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Supplementary Material

Vibrational Properties of the Isotopomers of the Water Dimer Derived from Experiment and Computations

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Abstract

The water dimer and its eleven deuterated isotopomers are investigated utilizing coupled cluster theory and experimental data as input for a perturbational determination of the isotopomer frequencies. Deuterium substitution reduces the H-bond stretching frequency by maximally 12 cm^{-1} from 143 to 131 cm^{-1}, which makes a spectroscopic differentiation of H- and D-bonds difficult. Utilizing however the 132 frequencies obtained in this work, the identification of all isotopomers is straightforward. The CCSD(T)/CBS value of the binding energy D_e is 5.00 kcal/mol. The binding energy D_0 of the water dimer increases upon deuterium substitution from 3.28 to maximally 3.71 kcal/mol reflecting a decrease in the zero point energy contribution. The entropy values of the D-isotopomers increase from 73 to 77 entropy units in line with the general observation that a mass increase leads to larger entropies. All 12 isotopomers possess positive free binding energies at 80 K and a reduced pressure of 110 Pa, which means that they can be spectroscopically observed under these conditions.

Water Dimer, **WD**

μ	Characterization of modes ω_μ in terms of modes ω^a
12	100.0% (H5-O4, H6-O4)
11	93.7% H2-O1, 6.2% H3-O1
10	99.4% (H5-O4, H6-O4)
9	92.5% H3-O1, 5.9% H2-O1
8	91.4% H3-O1-H2
7	94.1% H6-O4-H5
6	42.1% H5-O4-H3-O1, 38.8% O4-H3-O1-H2, 19.2% (H5-O4-H3, H6-O4-H3)
5	43.7% O4-H3-O1, 30.2% (H5-O4-H3, H6-O4-H3), 24.1% H3-O1-H2
4	64.9% O4-H3, 18.0% (H5-O4-H3, H6-O4-H3), 15.2% O4-H3-O1
3	43.6% O4-H3-O1, 33.4% (H5-O4-H3, H6-O4-H3), 17.5% O4-H3
2	41.0% (H5-O4-H3, H6-O4-H3), 30.5% H5-O4-H3-O1, 28.3% O4-H3-O1-H2
1	93.7% O4-H3-O1-H2

Table 1: Characterization of the normal modes ω_μ(Exp.) of the water dimer in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

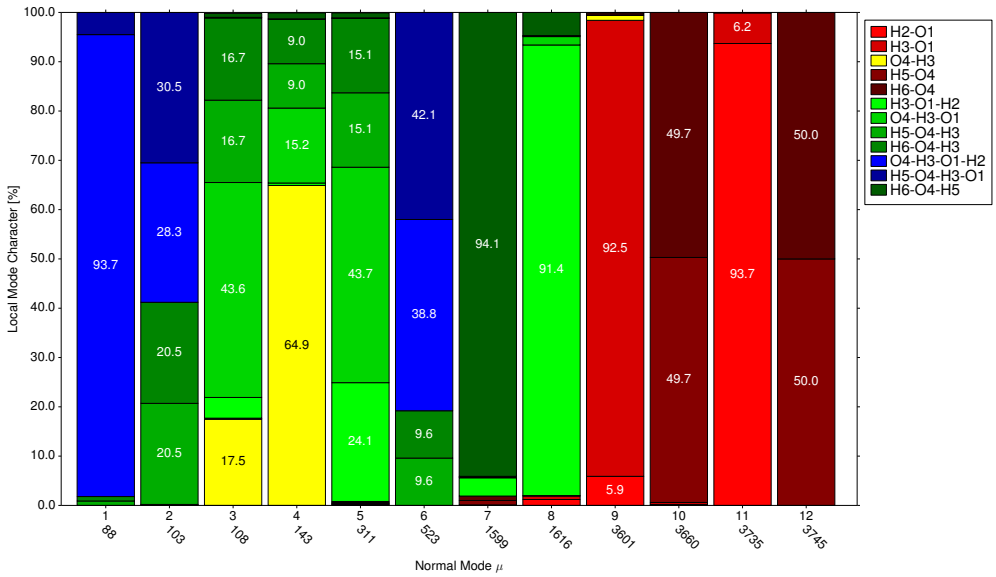
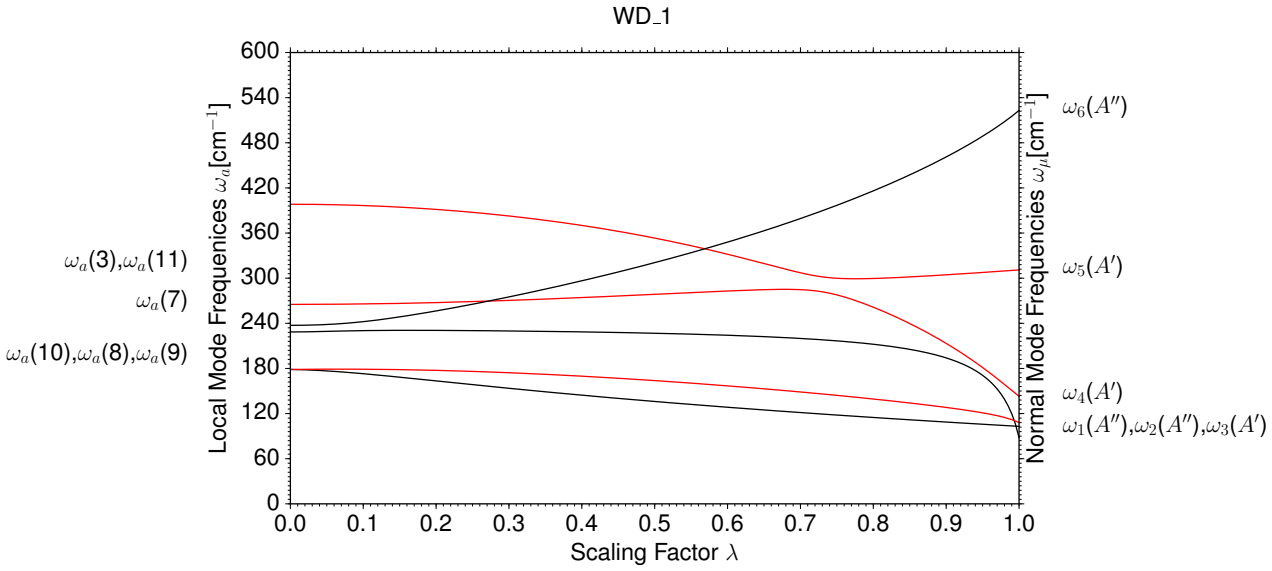
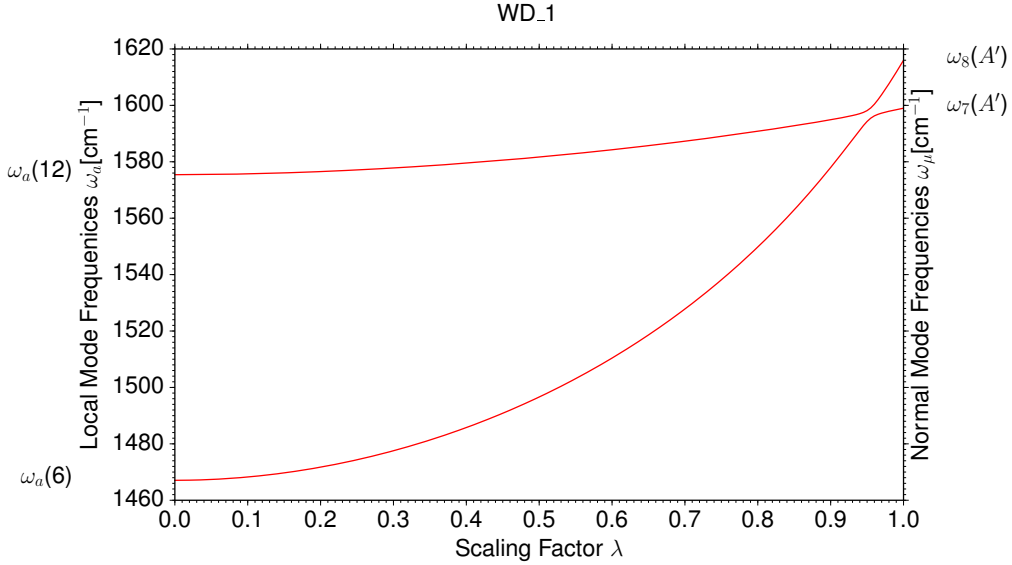


Figure 1: Decomposition of the 12 normal modes of the water dimer **WD** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


WD_1
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3),ω_a(11)
ω_a(7)
ω_a(10),ω_a(8),ω_a(9)
$\omega_6(A'')$
$\omega_5(A')$
$\omega_4(A')$
$\omega_1(A'')$,$\omega_2(A'')$,$\omega_3(A')$


WD_1
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(12)
ω_a(6)
$\omega_8(A')$
$\omega_7(A')$

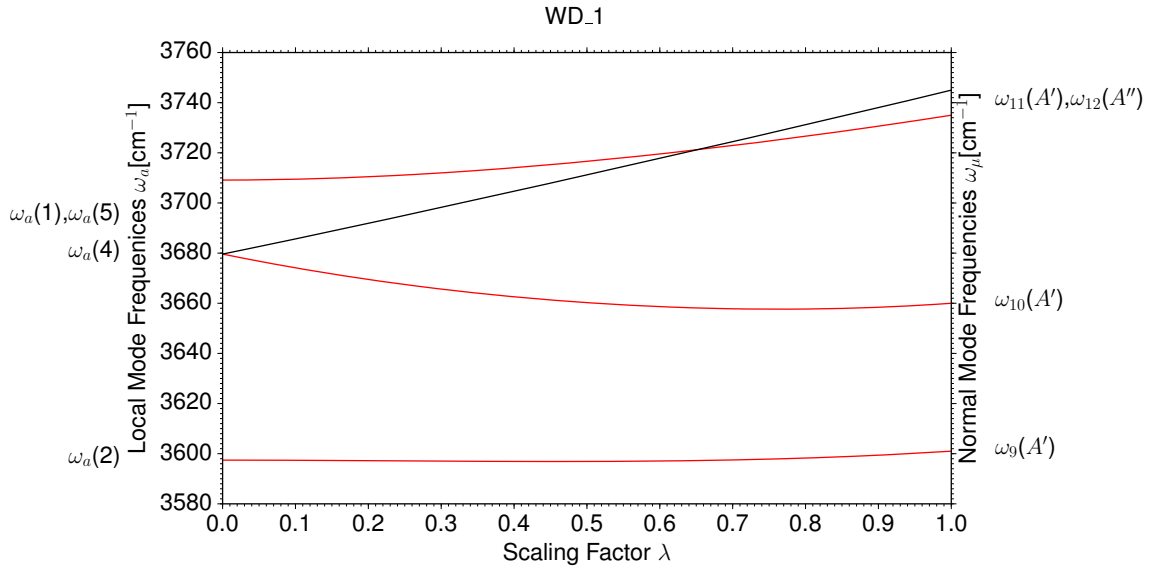


Figure 2: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the water dimer **WD**. **a**) Range from 0 to 600 cm^{-1}. **b**) Range from 1400 to 1600 cm^{-1}. **c**) Range from 3500 to 3800 cm^{-1}.

Deuterated Water Dimer **D2**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	100.0% (H5-O4, H6-O4)
11	99.2% (H5-O4, H6-O4)
10	97.9% H3-O1
9	99.8% H2-O1
8	97.9% H6-O4-H5
7	95.0% H3-O1-H2
6	42.6% H5-O4-H3-O1, 38.1% O4-H3-O1-H2, 19.4% (H5-O4-H3, H6-O4-H3)
5	42.2% (H5-O4-H3, H6-O4-H3), 28.2% O4-H3-O1, 26.5% H3-O1-H2
4	79.2% O4-H3, 10.4% O4-H3-O1
3	49.7% O4-H3-O1, 34.8% (H5-O4-H3, H6-O4-H3), 8.7% O4-H3, 5.3% H3-O1-H2
2	41.8% (H5-O4-H3, H6-O4-H3), 31.1% H5-O4-H3-O1, 27.0% O4-H3-O1-H2
1	98.9% O4-H3-O1-H2

Table 2: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D2** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

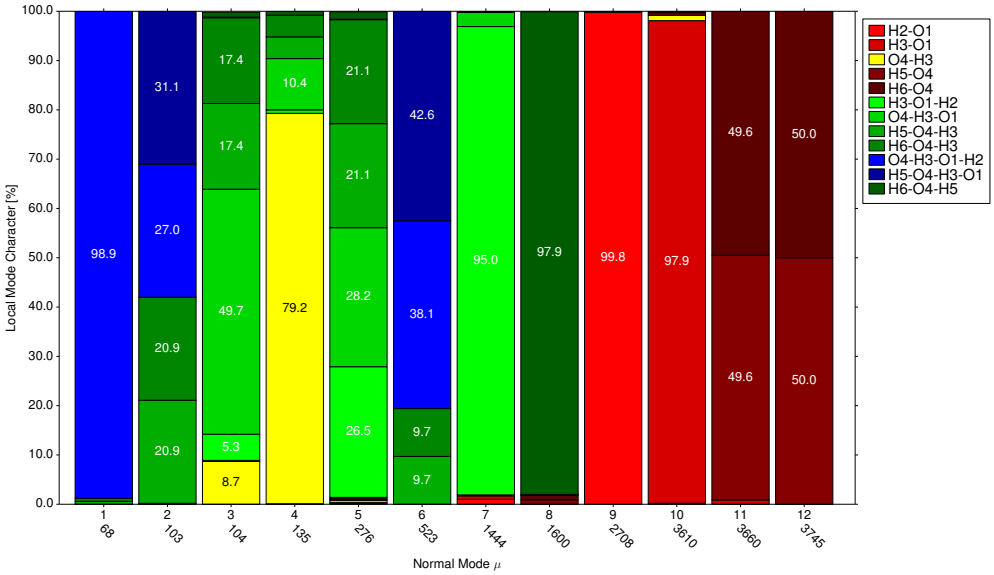
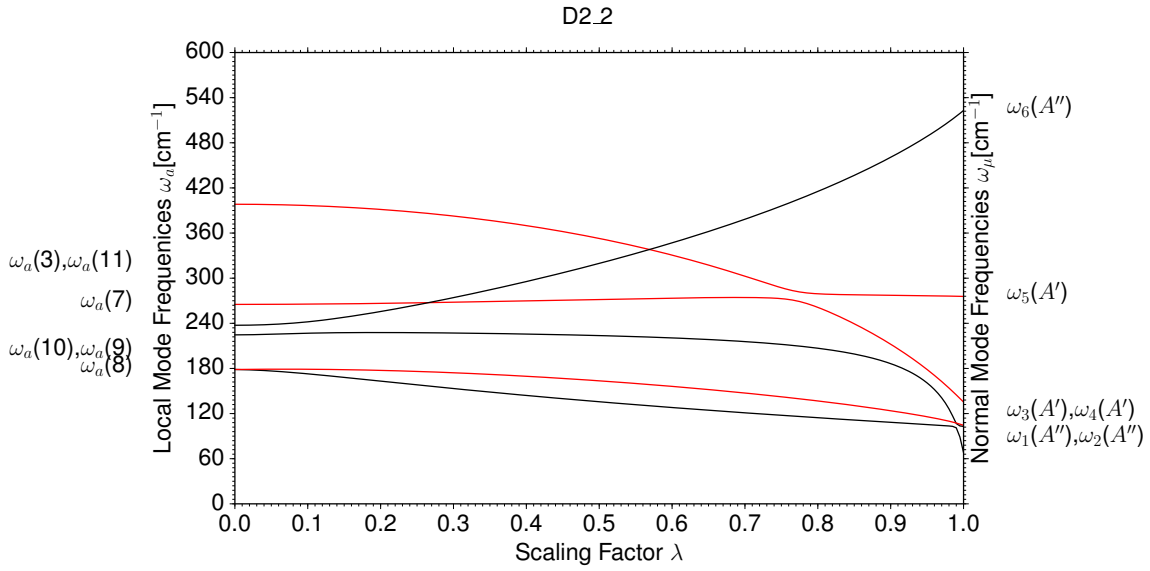
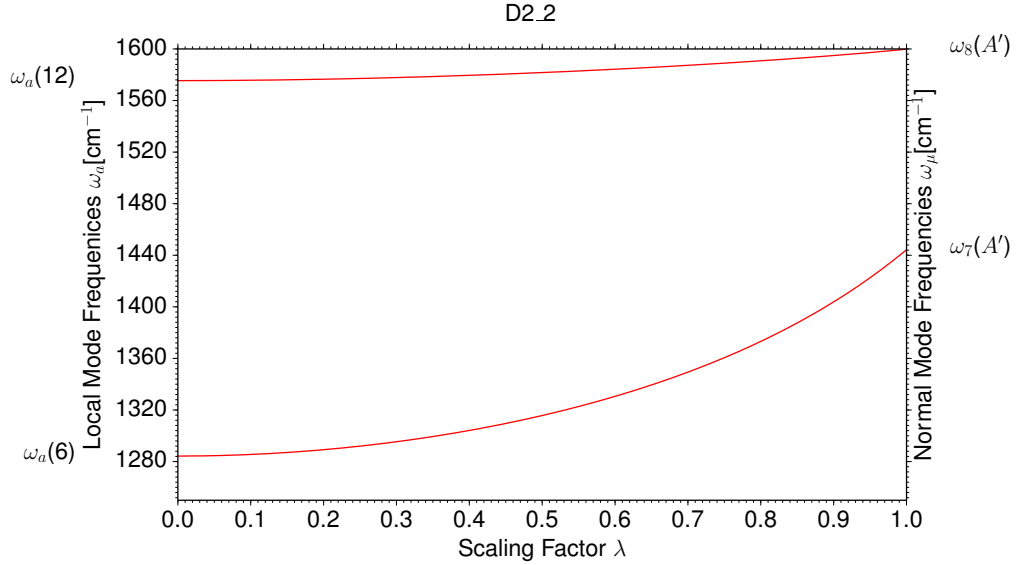


