1	4	3221.5286	0.0036	8	4	4	←	7	4	3	6155.0294	-0.0088	
3	1	2	←	2	0	2	3371.2326	0.0083	8	3	6	←	7	3	5	6158.7476	-0.0016	
5	1	5	←	4	1	4	3714.7044	0.0005	8	3	5	←	7	3	4	6169.1172	0.0083	
5	0	5	←	4	0	4	3804.3598	0.0009	8	2	6	←	7	2	5	6252.0748	-0.0071	
5	4	2	←	4	4	1	3842.9778	0.0038	8	1	7	←	7	1	6	6288.8973	0.0001	
5	3	3	←	4	3	2	3844.7124	-0.0040	5	2	3	←	4	1	3	6445.6506	-0.0012	
5	3	2	←	4	3	1	3845.5948	-0.0012	9	1	9	←	8	1	8	6657.3487	0.0029	
5	2	3	←	4	2	2	3869.8388	0.0052	9	0	9	←	8	0	8	6733.7075	0.0085	
5	1	4	←	4	1	3	3947.9027	-0.0015	9	2	8	←	8	2	7	6878.6116	0.0017	
4	1	3	←	3	0	3	4236.0744	0.0062	3	3	0	←	2	2	0	6936.2052	-0.0159	
2	2	0	←	1	1	0	4294.0595	0.0046	9	3	6	←	8	3	5	6949.6115	-0.0096	
2	2	1	←	1	1	1	4339.0983	0.0004	9	2	7	←	8	2	6	7054.5640	0.0133	
6	1	6	←	5	1	5	4453.3823	-0.0012	9	1	8	←	8	1	7	7059.9405	-0.0032	
6	0	6	←	5	0	5	4547.4548	0.0005	5	3	3	←	5	1	4	7085.5069	0.0002	
6	3	4	←	5	3	3	4615.4647	-0.0042	10	1	10	←	9	1	9	7388.0273	0.0095	
6	3	3	←	5	3	2	4617.8093	0.0031	10	0	10	←	9	0	9	7452.5805	0.0026	
6	2	4	←	5	2	3	4658.3000	0.0006	10	4	6	←	9	4	5	7701.4604	-0.0083	
6	1	5	←	5	1	4	4731.9385	-0.0037	7	2	5	←	6	1	5	7876.8273	-0.0037	
3	2	1	←	2	1	1	5022.1268	0.0024								RMS	6.3660 kHz	

Table S28 ^{18}O (0^+ state)