Figure 3: Decomposition of the 12 normal modes of the deuterated water dimer **D2** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


D2_2
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3),ω_a(11)
ω_a(7)
ω_a(10),ω_a(9)
ω_a(8)
$\omega_6(A'')$
$\omega_5(A')$
$\omega_3(A')$,$\omega_4(A')$
$\omega_1(A'')$,$\omega_2(A'')$


D2_2
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(12)
ω_a(6)
$\omega_8(A')$
$\omega_7(A')$

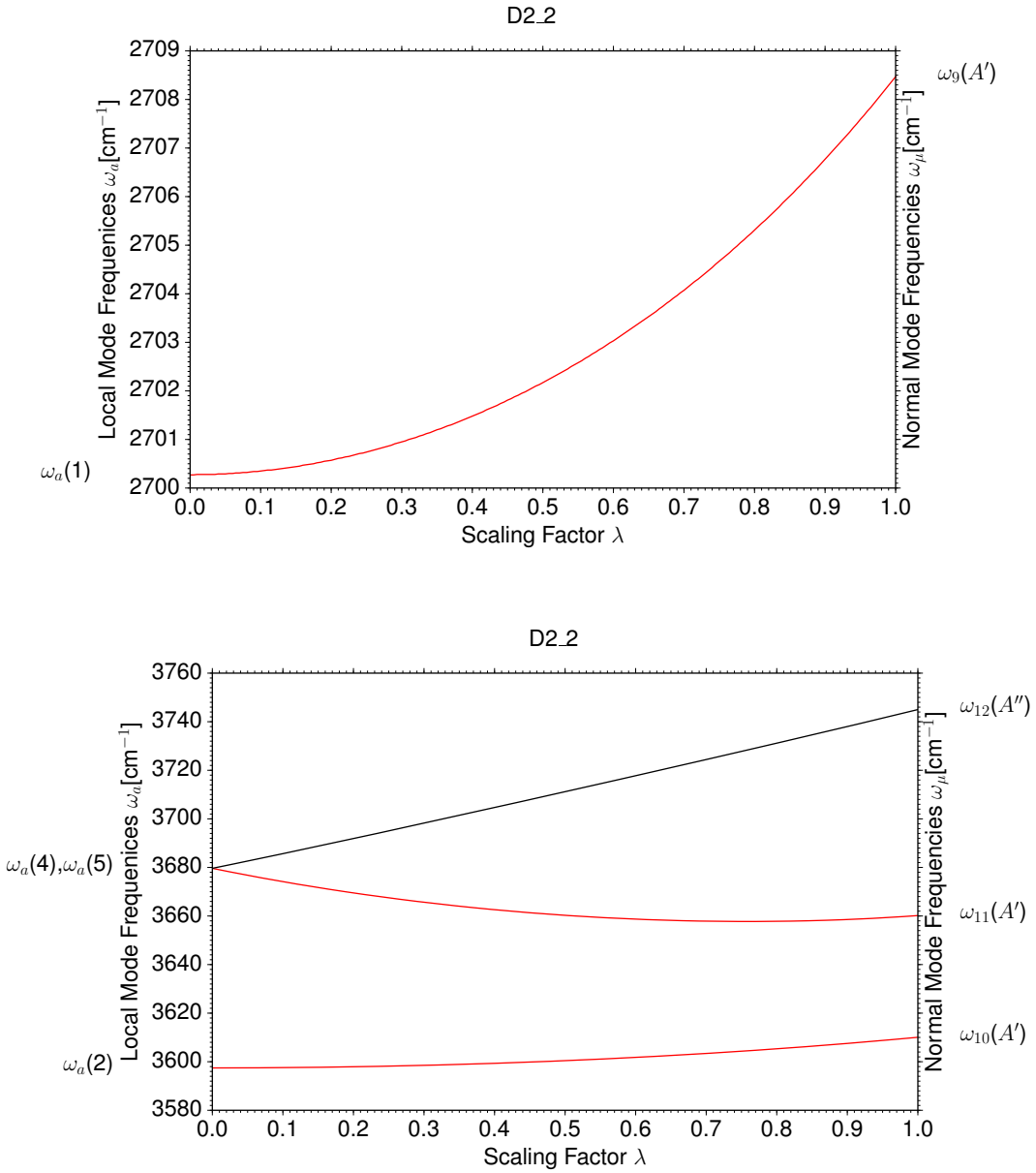


Figure 4: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D2**. **a**) Range from 0 to 600 cm^{-1}. **b**) Range from 1200 to 1600 cm^{-1}. **c**) Range from 2700 to 2710 cm^{-1}. **d**) Range from 3500 to 3800 cm^{-1}.

Deuterated Water Dimer **D3**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	100.0% (H5-O4, H6-O4)
11	99.9% H2-O1
10	100.0% (H5-O4, H6-O4)
9	98.9% H3-O1
8	97.9% H6-O4-H5
7	97.4% H3-O1-H2
6	35.4% H5-O4-H3-O1, 32.4% (H5-O4-H3, H6-O4-H3), 32.2% O4-H3-O1-H2
5	45.8% (H5-O4-H3, H6-O4-H3), 34.7% O4-H3-O1, 17.0% H3-O1-H2
4	74.5% O4-H3, 12.2% O4-H3-O1, 11.8% (H5-O4-H3, H6-O4-H3)
3	49.2% O4-H3-O1, 33.6% (H5-O4-H3, H6-O4-H3), 11.4% O4-H3
2	39.6% (H5-O4-H3, H6-O4-H3), 32.4% H5-O4-H3-O1, 27.8% O4-H3-O1-H2
1	97.1% O4-H3-O1-H2

Table 3: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D3** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

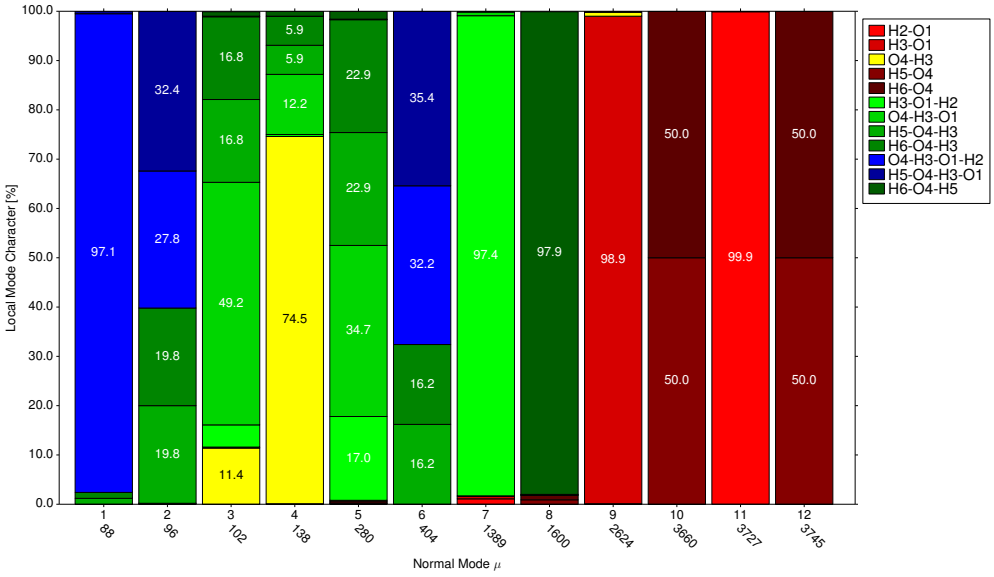
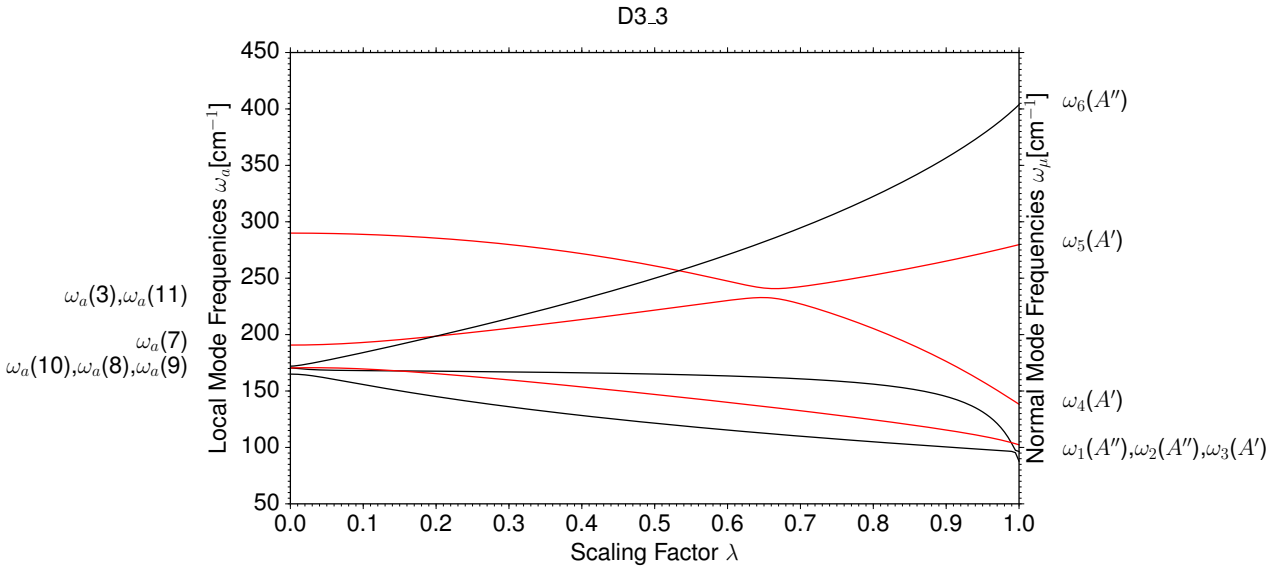
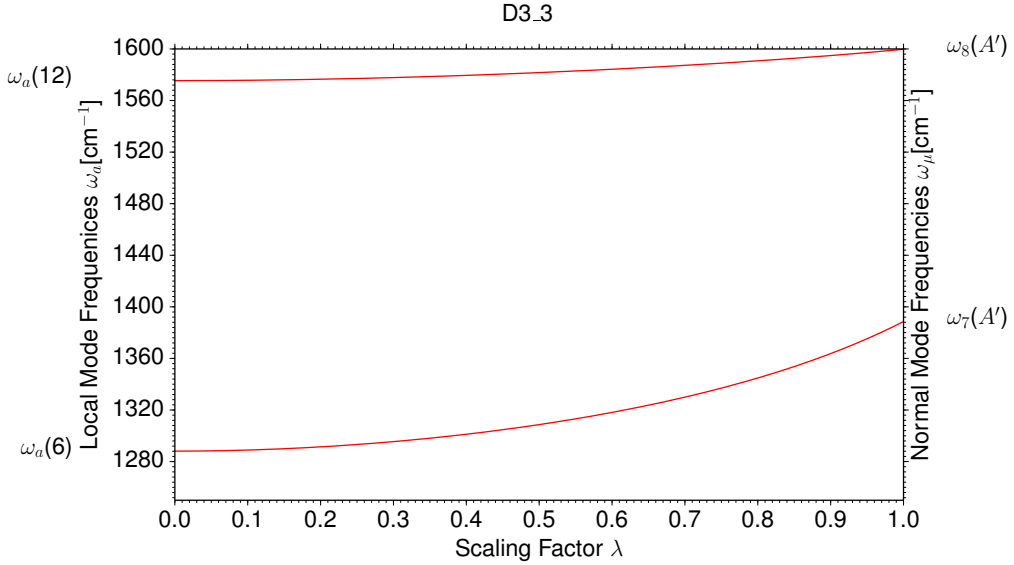


Figure 5: Decomposition of the 12 normal modes of the deuterated water dimer **D3** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


D3_3
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3),ω_a(11)
ω_a(7)
ω_a(10),ω_a(8),ω_a(9)
$\omega_6(A'')$
$\omega_5(A')$
$\omega_4(A')$
$\omega_1(A'')$,$\omega_2(A'')$,$\omega_3(A')$


D3_3
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(12)
ω_a(6)
$\omega_8(A')$
$\omega_7(A')$

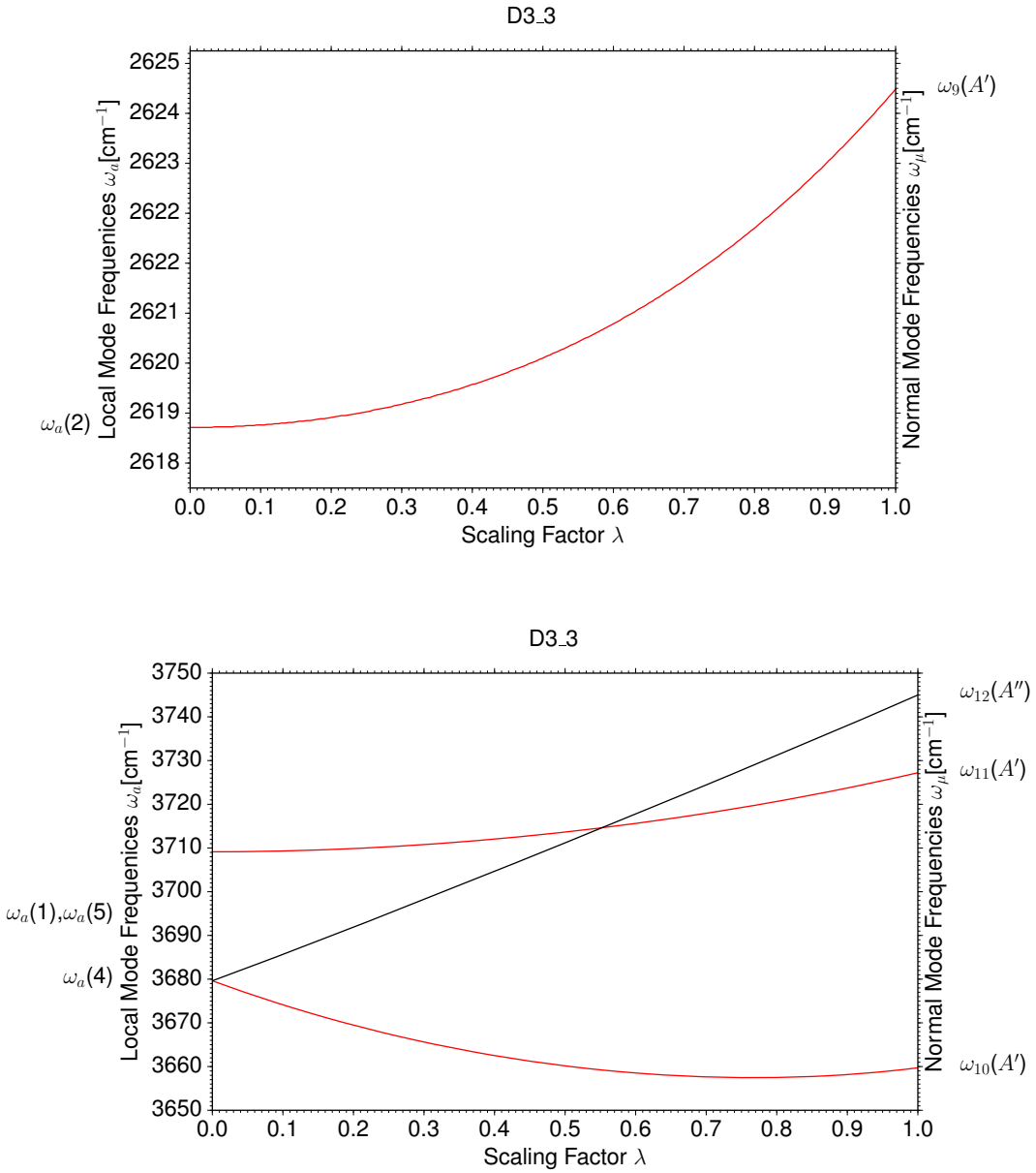


Figure 6: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D3**. **a**) Range from 0 to 450cm^{-1}. **b**) Range from 1250 to 1600 cm^{-1}. **c**) Range from 2610 to 2630 cm^{-1}. **d**) Range from 3650 to 3750cm^{-1}.