J'	K_a'	K_c'	J''	K_a''	K_c''	V_{obs}	$V_{\text{obs}}-V_{\text{calc}}$										
3	1	3	←	2	1	2	2231.8142	-0.0005	7	2	6	←	6	2	5	5360.8397	-0.0003
3	0	3	←	2	0	2	2296.3227	-0.0038	7	5	2	←	6	5	1	5381.0424	-0.0113
3	2	2	←	2	2	1	2303.4686	-0.0155	7	4	4	←	6	4	3	5383.6199	0.0028
3	1	2	←	2	1	1	2372.9172	-0.0017	7	4	3	←	6	4	2	5383.7212	0.0026
2	1	1	←	1	0	1	2530.3536	0.0001	7	3	5	←	6	3	4	5387.0962	0.0033
5	0	5	←	4	1	3	2622.7609	0.0153	7	3	4	←	6	3	3	5392.4316	0.0042
3	2	2	←	3	1	2	2632.3374	-0.0073	7	2	5	←	6	2	4	5453.7198	0.0026
4	1	4	←	3	1	3	2973.7469	-0.0064	7	1	6	←	6	1	5	5513.1292	0.0000
4	0	4	←	3	0	3	3053.5148	-0.0042	8	1	8	←	7	1	7	5923.5554	-0.0055
4	2	3	←	3	2	2	3069.9052	-0.0073	4	2	3	←	3	1	3	5984.5094	0.0007
4	3	2	←	3	3	1	3074.7639	0.0010	8	0	8	←	7	0	7	6009.7015	-0.0032
4	3	1	←	3	3	0	3075.0206	0.0008	6	1	5	←	5	0	5	6058.2306	0.0062
4	2	2	←	3	2	1	3087.7121	-0.0005	8	2	7	←	7	2	6	6120.7439	0.0005
4	1	3	←	3	1	2	3161.6887	-0.0037	8	6	2	←	7	6	1	6149.1916	-0.0051
3	1	2	←	2	0	2	3369.4026	-0.0033	8	4	5	←	7	4	4	6155.0295	0.0089
6	2	4	←	6	1	6	3400.1002	0.0124	8	4	4	←	7	4	3	6155.3134	0.0143
10	2	8	←	9	3	6	3575.8924	-0.0036	8	3	5	←	7	3	4	6169.5962	-0.0004
5	1	5	←	4	1	4	3714.1006	-0.0012	8	2	6	←	7	2	5	6253.3647	-0.0011
4	2	3	←	4	0	4	3721.8345	0.0168	8	1	7	←	7	1	6	6289.3789	-0.0009
5	0	5	←	4	0	4	3803.9956	-0.0026	5	2	3	←	4	1	3	6437.6183	0.0081
5	2	4	←	4	2	3	3835.1449	0.0017	9	4	5	←	9	3	7	6450.8794	-0.0154
5	4	1	←	4	4	0	3843.0968	0.0058	9	1	9	←	8	1	8	6655.9429	-0.0065
5	3	3	←	4	3	2	3844.8551	0.0043	9	0	9	←	8	0	8	6731.9917	-0.0056
5	3	2	←	4	3	1	3845.7476	-0.0007	4	2	2	←	3	0	3	6802.0951	-0.0025
5	2	3	←	4	2	2	3870.2840	-0.0001	5	2	4	←	4	1	4	6845.9011	0.0026
5	1	4	←	4	1	3	3948.4453	-0.0040	9	2	8	←	8	2	7	6878.3465	0.0117
4	1	3	←	3	0	3	4234.7725	0.0008	3	3	0	←	2	2	0	6923.4112	-0.0006
2	2	1	←	1	1	1	4331.5378	-0.0007	3	3	1	←	2	2	1	6925.1530	-0.0116
6	1	6	←	5	1	5	4452.6056	-0.0061	9	3	6	←	8	3	5	6950.3158	-0.0014
6	0	6	←	5	0	5	4546.8135	-0.0061	7	1	6	←	6	0	6	7024.5394	0.0054
6	2	5	←	5	2	4	4598.8776	-0.0039	9	2	7	←	8	2	6	7056.0909	0.0010
6	3	4	←	5	3	3	4615.6495	0.0006	9	1	8	←	8	1	7	7060.2666	-0.0014
6	3	3	←	5	3	2	4618.0377	0.0037	5	3	3	←	5	1	4	7063.4974	0.0003
5	3	2	←	5	2	4	4637.4304	-0.0054	6	2	4	←	5	1	4	7148.1581	-0.0033
6	2	4	←	5	2	3	4659.0000	-0.0006	10	1	10	←	9	1	9	7386.3777	-0.0057
7	3	4	←	7	2	6	4688.1945	0.0187	10	0	10	←	9	0	9	7450.5535	0.0090
9	0	9	←	8	1	7	4709.6114	0.0122	4	3	1	←	3	2	1	7687.7753	-0.0069
6	1	5	←	5	1	4	4732.5198	-0.0007	4	3	2	←	3	2	2	7696.4517	0.0083
9	3	6	←	9	2	8	4809.0123	0.0005	6	2	5	←	5	1	5	7730.6854	0.0072
3	2	1	←	2	1	1	5014.2216	-0.0031	10	3	7	←	9	3	6	7735.4265	0.0001
5	1	4	←	4	0	4	5129.7060	0.0039	10	1	9	←	9	1	8	7824.7210	-0.0034
3	2	2	←	2	1	2	5146.4145	0.0036	10	2	8	←	9	2	7	7859.6212	-0.0103
7	1	7	←	6	1	6	5189.1176	-0.0037	7	2	5	←	6	1	5	7869.3623	0.0042
2	2	0	←	1	0	1	5233.9283	-0.0004	6	3	3	←	6	1	6	7934.6494	-0.0054
7	0	7	←	6	0	6	5281.8058	-0.0049								RMS	6.4360 kHz