Deuterated Water Dimer **D5**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	93.6% H2-O1, 6.2% H3-O1
11	99.5% H6-O4
10	92.9% H3-O1, 6.0% H2-O1
9	99.7% H5-O4
8	96.1% H3-O1-H2
7	98.2% H6-O4-H5
6	43.5% H5-O4-H3-O1, 40.4% O4-H3-O1-H2, 9.6% H6-O4-H3, 6.2% H5-O4-H3
5	49.7% O4-H3-O1, 24.5% H3-O1-H2, 14.2% H6-O4-H3, 9.1% H5-O4-H3
4	72.6% O4-H3, 10.4% O4-H3-O1, 10.3% H6-O4-H3
3	38.7% H6-O4-H3, 25.2% O4-H3-O1, 12.2% H5-O4-H3-O1, 12.0% O4-H3-O1-H2, 8.7% O4-H3
2	67.2% O4-H3-O1-H2, 16.1% H5-O4-H3, 9.8% H5-O4-H3-O1
1	39.7% H5-O4-H3, 27.4% H5-O4-H3-O1, 17.6% O4-H3-O1-H2, 8.6% O4-H3-O1

Table 4: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D5** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

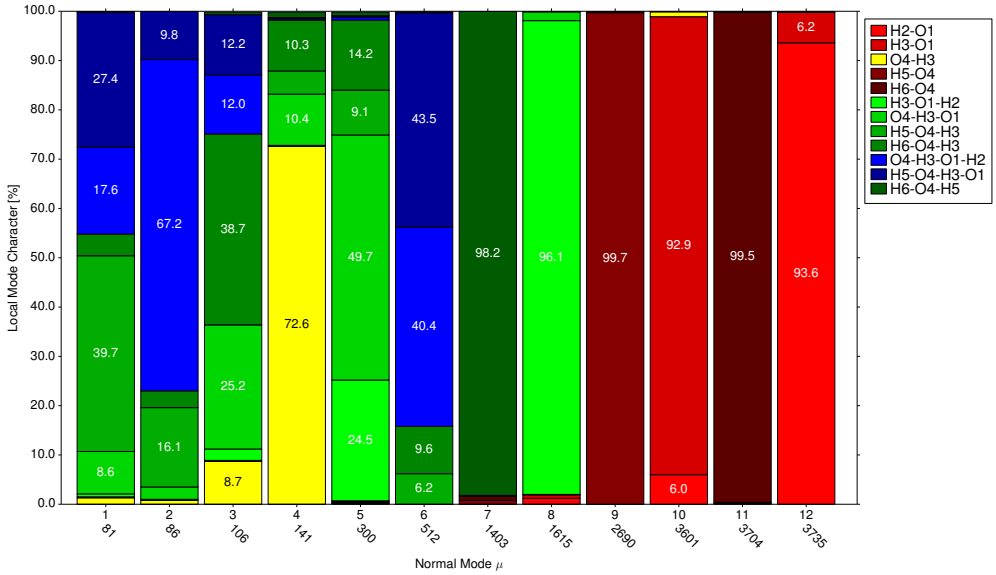
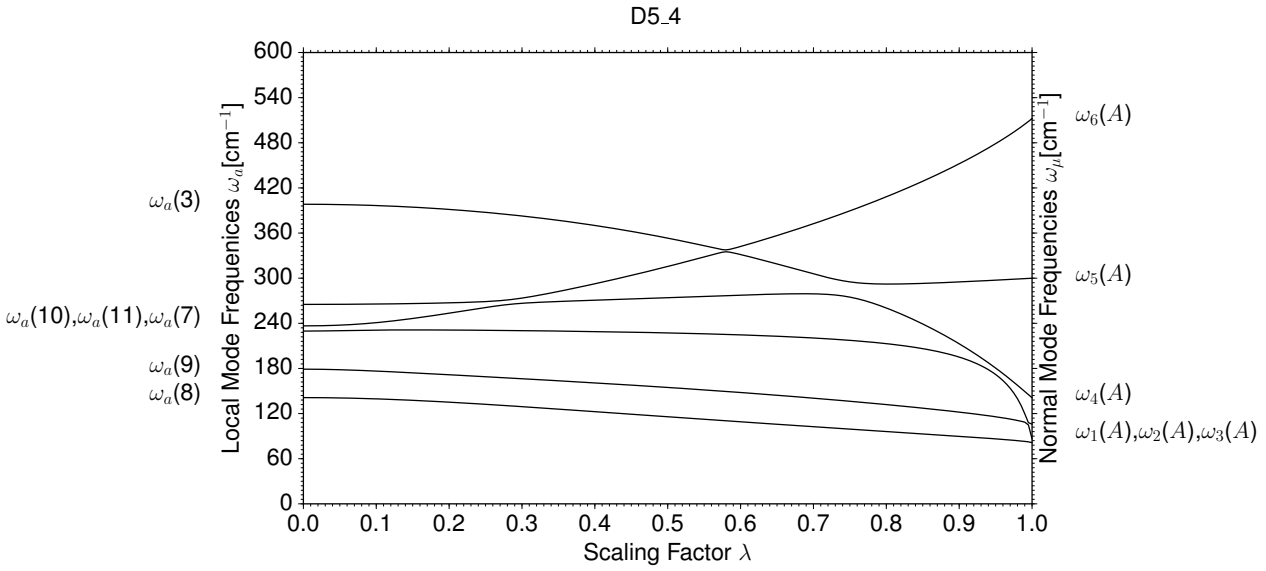
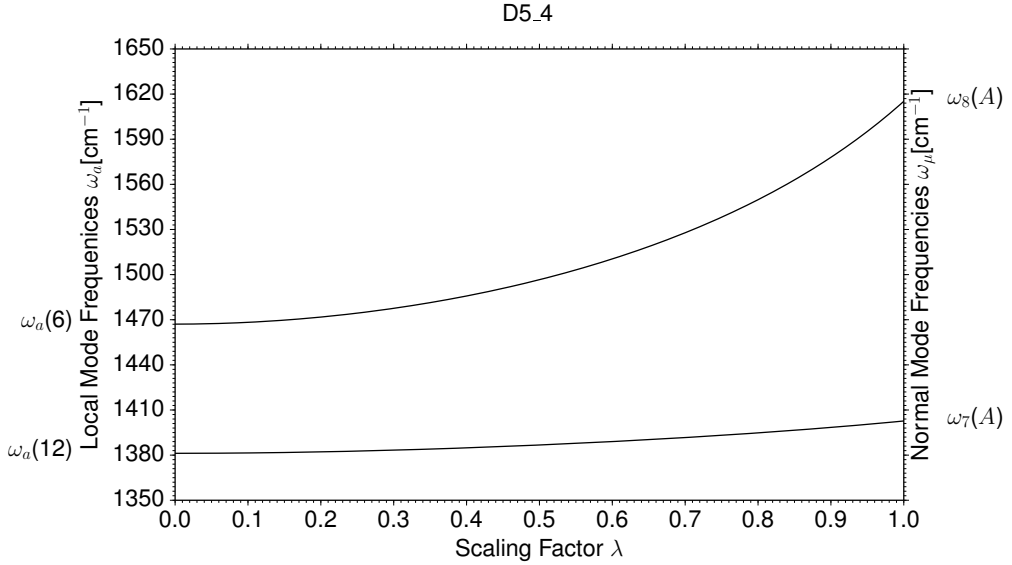


Figure 7: Decomposition of the 12 normal modes of the deuterated water dimer **D5** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


D5_4
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3)
ω_a(10),ω_a(11),ω_a(7)
ω_a(9)
ω_a(8)
$\omega_6(A)$
$\omega_5(A)$
$\omega_4(A)$
$\omega_1(A)$,$\omega_2(A)$,$\omega_3(A)$


D5_4
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(6)
ω_a(12)
$\omega_8(A)$
$\omega_7(A)$

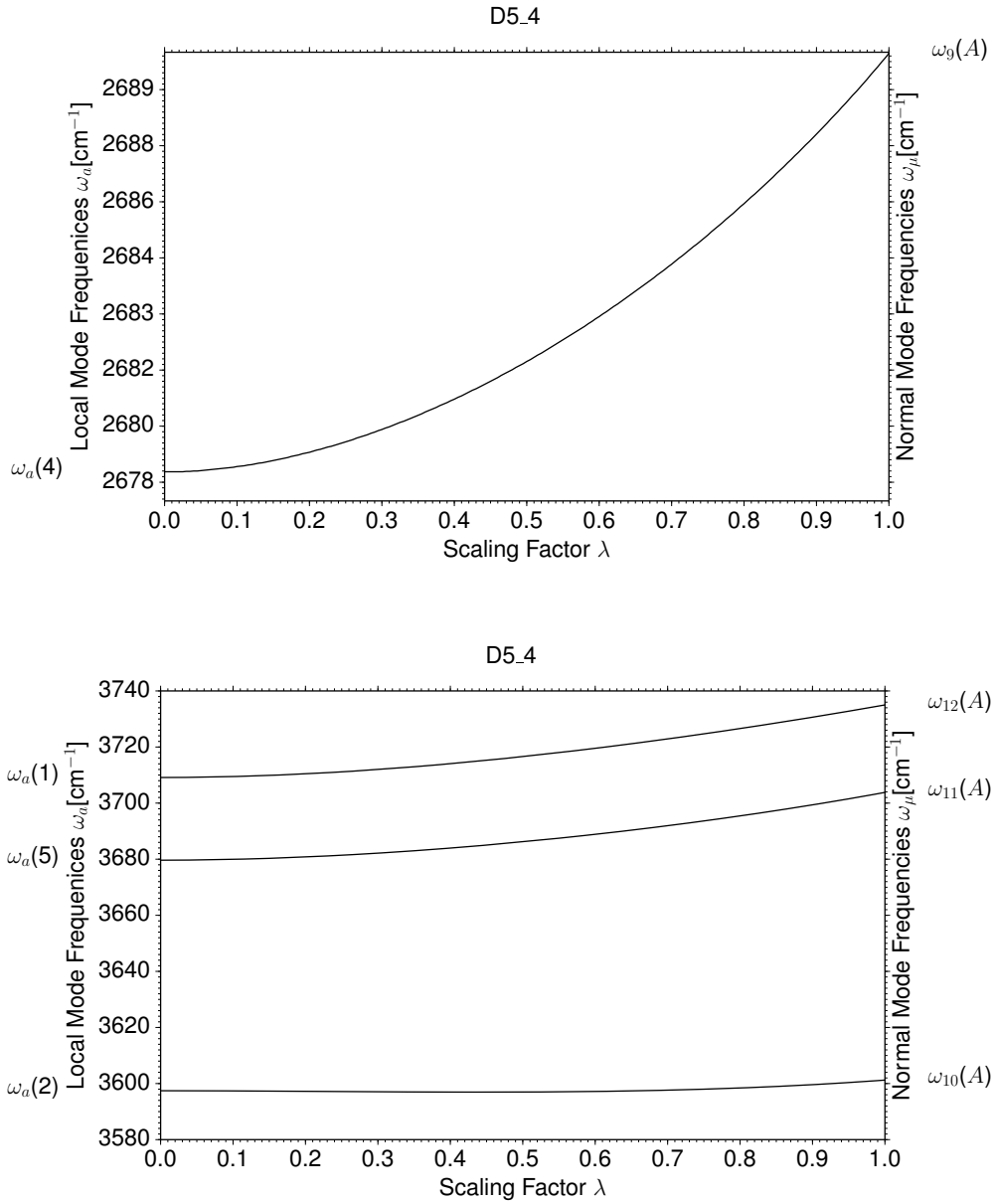


Figure 8: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D5**. **a**) Range from 0 to 600 cm^{-1}. **b**) Range from 1350 to 1650 cm^{-1}. **c**) Range from 2600 to 2690 cm^{-1}. **d**) Range from 3580 to 3740 cm^{-1}.

Deuterated Water Dimer **D2D3**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	100.0% (H5-O4, H6-O4)
11	100.0% (H5-O4, H6-O4)
10	83.8% H2-O1, 16.0% H3-O1
9	83.1% H3-O1, 16.0% H2-O1
8	97.9% H6-O4-H5
7	96.8% H3-O1-H2
6	35.8% H5-O4-H3-O1, 32.6% (H5-O4-H3, H6-O4-H3), 31.5% O4-H3-O1-H2
5	54.6% (H5-O4-H3, H6-O4-H3), 22.1% O4-H3-O1, 19.4% H3-O1-H2
4	86.3% O4-H3, 7.4% O4-H3-O1
3	53.9% O4-H3-O1, 33.8% (H5-O4-H3, H6-O4-H3), 5.5% H3-O1-H2, 5.3% O4-H3
2	40.0% (H5-O4-H3, H6-O4-H3), 32.7% H5-O4-H3-O1, 27.3% O4-H3-O1-H2
1	94.9% O4-H3-O1-H2

Table 5: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D2D3** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

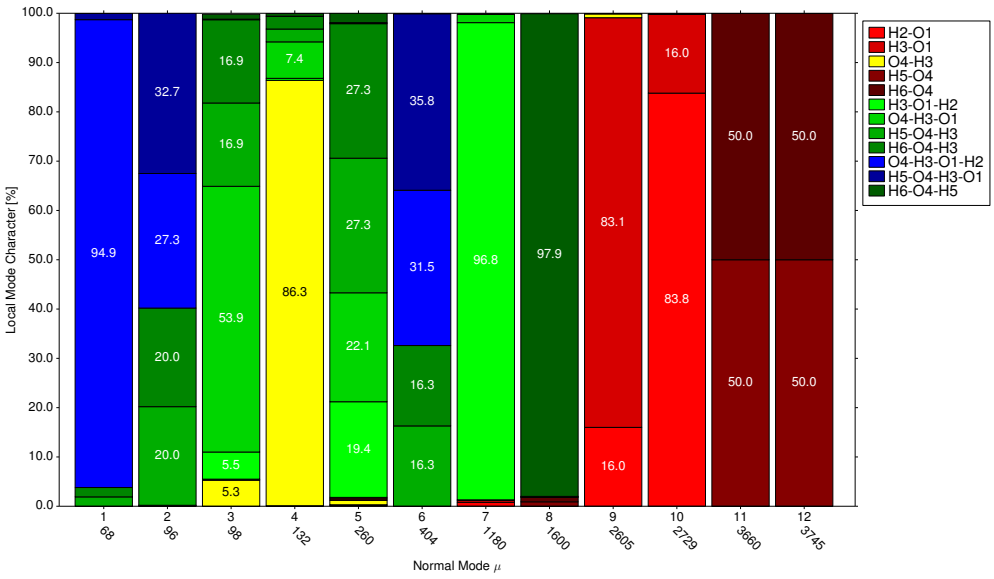
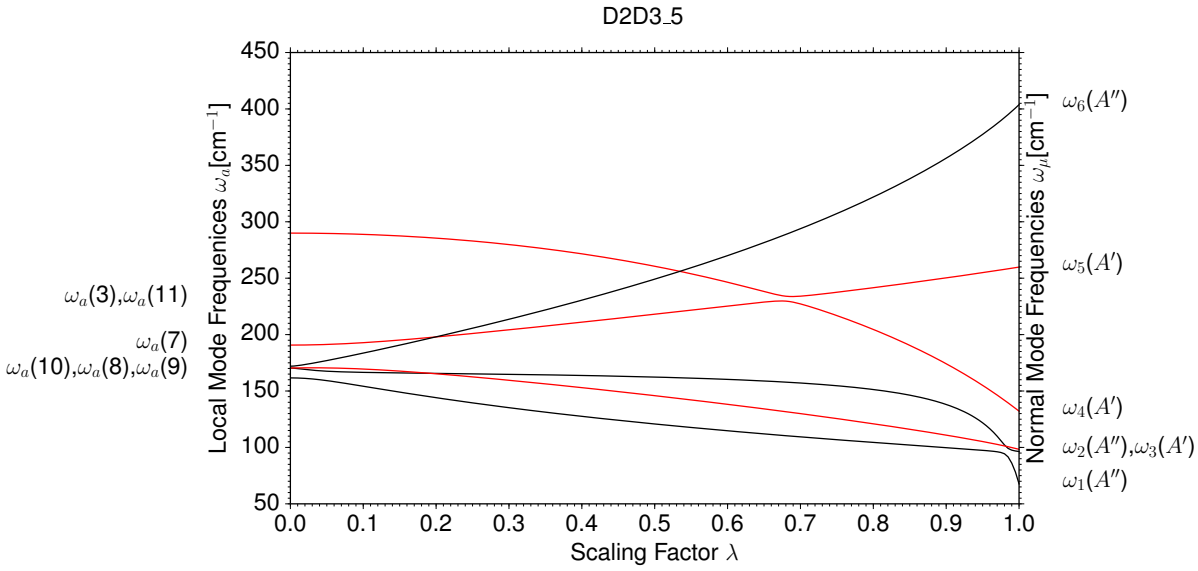
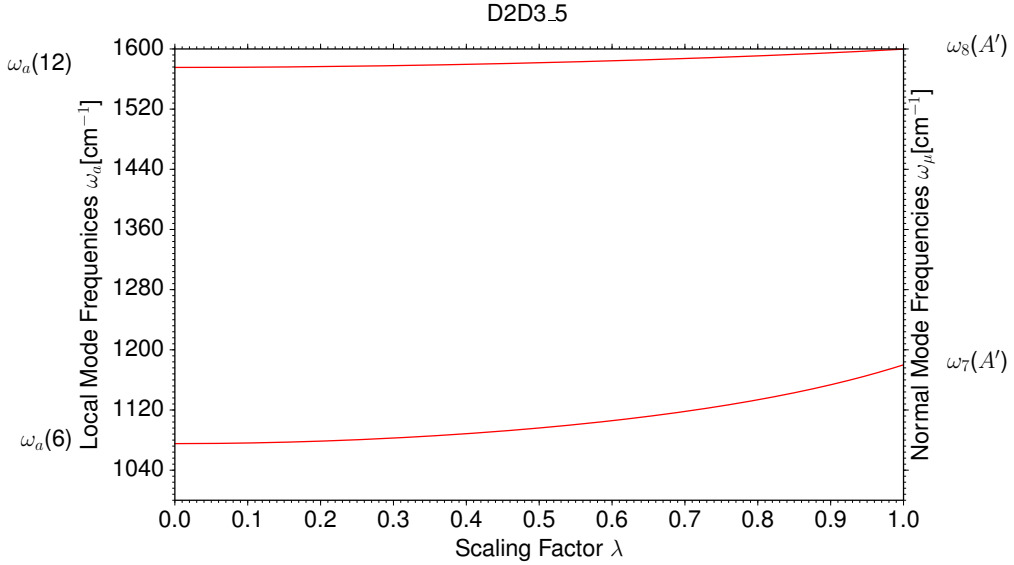


Figure 9: Decomposition of the 12 normal modes of the deuterated water dimer **D2D3** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


D2D3_5
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3),ω_a(11)
ω_a(7)
ω_a(10),ω_a(8),ω_a(9)
$\omega_6(A'')$
$\omega_5(A')$
$\omega_4(A')$
$\omega_2(A'')$,$\omega_3(A')$
$\omega_1(A'')$


D2D3_5
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(12)
ω_a(6)
$\omega_8(A')$
$\omega_7(A')$

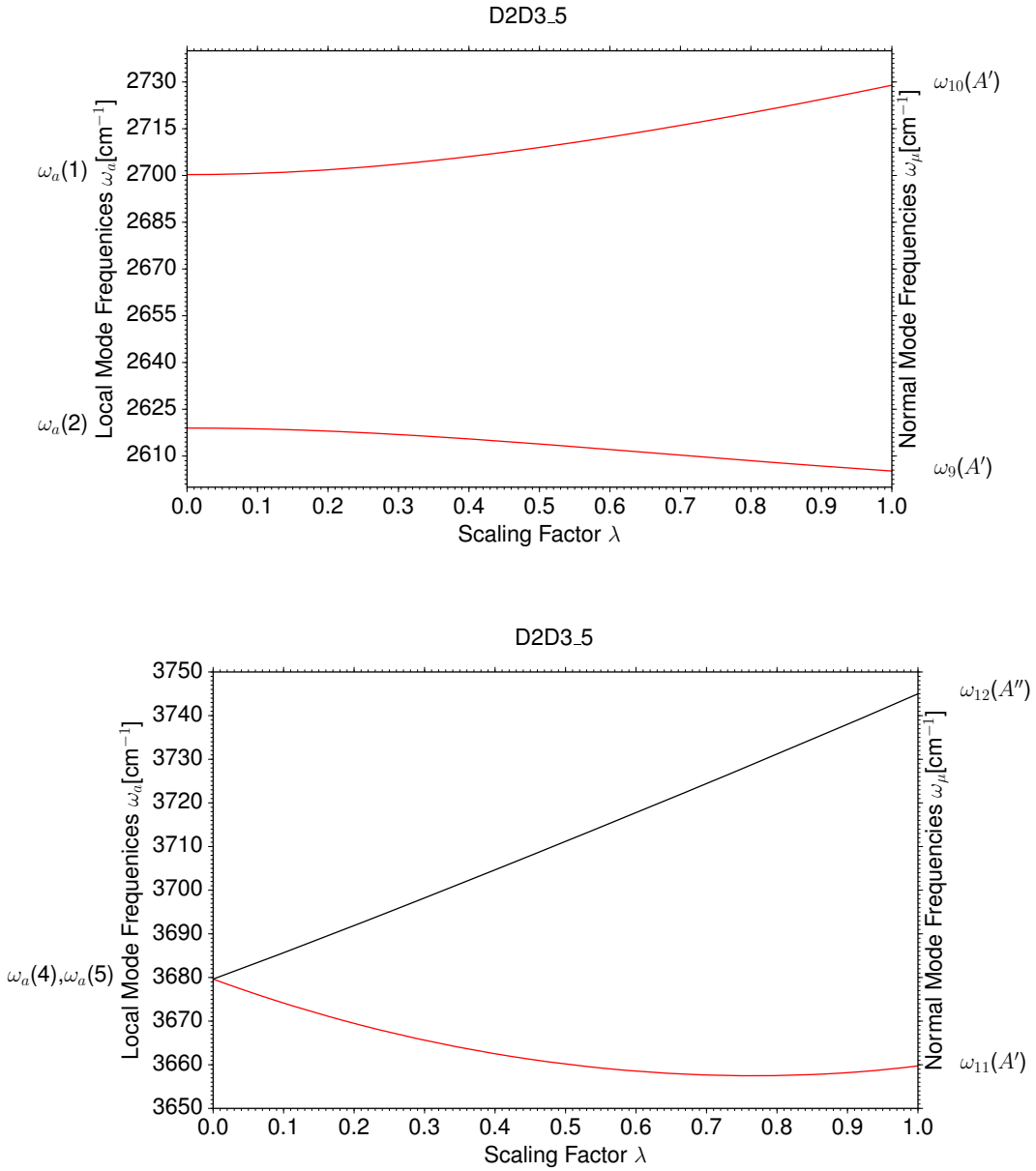


Figure 10: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D2D3**. **a**) Range from 50 to 450 cm^{-1}. **b**) Range from 1030 to 1600 cm^{-1}. **c**) Range from 2600 to 2740 cm^{-1}. **d**) Range from 3650 to 3750 cm^{-1}.

Deuterated Water Dimer **D2D5**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	99.7% H6-O4
11	98.7% H3-O1
10	99.8% H2-O1
9	99.7% H5-O4
8	94.5% H3-O1-H2
7	97.7% H6-O4-H5
6	44.0% H5-O4-H3-O1, 39.9% O4-H3-O1-H2, 9.6% H6-O4-H3, 6.4% H5-O4-H3
5	34.9% O4-H3-O1, 27.6% H3-O1-H2, 21.5% H6-O4-H3, 12.3% H5-O4-H3
4	82.6% O4-H3, 8.2% O4-H3-O1
3	39.4% H6-O4-H3, 26.4% O4-H3-O1, 13.5% H5-O4-H3-O1, 12.9% O4-H3-O1-H2
2	38.3% H5-O4-H3, 24.6% H5-O4-H3-O1, 21.3% O4-H3-O1-H2, 10.0% O4-H3-O1
1	95.2% O4-H3-O1-H2

Table 6: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D2D5** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

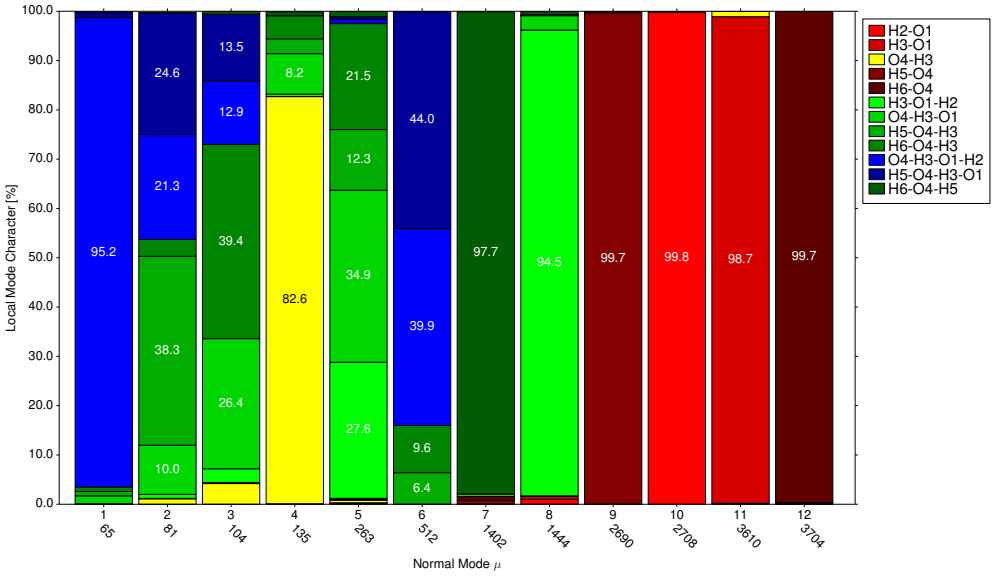
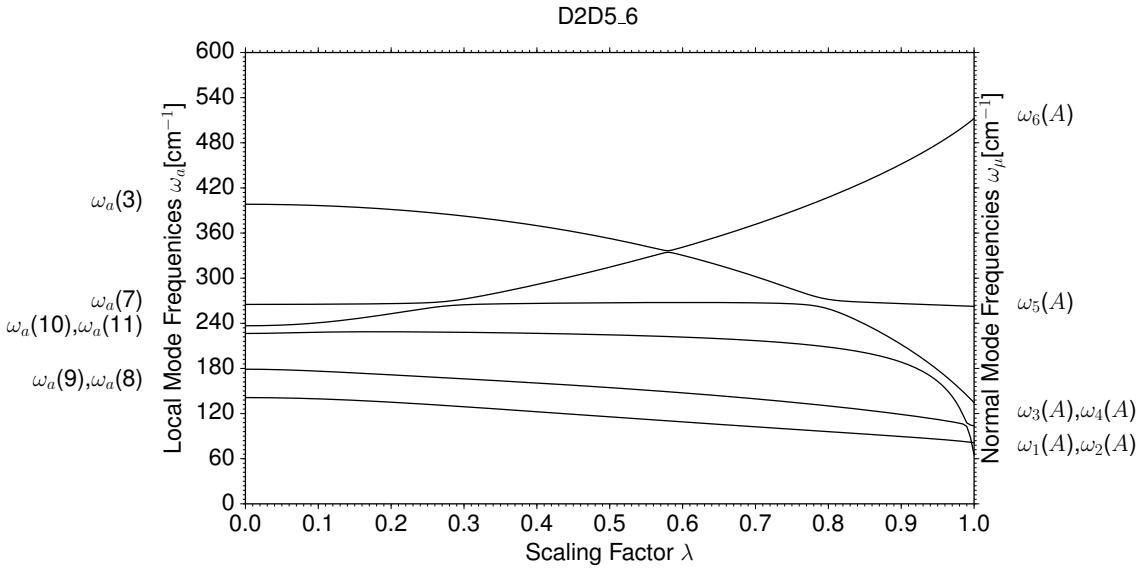
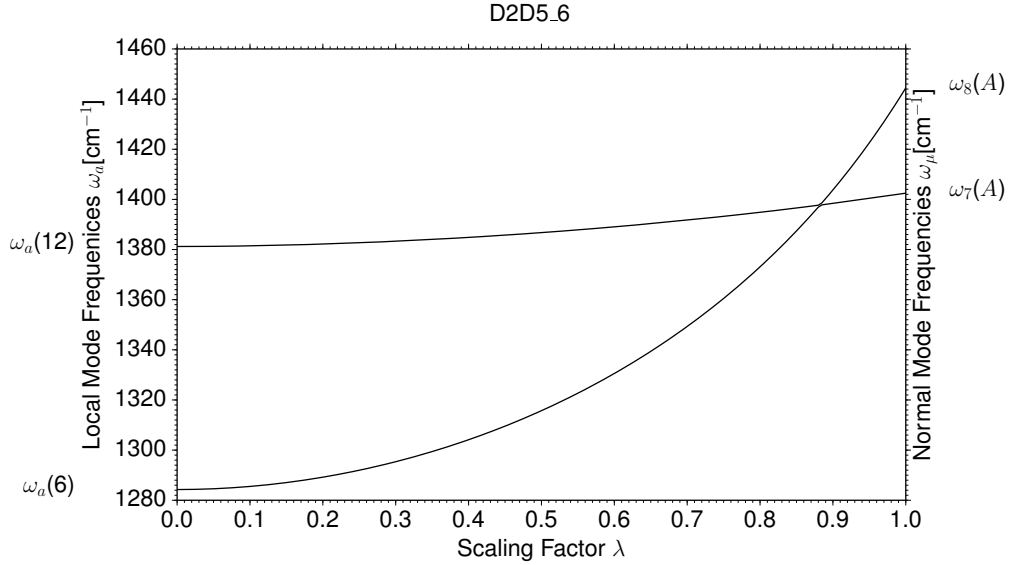


Figure 11: Decomposition of the 12 normal modes of the deuterated water dimer **D2D5** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


D2D5_6
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3)
ω_a(7)
ω_a(10),ω_a(11)
ω_a(9),ω_a(8)
$\omega_6(A)$
$\omega_5(A)$
$\omega_3(A)$,$\omega_4(A)$
$\omega_1(A)$,$\omega_2(A)$


D2D5_6
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(12)
ω_a(6)
$\omega_8(A)$
$\omega_7(A)$

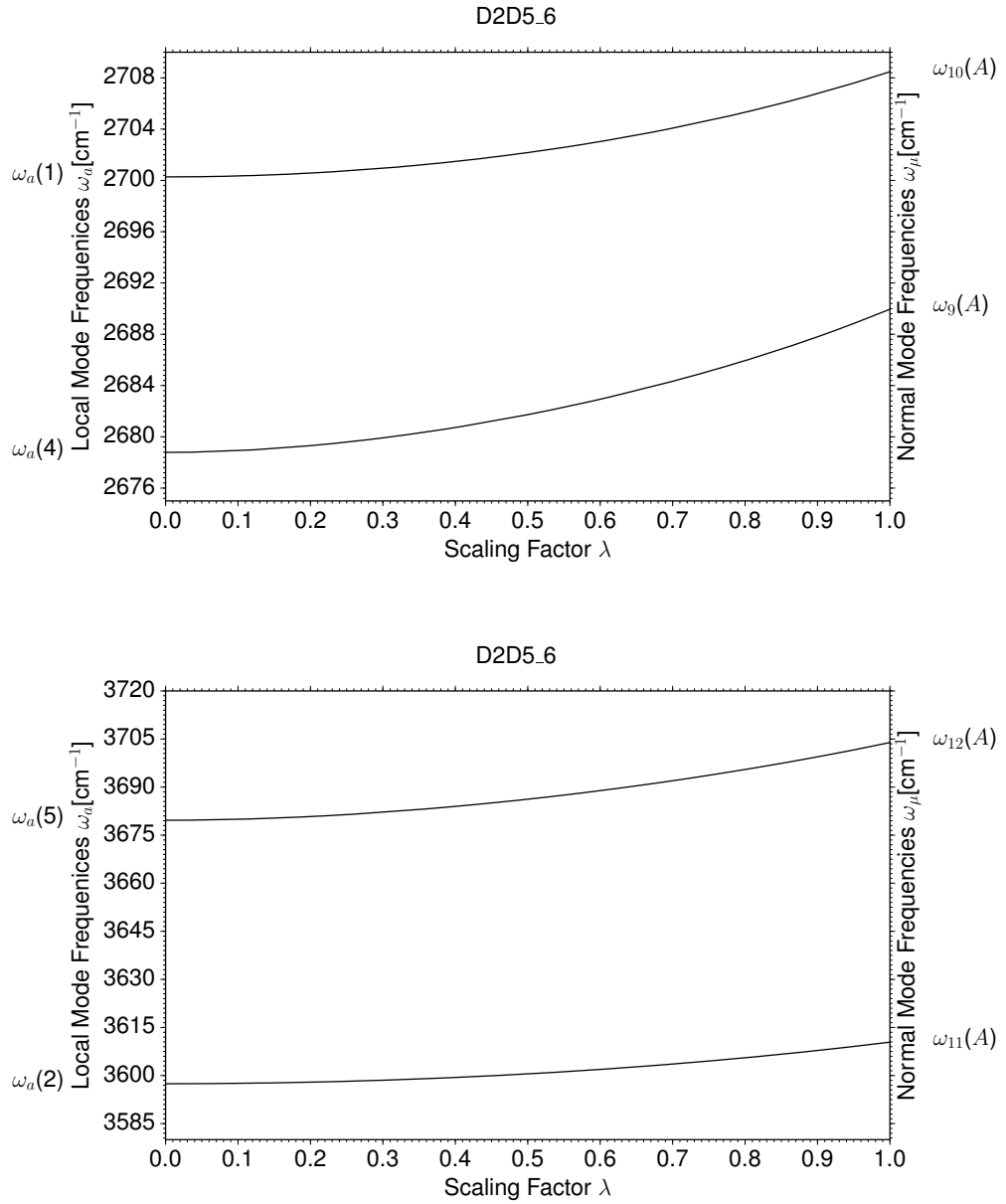


Figure 12: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D2D5**. **a**) Range from 0 to 600 cm^{-1}. **b**) Range from 1280 to 1460 cm^{-1}. **c**) Range from 2670 to 2710 cm^{-1}. **d**) Range from 3585 to 3720 cm^{-1}.