Table S29 Experimental positions of all the atoms obtained from the Kraitchman fit for the DPE-H₂O OH- π isomer. The signs of the coordinates are assigned with the help of the calculated structure at the B3LYP-D3(BJ)/def2-TZVP level.

	a	b	c
O(1)	1.54869(97)	2.66406(57)	0.5866(25)
C(1)	1.4729(23)	0.8737(39)	0.329(10)
C(2)	2.6942(13)	1.4427(25)	-0.171(28)
C(3)	3.7852(66)	0.6131(41)	-0.4139(61)
C(4)	3.6537(13)	-0.7722(62)	-0.348(13)
C(5)	2.4400(13)	-1.3414(25)	0.000(30)
C(6)	1.3382(20)	-0.4937(55)	0.4124(66)
C(7)	-0.9715(27)	-0.7623(34)	0.211(12)
C(8)	-2.1140(18)	-0.8877(43)	1.0509(37)
C(9)	-3.3714(10)	-0.5832(62)	0.5268(68)
C(10)	-3.49590(85)	-0.250(11)	-0.8092(37)
C(11)	-2.3619(18)	0.000(42)	-1.5813(28)
C(12)	-1.0995(27)	-0.3176(95)	-1.0676(28)

Table S30 Line list for DPE-water OH-O isomer.

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
2	1	2	←	1	0	1	2092.9298	0.0057
9	2	7	←	9	1	8	2357.8528	0.0095
5	1	4	←	4	2	3	2485.0170	-0.0061
4	0	4	←	3	1	3	2584.6904	-0.0020
5	2	4	←	5	1	5	2728.5845	-0.0112
3	1	3	←	2	0	2	2738.4819	0.0051
8	1	7	←	8	0	8	3082.1653	0.0037
4	1	4	←	3	0	3	3354.2773	0.0060
5	0	5	←	4	1	4	3400.5898	0.0158
6	1	5	←	5	2	4	3465.8026	-0.0116
5	1	5	←	4	0	4	3957.3056	-0.0077
7	1	6	←	6	2	5	4446.8663	-0.0124
6	1	6	←	5	0	5	4564.6093	0.0010
4	2	3	←	3	1	2	4857.8368	-0.0020
7	0	7	←	6	1	6	4947.9545	0.0167
7	1	7	←	6	0	6	5187.2155	-0.0099
5	2	4	←	4	1	3	5454.1581	0.0011
4	2	2	←	3	1	3	5532.6811	0.0102
8	1	8	←	7	0	7	5828.2133	0.0093
6	2	5	←	5	1	4	6010.7567	-0.0020
9	1	8	←	8	2	7	6338.6940	0.0074
9	0	9	←	8	1	8	6399.6741	-0.0171
9	1	9	←	8	0	8	6485.0772	-0.0051
7	2	6	←	6	1	5	6536.2215	0.0106
8	2	7	←	7	1	6	7043.6782	0.0040
10	1	10	←	9	0	9	7153.5393	-0.0030
10	1	9	←	9	2	8	7220.6337	0.0097

9	2	8	←	8	1	7	7550.0858	-0.0014
4	4	0	←	3	3	1	7825.1382	-0.0099
6	2	4	←	5	1	5	7895.9951	-0.0063
							RMS	8.7 kHz