Deuterated Water Dimer **D3D5**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	99.8% H2-O1
11	99.7% H6-O4
10	99.6% H5-O4
9	98.8% H3-O1
8	97.0% H6-O4-H5
7	95.9% H3-O1-H2
6	38.4% H5-O4-H3-O1, 35.0% O4-H3-O1-H2, 17.7% H6-O4-H3, 8.3% H5-O4-H3
5	42.7% O4-H3-O1, 20.2% H6-O4-H3, 17.9% H3-O1-H2, 15.1% H5-O4-H3
4	79.1% O4-H3, 9.2% O4-H3-O1, 6.5% H6-O4-H3
3	37.7% H6-O4-H3, 29.5% O4-H3-O1, 12.0% H5-O4-H3-O1, 11.1% O4-H3-O1-H2, 6.1% O4-H3
2	88.9% O4-H3-O1-H2
1	36.6% H5-O4-H3, 27.3% H5-O4-H3-O1, 21.4% O4-H3-O1-H2, 8.1% O4-H3-O1

Table 7: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D3D5** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

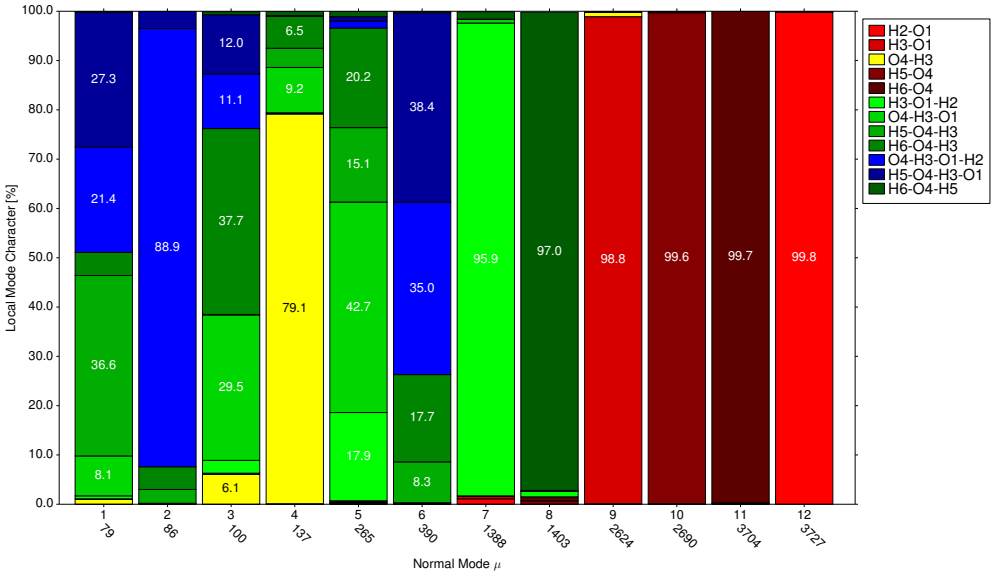
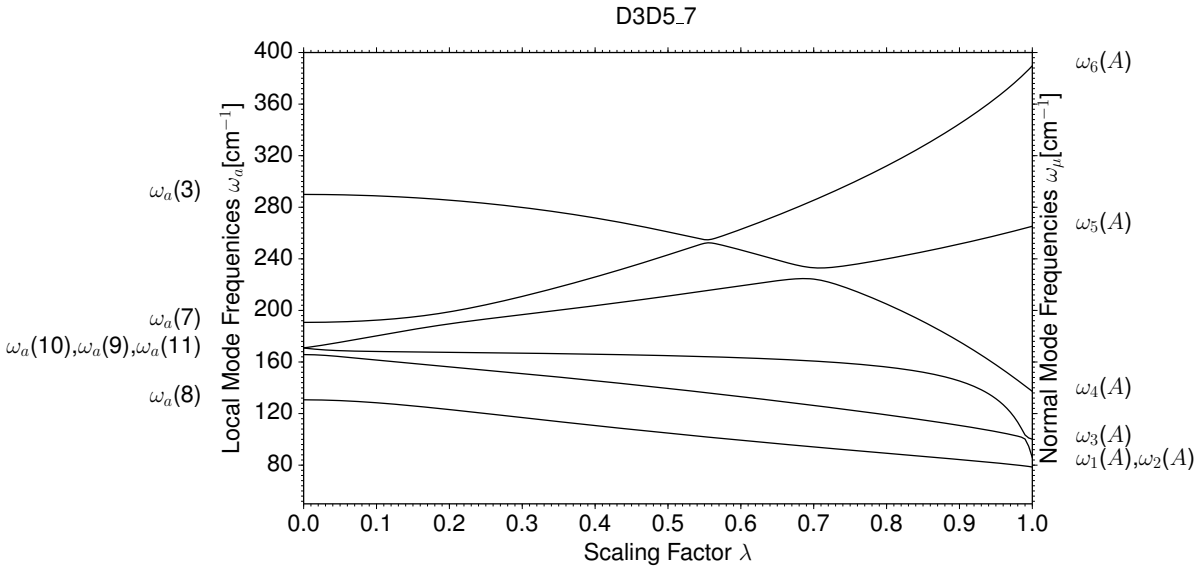
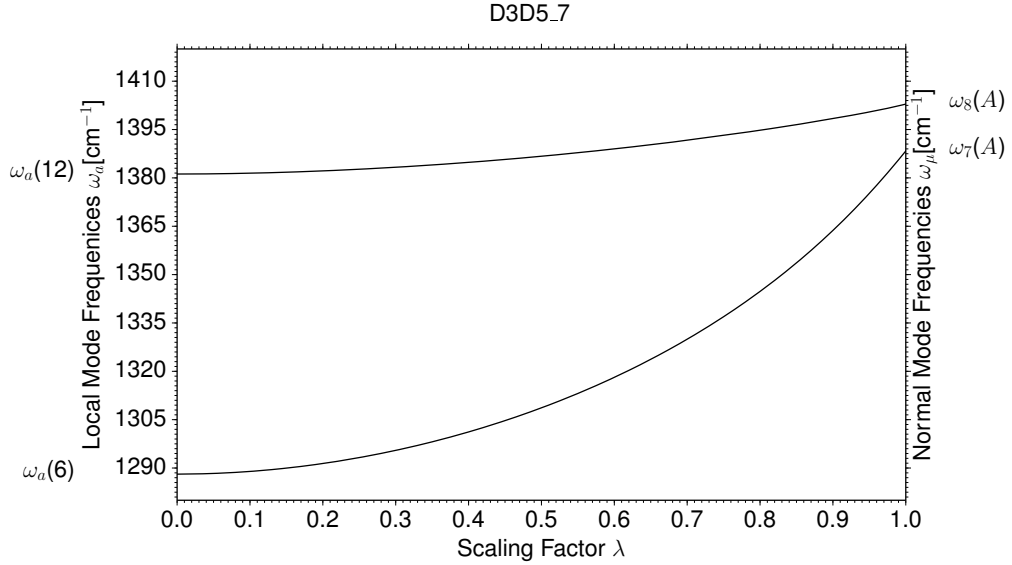


Figure 13: Decomposition of the 12 normal modes of the deuterated water dimer **D3D5** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


D3D5_7
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3)
ω_a(7)
ω_a(10),ω_a(9),ω_a(11)
ω_a(8)
$\omega_6(A)$
$\omega_5(A)$
$\omega_4(A)$
$\omega_3(A)$
$\omega_1(A)$,$\omega_2(A)$


D3D5_7
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(12)
ω_a(6)
$\omega_8(A)$
$\omega_7(A)$

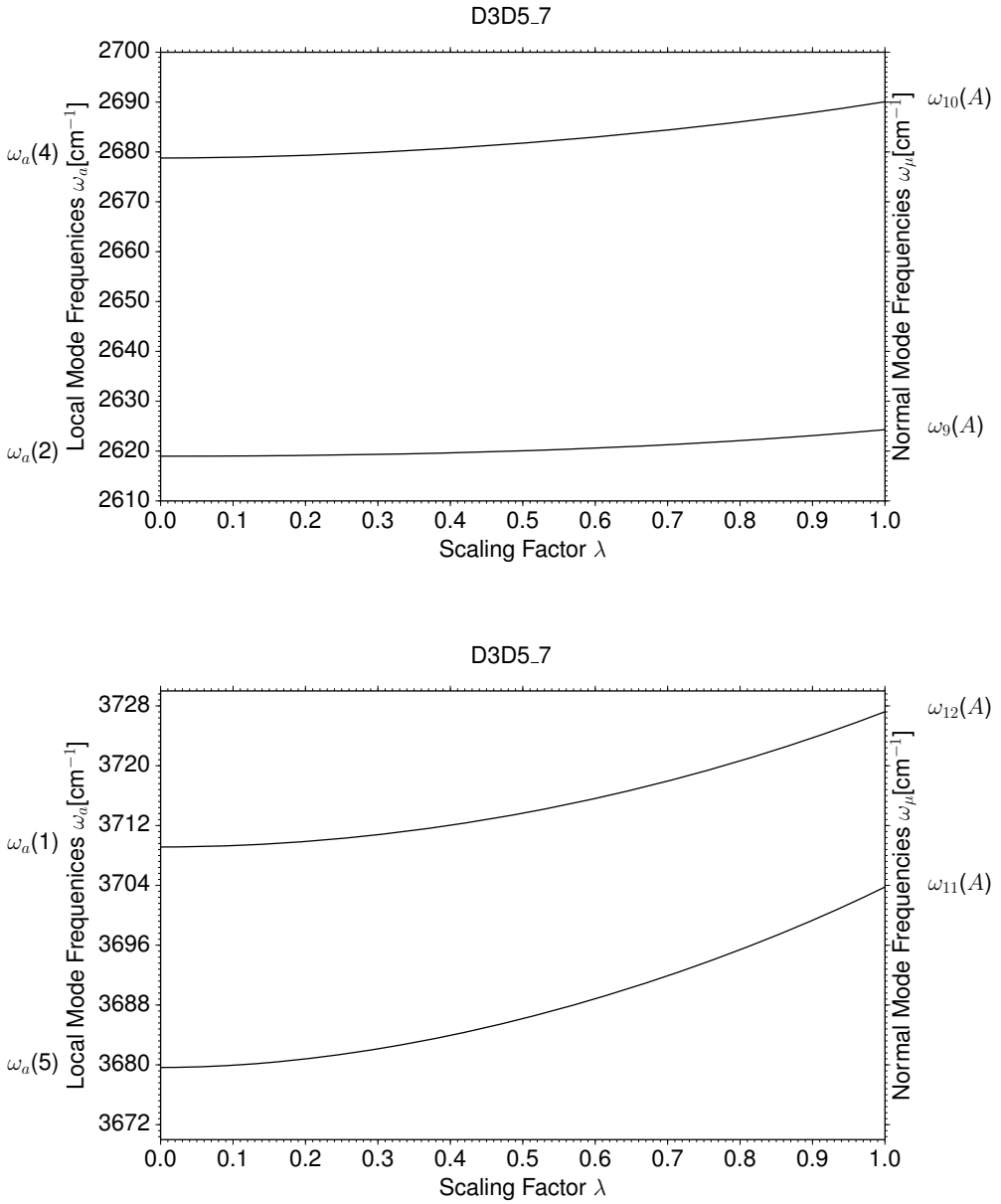


Figure 14: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D3D5**. **a**) Range from 0 to 400 cm^{-1}. **b**) Range from 1290 to 1410 cm^{-1}. **c**) Range from 2610 to 2700 cm^{-1}. **d**) Range from 3670 to 3730 cm^{-1}.

Deuterated Water Dimer **D5D6**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	93.8% H2-O1, 6.1% H3-O1
11	93.0% H3-O1, 6.0% H2-O1
10	100.0% (H5-O4, H6-O4)
9	100.0% (H5-O4, H6-O4)
8	96.1% H3-O1-H2
7	98.6% H6-O4-H5
6	44.9% H5-O4-H3-O1, 42.2% O4-H3-O1-H2, 12.8% (H5-O4-H3, H6-O4-H3)
5	56.8% O4-H3-O1, 25.1% H3-O1-H2, 16.8% (H5-O4-H3, H6-O4-H3)
4	82.6% O4-H3, 10.4% (H5-O4-H3, H6-O4-H3), 5.7% O4-H3-O1
3	44.3% O4-H3-O1, 43.2% (H5-O4-H3, H6-O4-H3), 7.4% O4-H3
2	86.1% O4-H3-O1-H2
1	43.6% (H5-O4-H3, H6-O4-H3), 31.0% H5-O4-H3-O1, 25.2% O4-H3-O1-H2

Table 8: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D5D6** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

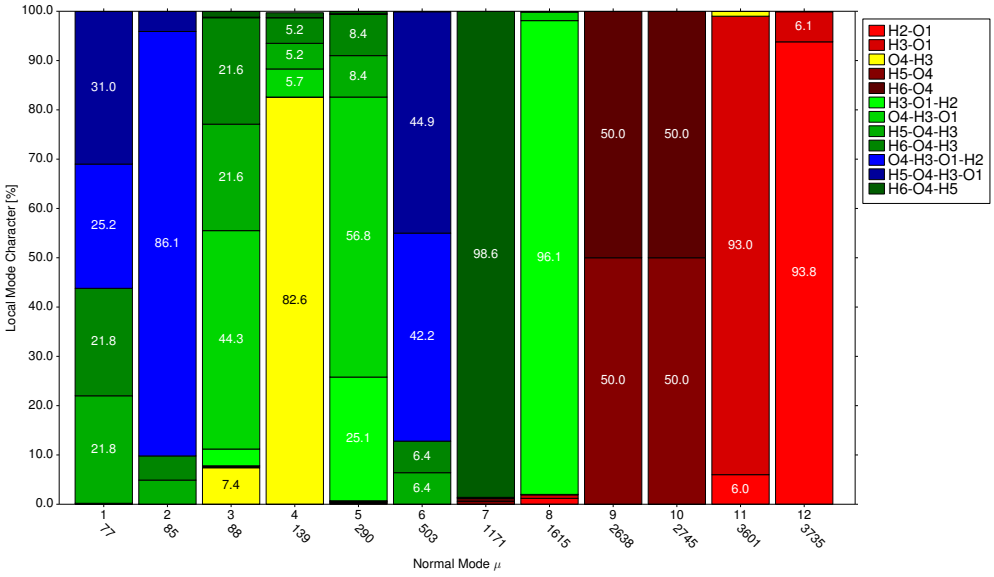
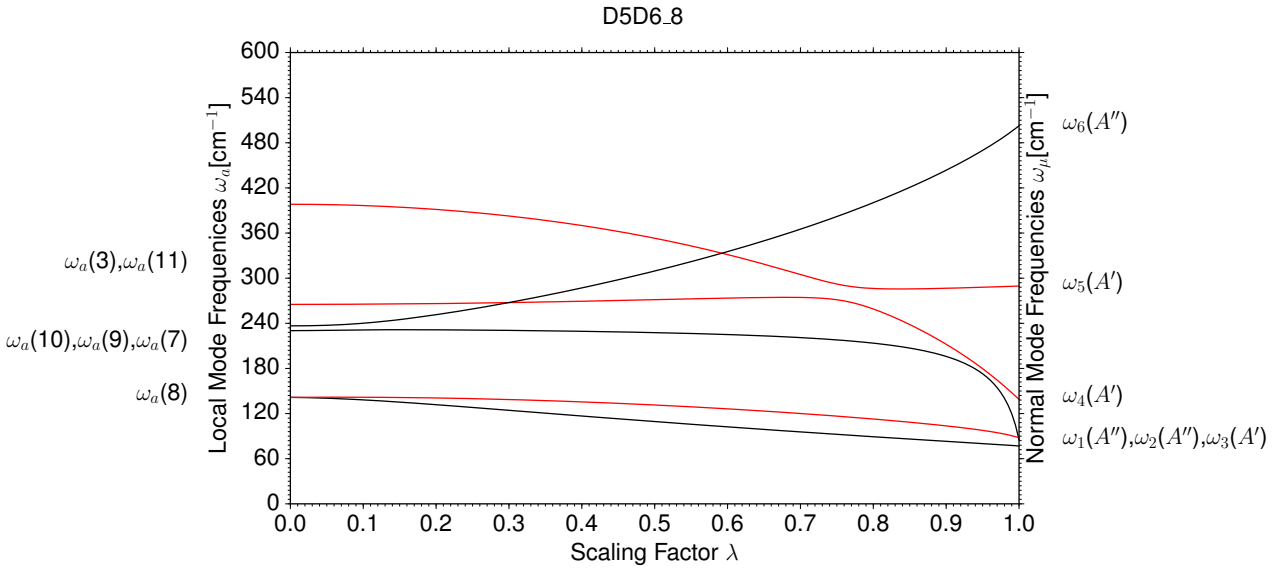
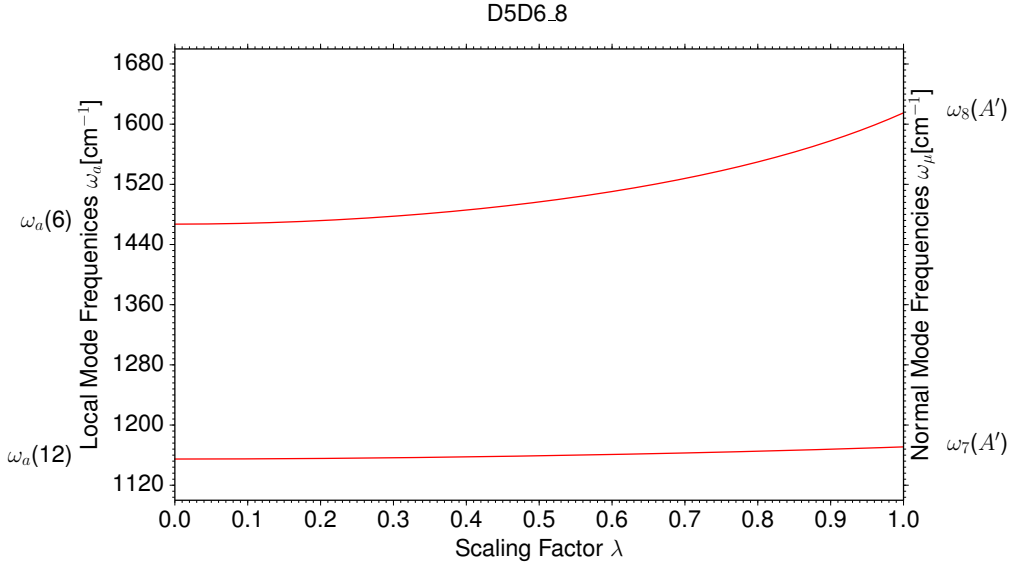