Table S31 Line list for ^{18}O

J'	K _a '	K _c '		J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}
2	1	2	←	1	0	1	2020.2363	0.0031
3	2	2	←	3	1	3	2160.1259	-0.0094
8	3	5	←	8	2	6	2415.1943	-0.0021
3	1	3	←	2	0	2	2651.8587	0.0092
4	1	4	←	3	0	3	3254.3129	0.0023
5	0	5	←	4	1	4	3399.3008	0.0039
5	1	5	←	4	0	4	3847.5673	0.0011
3	2	2	←	2	1	1	4034.6552	-0.0063
8	2	6	←	7	3	5	4134.2752	-0.0018
6	0	6	←	5	1	5	4163.3872	-0.0149
4	4	0	←	4	3	1	4325.1451	-0.0076
10	1	9	←	10	0	10	4359.6951	-0.0032
3	2	1	←	2	1	2	4379.3940	-0.0030
6	1	6	←	5	0	5	4449.6251	-0.0044
4	2	3	←	3	1	2	4660.4063	0.0031
7	1	7	←	6	0	6	5069.8097	-0.0141
5	2	4	←	4	1	3	5239.3098	0.0065
3	3	1	←	2	2	0	5417.4460	-0.0143
12	1	11	←	12	0	12	5470.1950	0.0045
8	1	8	←	7	0	7	5708.4652	-0.0094
6	2	5	←	5	1	4	5777.7822	0.0104
13	2	12	←	13	1	13	6050.3609	0.0058
7	2	6	←	6	1	5	6287.3826	0.0142
9	1	9	←	8	0	8	6361.3528	-0.0110
8	2	7	←	7	1	6	6785.2210	0.0078
10	1	9	←	9	2	8	7234.1699	-0.0011
9	2	8	←	8	1	7	7291.5017	0.0063
11	1	11	←	10	0	10	7691.7594	0.0034
10	2	9	←	9	1	8	7823.5602	0.0052
							RMS	6.9 kHz

Table S32 Line list for the DPE-AdOH OH-O isomer

J'	K _a '	K _c '	J''	K _a ''	K _c ''	V _{obs}	V _{obs} -V _{calc}											
4	3	1	←	3	2	1	2210.4947	-0.0005	11	8	4	←	10	7	4	6355.2632	0.0068	
9	2	7	←	8	3	6	2383.6780	0.0014	11	8	3	←	10	7	3	6355.2632	0.0126	
5	3	3	←	4	2	2	2489.1797	0.0175	11	8	3	←	10	7	4	6355.2632	0.0062	
5	3	3	←	4	2	3	2563.3437	-0.0127	11	8	4	←	10	7	3	6355.2632	0.0132	
5	4	2	←	4	3	2	2925.2917	0.0012	11	4	8	←	10	1	9	6388.0476	-0.0012	
5	4	1	←	4	3	2	2925.6275	0.0109	10	9	2	←	9	8	2	6429.7050	0.0063	
7	2	6	←	6	1	6	3143.4405	0.0102	10	9	1	←	9	8	1	6429.7050	0.0063	
6	4	3	←	5	3	2	3228.0738	-0.0120	10	9	2	←	9	8	1	6429.7050	0.0063	
6	4	2	←	5	3	2	3229.6819	-0.0123	10	9	1	←	9	8	2	6429.7050	0.0063	
6	4	3	←	5	3	3	3241.2259	-0.0022	13	7	6	←	12	6	6	6584.7646	-0.0099	
8	2	6	←	7	1	6	3251.7813	-0.0034	13	7	7	←	12	6	7	6587.0920	-0.0147	
7	4	4	←	6	3	4	3560.4292	-0.0122	11	9	3	←	10	8	3	6743.2709	0.0052	
7	4	3	←	6	3	4	3566.2087	-0.0005	11	9	2	←	10	8	2	6743.2709	0.0053	
6	5	1	←	5	4	2	3625.3770	0.0077	11	9	2	←	10	8	3	6743.2709	0.0052	
8	3	6	←	7	2	6	3633.0518	-0.0036	11	9	3	←	10	8	2	6743.2709	0.0053	
13	0	13	←	12	1	12	3658.6083	0.0104	10	10	1	←	9	9	1	6817.0162	-0.0138	
8	4	4	←	7	3	5	3902.2676	-0.0118	10	10	0	←	9	9	0	6817.0162	-0.0138	
7	5	2	←	6	4	2	3937.2362	0.0083	10	10	1	←	9	9	0	6817.0162	-0.0138	
7	5	3	←	6	4	3	3938.6853	0.0098	10	10	0	←	9	9	1	6817.0162	-0.0138	
7	5	2	←	6	4	3	3938.8512	0.0148	14	7	7	←	13	6	7	6889.9601	-0.0058	
9	3	7	←	8	2	7	4021.2235	0.0018	13	8	5	←	12	7	5	6979.5536	0.0136	
8	5	4	←	7	4	3	4246.0554	-0.0162	12	9	3	←	11	8	4	7056.5631	0.0044	
8	5	3	←	7	4	3	4246.7487	-0.0099	12	9	4	←	11	8	3	7056.5631	0.0049	
5	4	2	←	4	1	3	4322.9056	-0.0110	11	10	2	←	10	9	2	7130.7515	-0.0098	
7	6	2	←	6	5	2	4326.4273	0.0180	11	10	1	←	10	9	1	7130.7515	-0.0098	
7	6	1	←	6	5	2	4326.4273	0.0160	11	10	2	←	10	9	1	7130.7515	-0.0098	
11	3	8	←	10	2	8	4429.6135	-0.0043	11	10	1	←	10	9	2	7130.7515	-0.0098	
9	5	4	←	8	4	5	4567.8324	-0.0172	16	1	15	←	15	0	15	7165.7933	-0.0113	
10	5	5	←	9	4	6	4887.8930	-0.0174	18	5	13	←	17	4	13	7184.0640	0.0069	
9	6	3	←	8	5	3	4951.6643	0.0141	15	7	9	←	14	6	9	7204.0264	-0.0085	
9	6	4	←	8	5	4	4952.2788	0.0116	15	7	8	←	14	6	9	7206.7238	-0.0143	
10	6	5	←	9	5	4	5261.7266	-0.0078	14	8	6	←	13	7	6	7290.1092	-0.0090	
10	6	4	←	9	5	4	5262.0067	-0.0035	14	8	7	←	13	7	7	7290.4387	0.0129	
10	6	5	←	9	5	5	5264.0827	-0.0055	17	5	13	←	16	4	13	7359.0937	-0.0114	
10	6	4	←	9	5	5	5264.3555	-0.0085	13	9	5	←	12	8	5	7369.4393	0.0022	
12	4	9	←	11	3	9	5302.8377	0.0037	13	9	4	←	12	8	4	7369.4393	0.0046	
9	7	3	←	8	6	3	5340.9347	0.0146	13	9	4	←	12	8	5	7369.4393	0.0020	
9	7	2	←	8	6	3	5340.9347	0.0134	13	9	5	←	12	8	4	7369.4393	0.0049	
18	2	16	←	17	3	15	5387.1197	-0.0164	12	10	3	←	11	9	3	7444.3618	-0.0090	
18	4	15	←	17	3	14	5667.0297	0.0105	12	10	2	←	11	9	2	7444.3618	-0.0090	
11	7	4	←	10	6	4	5965.7013	-0.0031	12	10	3	←	11	9	2	7444.3618	-0.0090	
11	7	5	←	10	6	5	5965.9578	0.0060	12	10	2	←	11	9	3	7444.3618	-0.0090	
15	4	11	←	14	3	11	6020.0991	0.0187	16	7	10	←	15	6	10	7512.1897	0.0083	
10	8	3	←	9	7	3	6042.1388	0.0163	15	8	7	←	14	7	7	7599.0971	0.0095	
10	8	2	←	9	7	2	6042.1388	0.0173	15	8	8	←	14	7	8	7599.9764	0.0017	
10	8	2	←	9	7	3	6042.1388	0.0162	15	8	7	←	14	7	8	7600.1099	0.0066	
10	8	3	←	9	7	2	6042.1388	0.0174	14	9	6	←	13	8	6	7681.7399	0.0022	
9	9	1	←	8	8	1	6115.9817	0.0052	14	9	5	←	13	8	5	7681.7399	0.0122	
9	9	0	←	8	8	0	6115.9817	0.0052	14	9	5	←	13	8	6	7681.7399	0.0012	
9	9	1	←	8	8	0	6115.9817	0.0052	13	10	4	←	12	9	4	7757.7576	-0.0096	
9	9	0	←	8	8	1	6115.9817	0.0052	13	10	3	←	12	9	3	7757.7576	-0.0095	
14	5	10	←	13	4	10	6214.1406	0.0014	13	10	3	←	12	9	4	7757.7576	-0.0096	
14	2	13	←	13	1	13	6258.5843	0.0040	13	10	4	←	12	9	3	7757.7576	-0.0095	
12	7	6	←	11	6	5	6276.1761	-0.0120	17	7	11	←	16	6	11	7821.9475	0.0046	
12	7	5	←	11	6	5	6276.2830	-0.0115	16	8	8	←	15	7	8	7905.7807	0.0015	
12	7	6	←	11	6	6	6277.0971	-0.0093	16	8	8	←	15	7	8	7905.7807	0.0015	
12	7	5	←	11	6	6	6277.2084	-0.0044	16	8	9	←	15	7	9	7908.1170	0.0109	
																RMS		10.14 kHz