Figure 15: Decomposition of the 12 normal modes of the deuterated water dimer **D5D6** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


D5D6_8
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3),ω_a(11)
ω_a(10),ω_a(9),ω_a(7)
ω_a(8)
$\omega_6(A'')$
$\omega_5(A')$
$\omega_4(A')$
$\omega_1(A'')$,$\omega_2(A'')$,$\omega_3(A')$


D5D6_8
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(6)
ω_a(12)
$\omega_8(A')$
$\omega_7(A')$

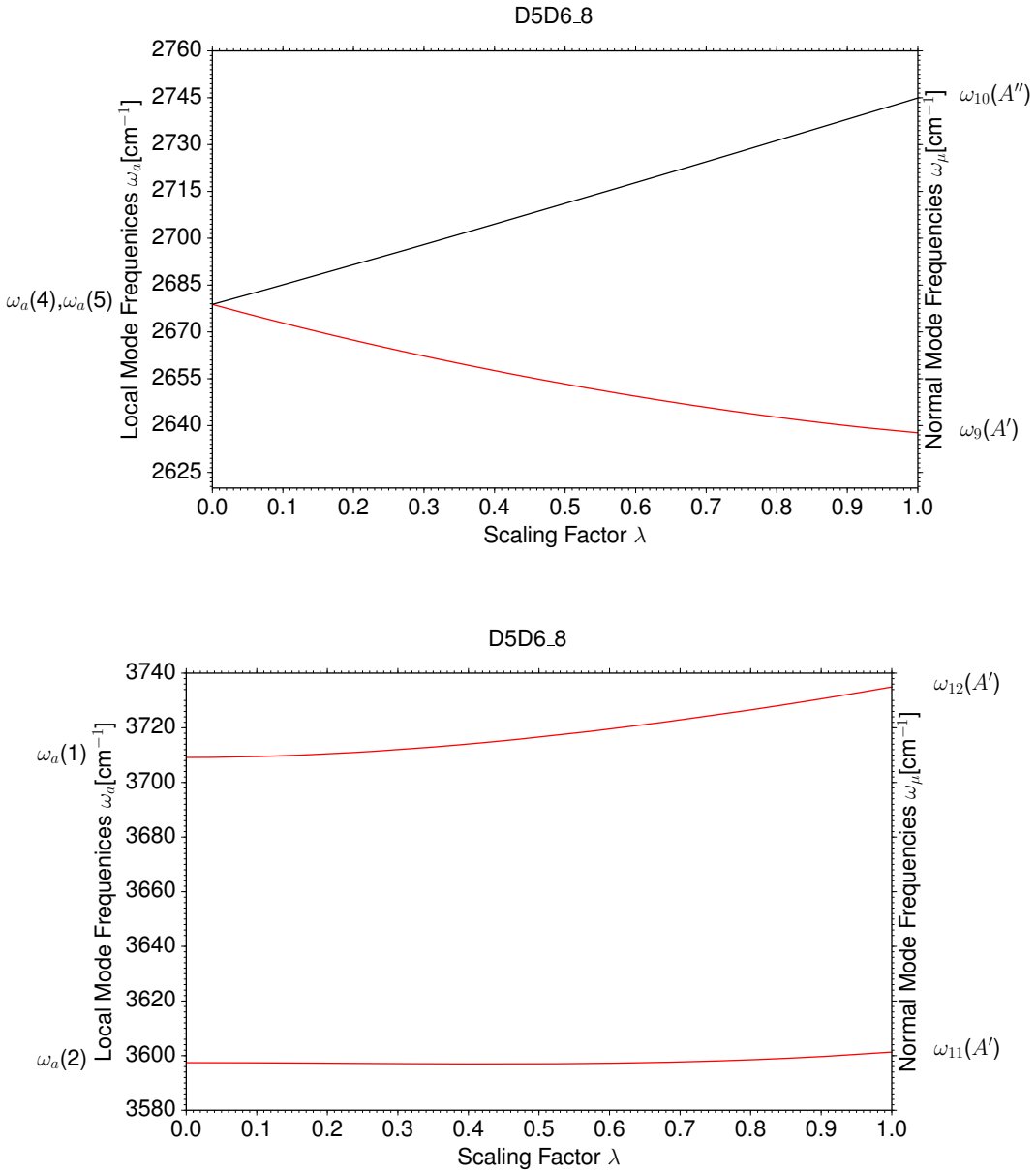


Figure 16: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D5D6**. **a**) Range from 0 to 600 cm^{-1}. **b**) Range from 1110to 1690 cm^{-1}. **c**) Range from 2620to 2760 cm^{-1}. **d**) Range from 3580 to 3740 cm^{-1}.

Deuterated Water Dimer **D2D3D5**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	99.8% H6-O4
11	83.7% H2-O1, 16.0% H3-O1
10	99.5% H5-O4
9	83.1% H3-O1, 16.0% H2-O1
8	98.2% H6-O4-H5
7	96.8% H3-O1-H2
6	38.8% H5-O4-H3-O1, 34.5% O4-H3-O1-H2, 17.6% H6-O4-H3, 8.6% H5-O4-H3
5	29.2% O4-H3-O1, 26.4% H6-O4-H3, 20.7% H3-O1-H2, 17.7% H5-O4-H3
4	87.4% O4-H3, 6.7% O4-H3-O1
3	37.8% H6-O4-H3, 29.4% O4-H3-O1, 13.7% H5-O4-H3-O1, 12.6% O4-H3-O1-H2
2	37.0% H5-O4-H3, 25.7% H5-O4-H3-O1, 21.4% O4-H3-O1-H2, 10.2% O4-H3-O1
1	95.9% O4-H3-O1-H2

Table 9: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D2D3D5** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

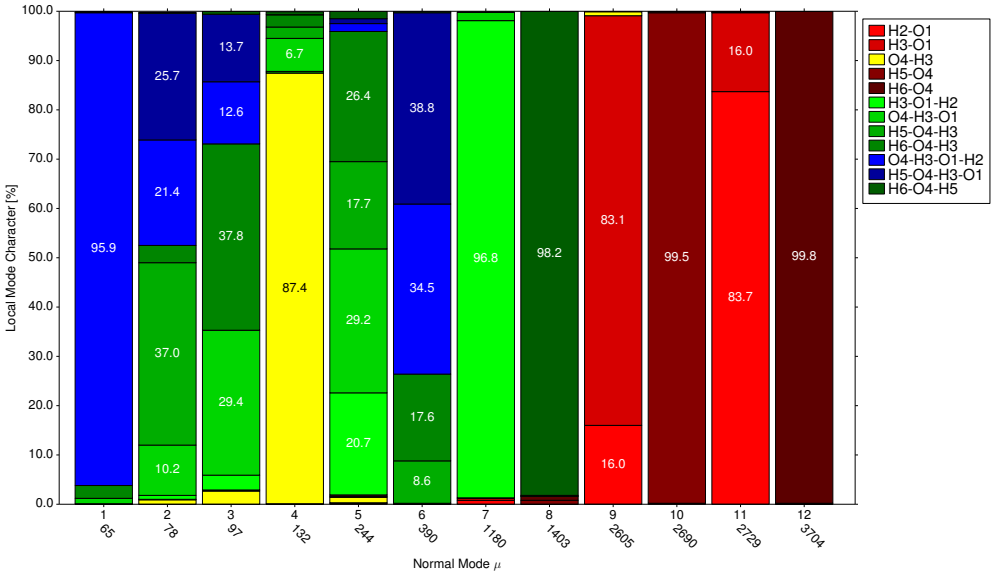
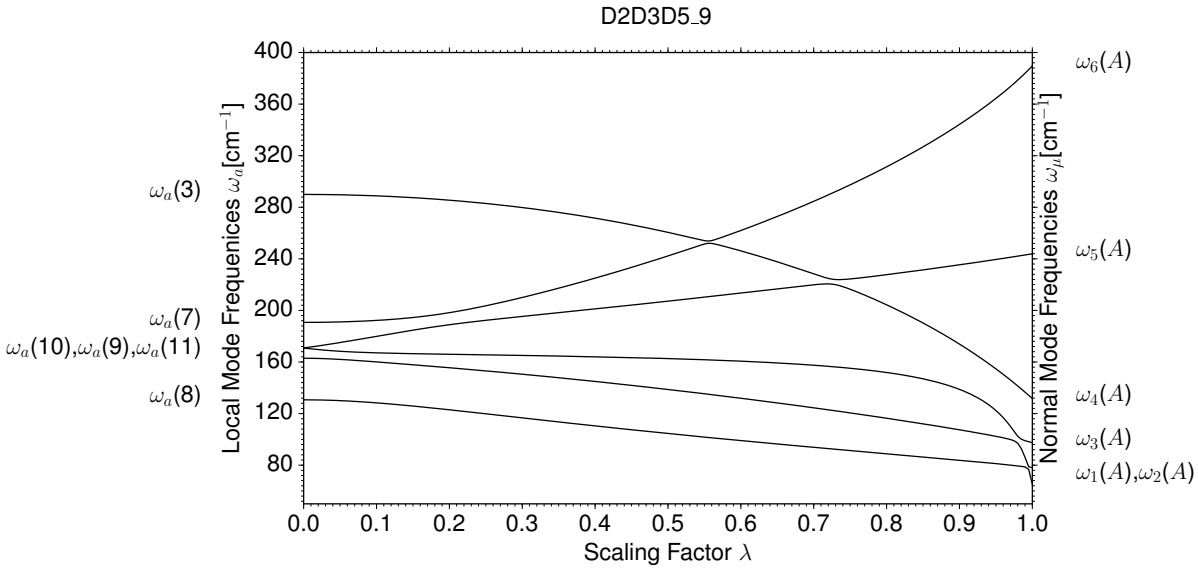
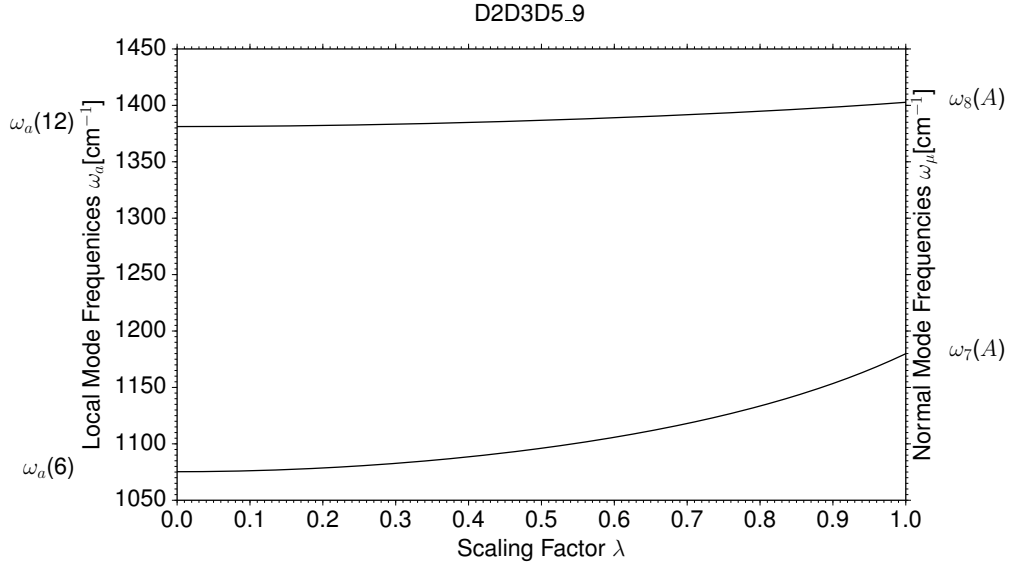


Figure 17: Decomposition of the 12 normal modes of the deuterated water dimer **D2D3D5** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


D2D3D5_9
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3)
ω_a(7)
ω_a(10),ω_a(9),ω_a(11)
ω_a(8)
$\omega_6(A)$
$\omega_5(A)$
$\omega_4(A)$
$\omega_3(A)$
$\omega_1(A)$,$\omega_2(A)$


D2D3D5_9
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(12)
ω_a(6)
$\omega_8(A)$
$\omega_7(A)$