References

- [1] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.
- [2] A. Hellweg, S. A. Grün, C. Hättig, *Phys. Chem. Chem. Phys.* **2008**, *10*, 4119.
- [3] F. Weigend, A. Köhn, C. Hättig, *J. Chem. Phys.* **2002**, *116*, 3175.
- [4] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs: Comput. Mol. Sci.* **2014**, *4*, 91.
- [5] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, *WIREs: Comput. Mol. Sci.* **2012**, *2*, 242.
- [6] A. Wuttke, R. A. Mata, *J. Comput. Chem.* **2017**, *38*, 15.
- [7] D. Schmitz, V. A. Shubert, T. Betz, M. Schnell, *J. Mol. Spectrosc.* **2012**, *280*, 77.
- [8] David Plusquellic, *JB95*, NIST.
- [9] Z. Kisiel, L. Pszczółkowski, I. R. Medvedev, M. Winnewisser, F. C. de Lucia, E. Herbst, *J. Mol. Spectrosc.* **2005**, *233*, 231.
- [10] J. Kraitchman, *Am. J. Phys.* **1953**, *21*, 17.
- [11] a) M. Gerhards, C. Unterberg, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1760; b) C. Unterberg, A. Jansen, M. Gerhards, *J. Chem. Phys.* **2000**, *113*, 7945.
- [12] C. Medcraft, S. Zinn, M. Schnell, A. Poblitzki, J. Altnöder, M. Heger, M. A. Suhm, D. Bernhard, A. Stamm, F. Dietrich, M. Gerhards, *Phys. Chem. Chem. Phys.* **2016**, *18*, 25975.
- [13] D. Bernhard, F. Dietrich, A. Poblitzki, M. Farima, C. Perez, G. Jansen, M. Schnell, M. Suhm, and M. Gerhards, *Phys. Chem. Chem. Phys.* **2017**, *19*, 18076-18088.
- [14] a) A. C. S. Paiva, P. G. Kistemaker, T. L. Weeding, *Int. J. Mass Spectrom.* **2002**, *221*, 107; b) D. Bernhard, C. Holzer, F. Dietrich, A. Stamm, W. Klopper, M. Gerhards, *ChemPhysChem* **2017**, *18*, 3634.