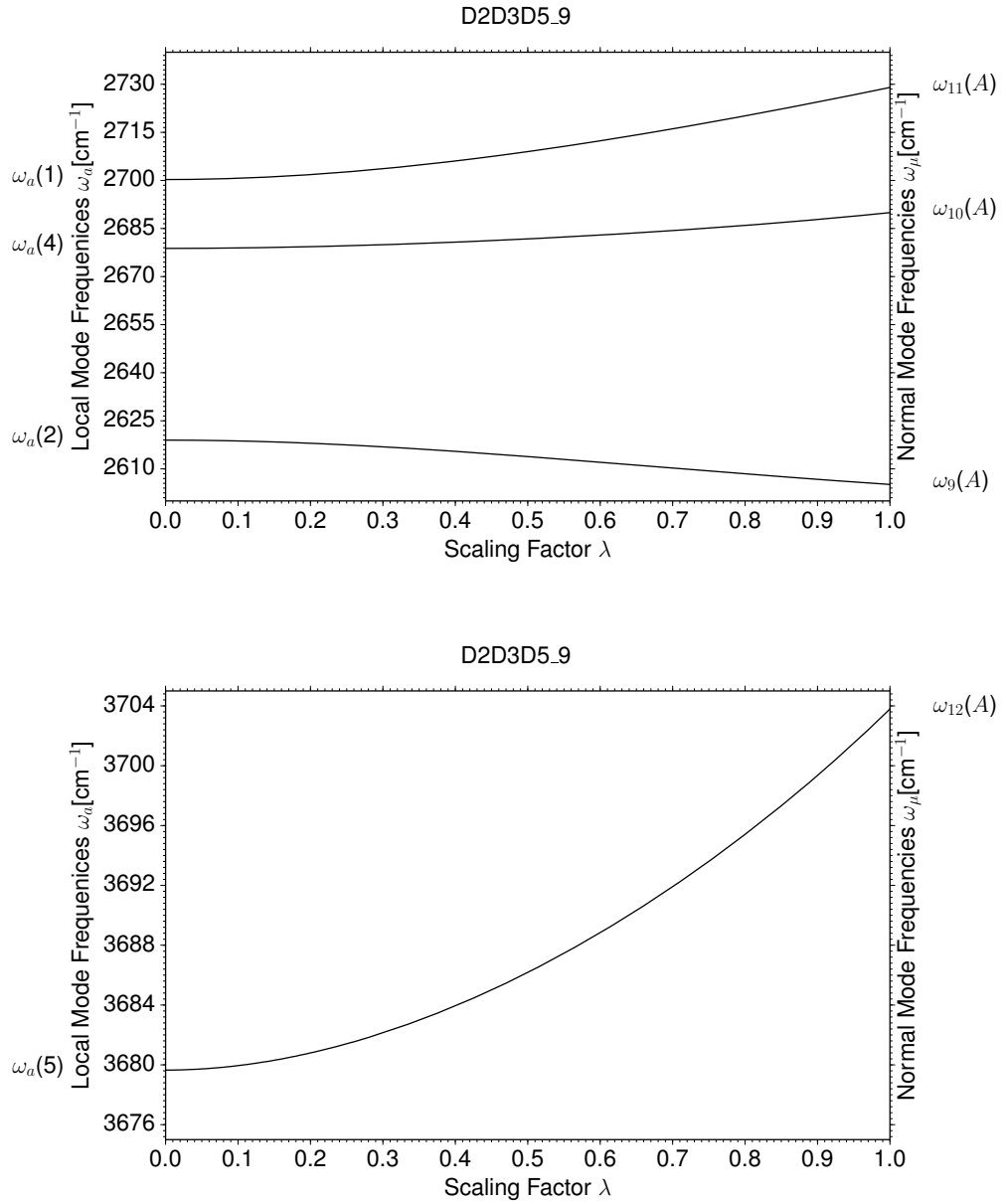
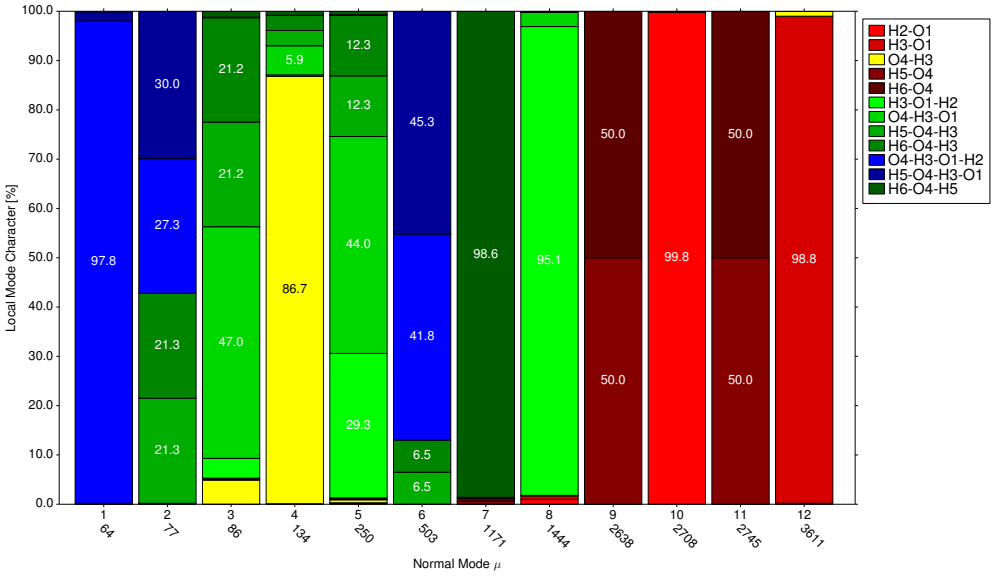


Figure 18: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D2D3D5**. **a**) Range from 0 to 400 cm^{-1}. **b**) Range from 1050 to 1450cm^{-1}. **c**) Range from 2610 to 2740 cm^{-1}. **d**) Range from 3670 to 3710 cm^{-1}.

Deuterated Water Dimer **D2D5D6**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	98.8% H3-O1
11	100.0% (H5-O4, H6-O4)
10	99.8% H2-O1
9	100.0% (H5-O4, H6-O4)
8	95.1% H3-O1-H2
7	98.6% H6-O4-H5
6	45.3% H5-O4-H3-O1, 41.8% O4-H3-O1-H2, 13.0% (H5-O4-H3, H6-O4-H3)
5	44.0% O4-H3-O1, 29.3% H3-O1-H2, 24.6% (H5-O4-H3, H6-O4-H3)
4	86.7% O4-H3, 5.9% O4-H3-O1
3	47.0% O4-H3-O1, 42.4% (H5-O4-H3, H6-O4-H3)
2	42.6% (H5-O4-H3, H6-O4-H3), 30.0% H5-O4-H3-O1, 27.3% O4-H3-O1-H2
1	97.8% O4-H3-O1-H2

Table 10: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D2D5D6** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.



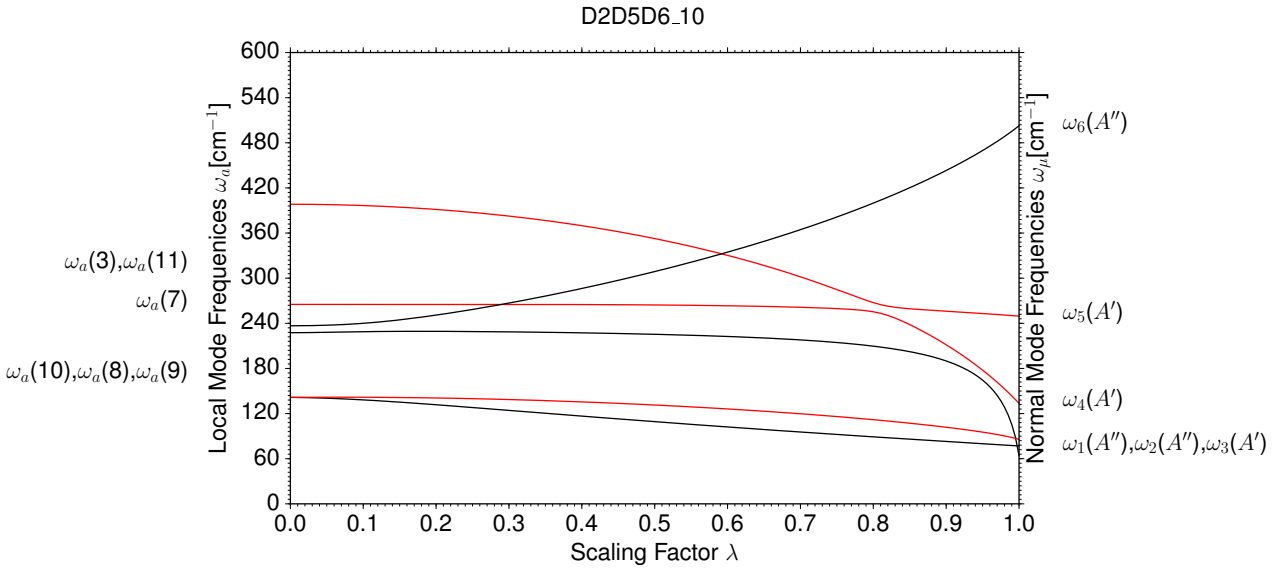
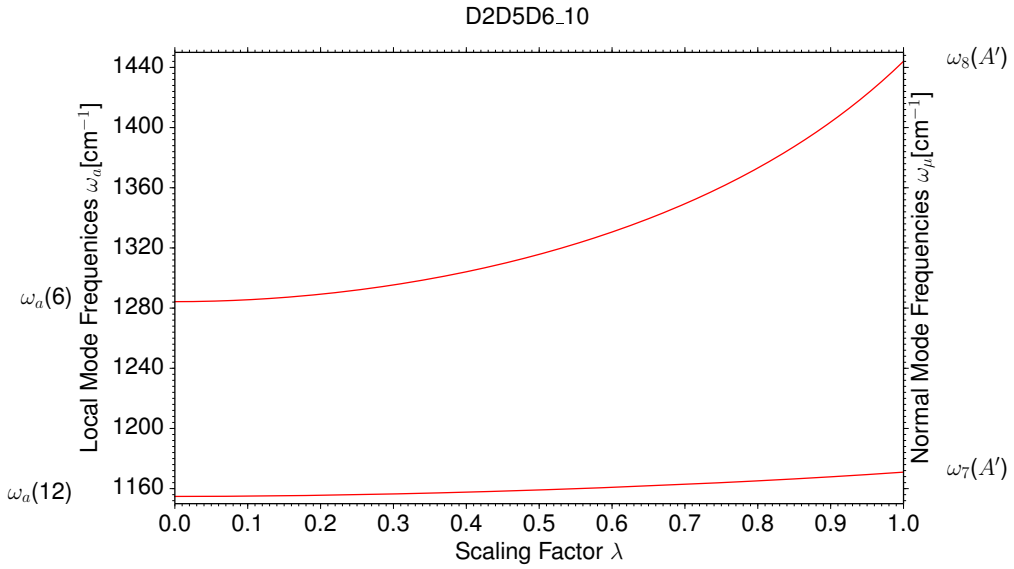


Figure 19: Decomposition of the 12 normal modes of the deuterated water dimer **D2D5D6** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).



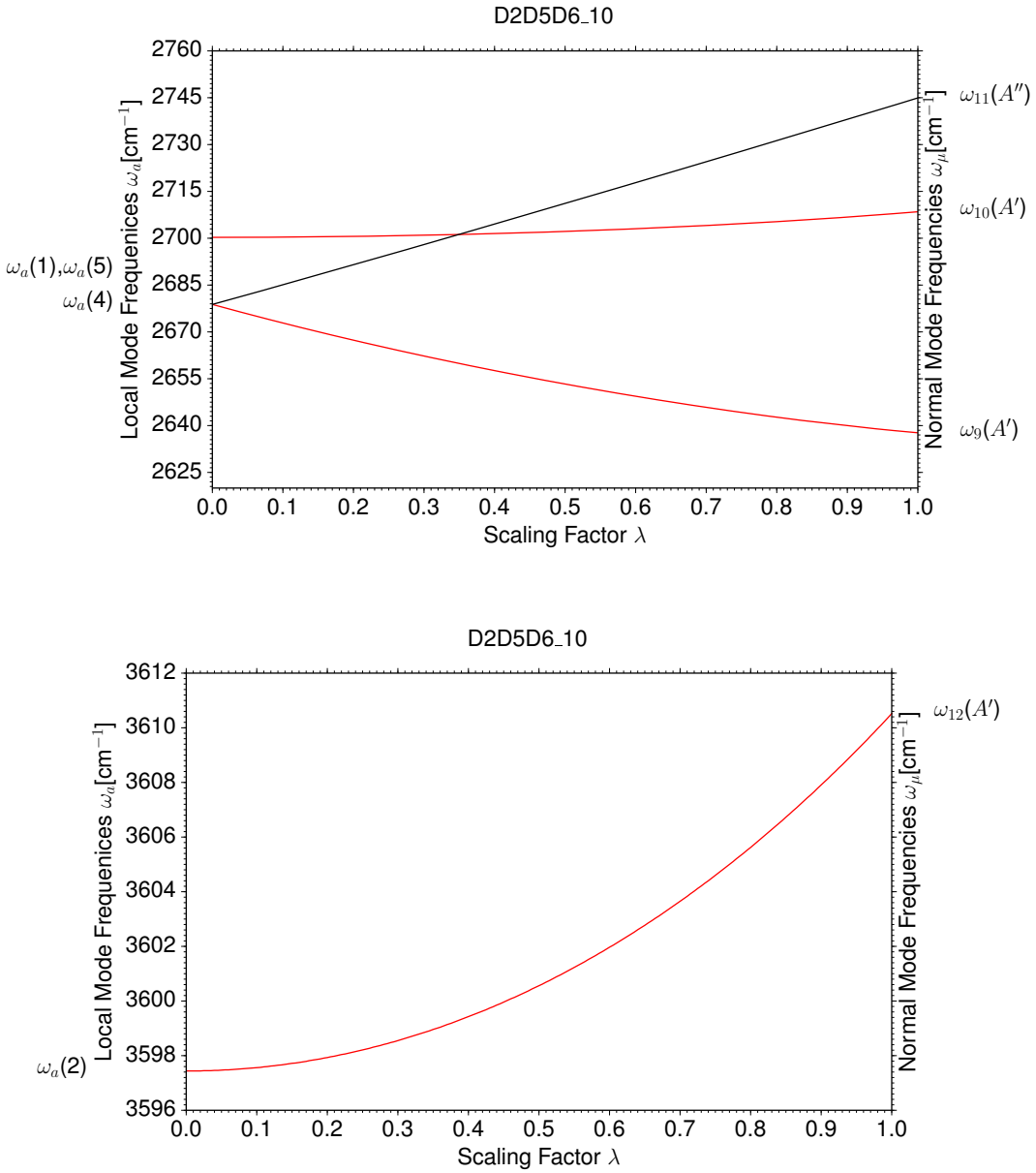
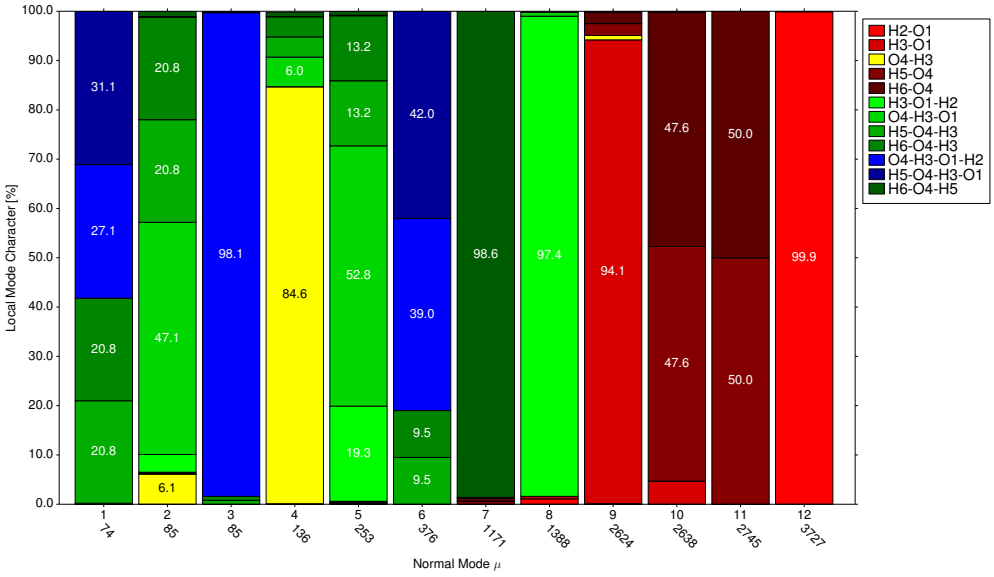


Figure 20: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D2D5D6**. **a**) Range from 0 to 600 cm^{-1}. **b**) Range from 1160to 1440 cm^{-1}. **c**) Range from 2620 to 2760 cm^{-1}. **d**) Range from 3596 to 3612 cm^{-1}.

Deuterated Water Dimer **D3D5D6**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	99.9% H2-O1
11	100.0% (H5-O4, H6-O4)
10	95.2% (H5-O4, H6-O4)
9	94.1% H3-O1
8	97.4% H3-O1-H2
7	98.6% H6-O4-H5
6	42.0% H5-O4-H3-O1, 39.0% O4-H3-O1-H2, 19.0% (H5-O4-H3, H6-O4-H3)
5	52.8% O4-H3-O1, 26.4% (H5-O4-H3, H6-O4-H3), 19.3% H3-O1-H2
4	84.6% O4-H3, 6.0% O4-H3-O1
3	98.1% O4-H3-O1-H2
2	47.1% O4-H3-O1, 41.6% (H5-O4-H3, H6-O4-H3), 6.1% O4-H3
1	41.6% (H5-O4-H3, H6-O4-H3), 31.1% H5-O4-H3-O1, 27.1% O4-H3-O1-H2

Table 11: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **D3D5D6** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.



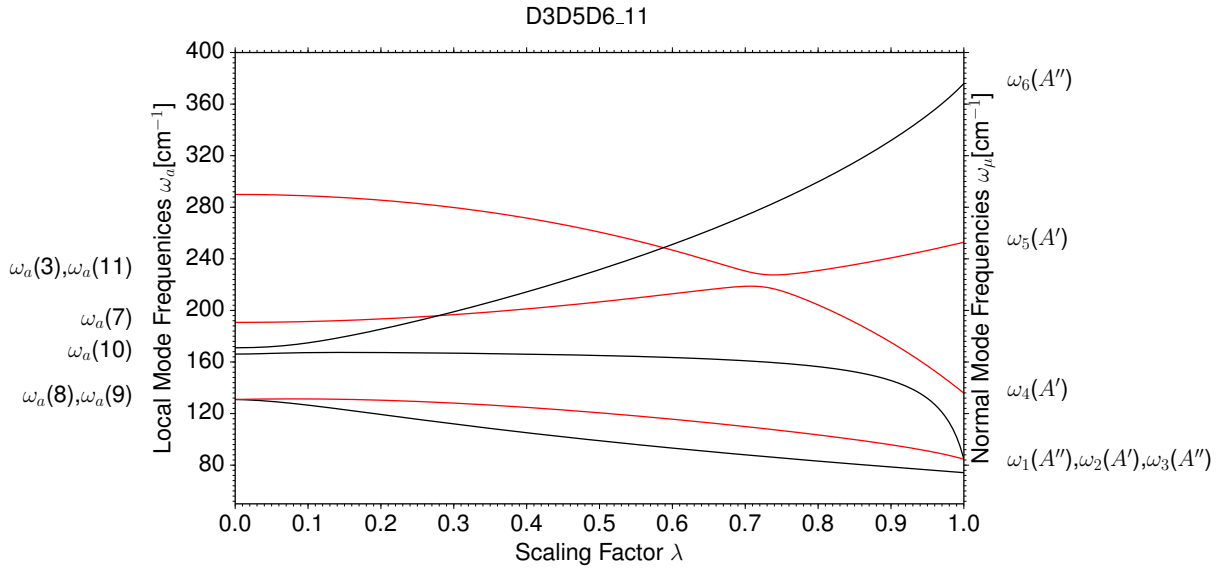
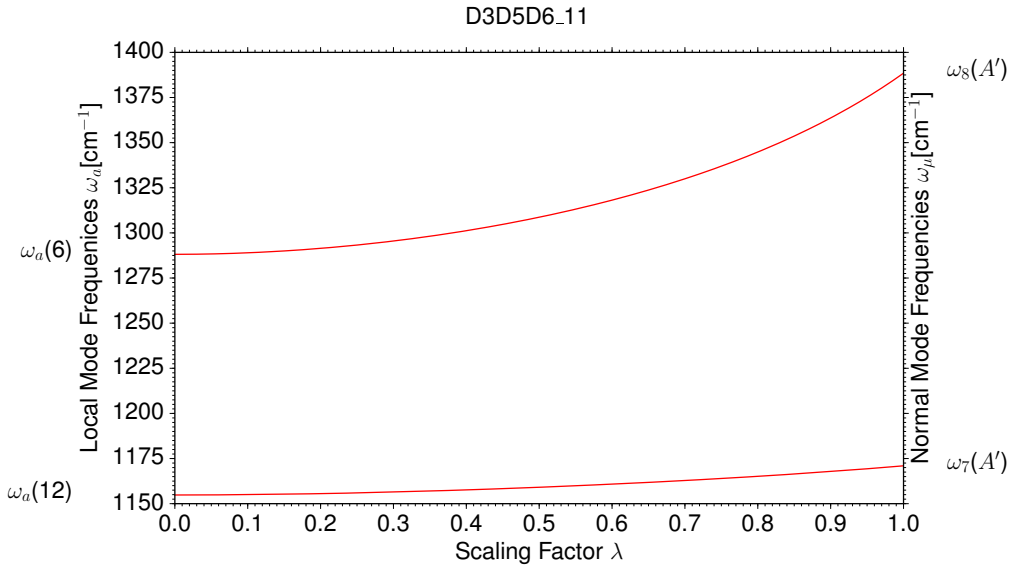


Figure 21: Decomposition of the 12 normal modes of the deuterated water dimer **D3D5D6** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).



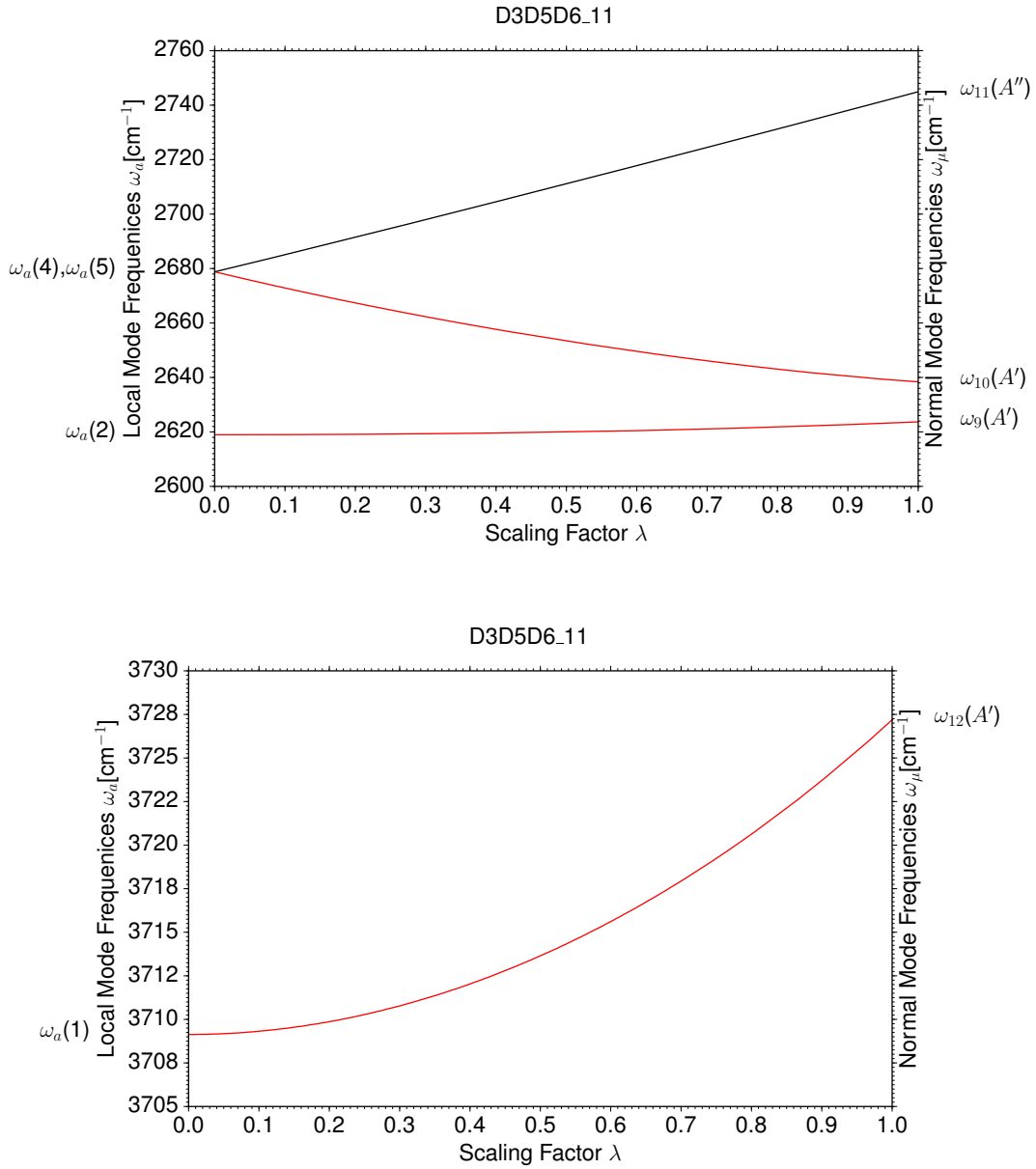


Figure 22: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **D3D5D6**. **a**) Range from 0 to 400 cm^{-1}. **b**) Range from 1150 to 1400 cm^{-1}. **c**) Range from 2600 to 2760 cm^{-1}. **d**) Range from 3705 to 3730 cm^{-1}.

Deuterated Water Dimer **All D**

μ	Characterization of modes ω_μ in terms of modes ω_a
12	100.0% (H5-O4, H6-O4)
11	83.8% H2-O1, 16.0% H3-O1
10	99.2% (H5-O4, H6-O4)
9	82.7% H3-O1, 15.8% H2-O1
8	95.2% H3-O1-H2
7	97.2% H6-O4-H5
6	42.3% H5-O4-H3-O1, 38.5% O4-H3-O1-H2, 19.2% (H5-O4-H3, H6-O4-H3)
5	39.5% O4-H3-O1, 34.2% (H5-O4-H3, H6-O4-H3), 23.1% H3-O1-H2
4	88.6% O4-H3, 5.8% O4-H3-O1
3	49.5% O4-H3-O1, 40.6% (H5-O4-H3, H6-O4-H3)
2	41.8% (H5-O4-H3, H6-O4-H3), 31.1% H5-O4-H3-O1, 27.0% O4-H3-O1-H2
1	98.3% O4-H3-O1-H2

Table 12: Characterization of the normal modes ω_μ(Exp.) of the deuterated water dimer **All D** in terms of the local mode contributions ω_a(Exp.). Only local mode contributions larger than 5.0% are given.

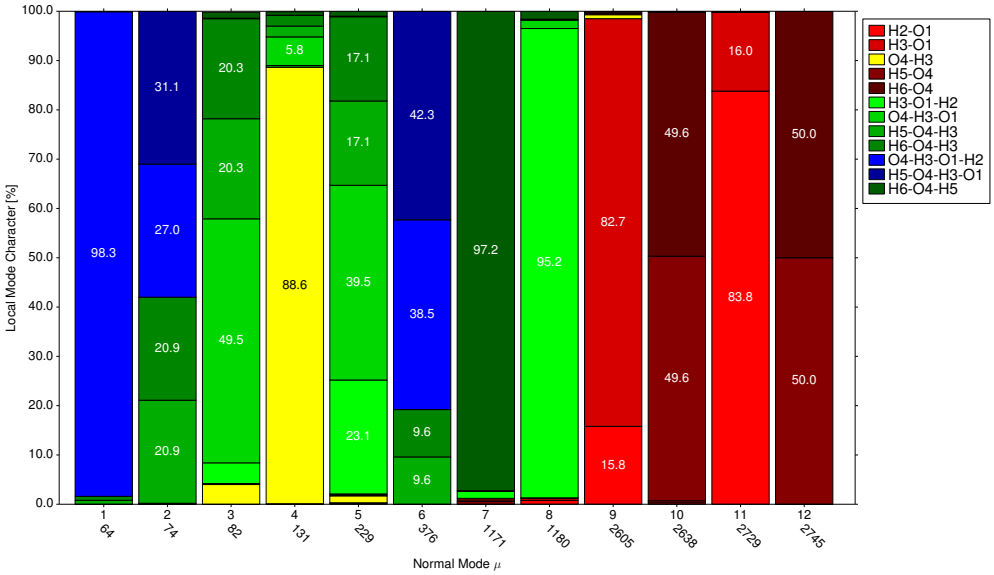
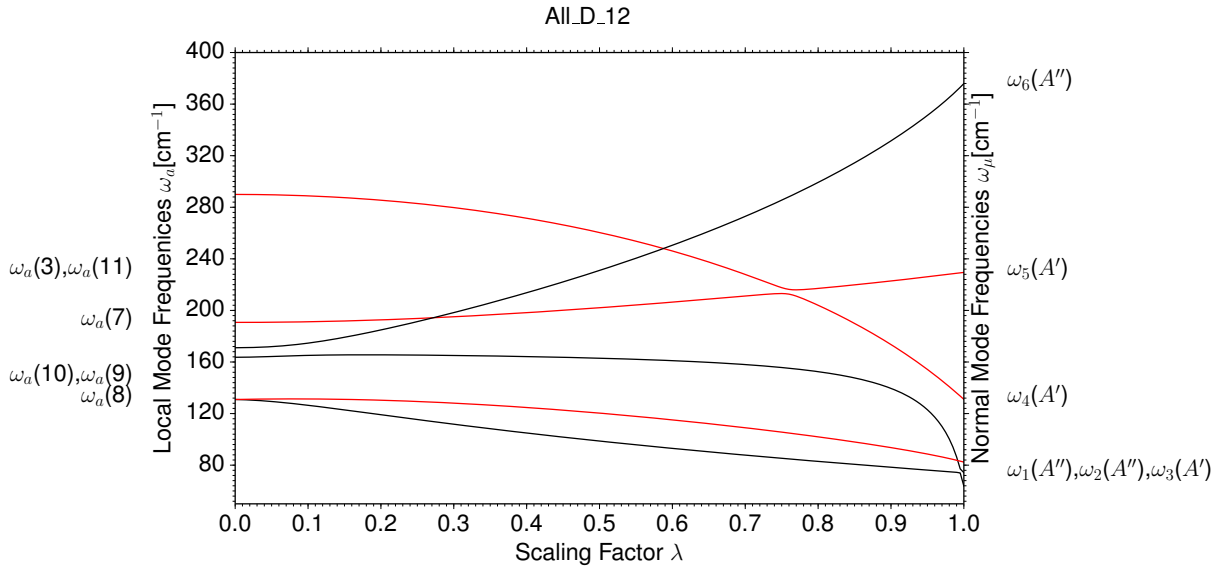
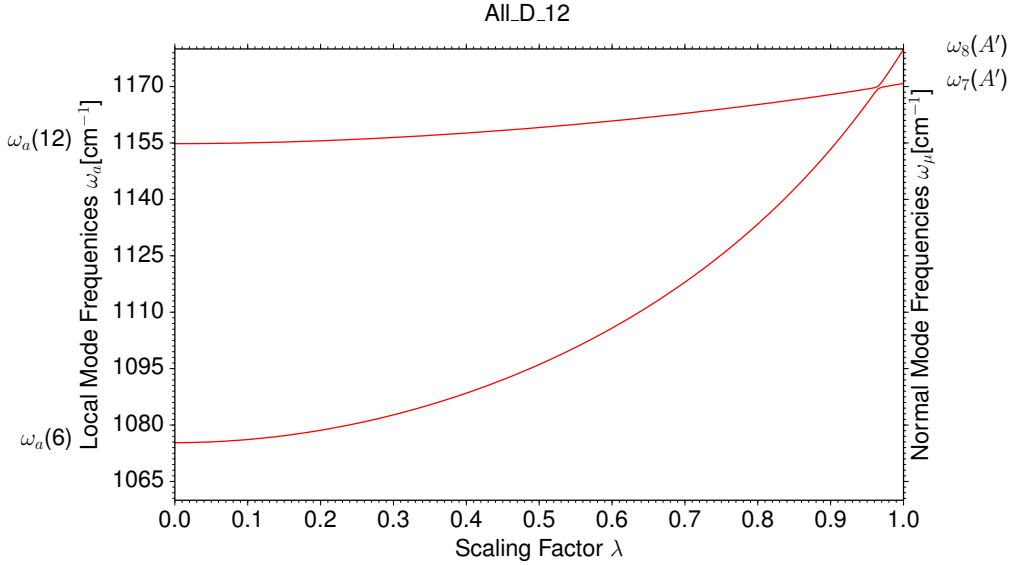


Figure 23: Decomposition of the 12 normal modes of the deuterated water dimer **All D** into local modes. Contributions are given in % and are color-coded for the local modes (identified via the internal coordinate driving a local mode and given on the right).


All_D_12
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(3),ω_a(11)
ω_a(7)
ω_a(10),ω_a(9)
ω_a(8)
$\omega_6(A'')$
$\omega_5(A')$
$\omega_4(A')$
$\omega_1(A''),\omega_2(A''),\omega_3(A')$


All_D_12
Local Mode Frequenices ω_a[cm^{-1}]
Normal Mode Frequencies ω_μ[cm^{-1}]
Scaling Factor λ
ω_a(12)
ω_a(6)
$\omega_8(A')$
$\omega_7(A')$

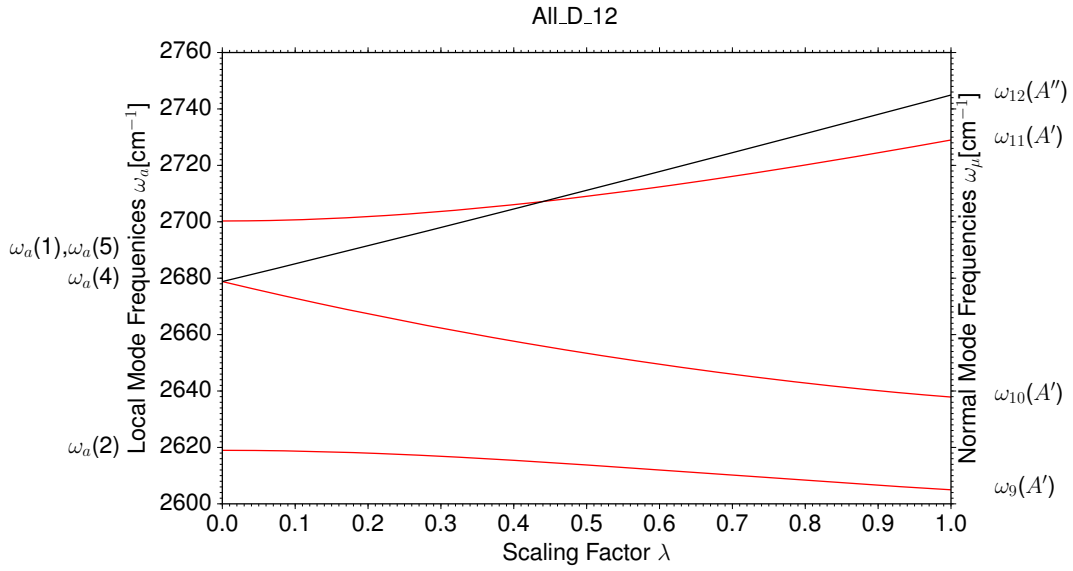


Figure 24: Adiabatic connection scheme relating local mode frequencies (left) to the measured normal mode frequencies (right) of the deuterated water dimer **All D**. **a**) Range from 0 to 400 cm^{-1}. **b**) Range from 1060 to 1180 cm^{-1}. **c**) Range from 2600 to 2760 cm^{-1}.