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

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The water dimer and its 11 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. However, utilizing 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^{-1}. The binding energy D_0 of the water dimer increases upon deuterium substitution from 3.28 to maximally 3.71 kcal mol^{-1} 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.

Introduction

The water dimer (**WD**) is the prototype of a H-bonded complex and therefore a large number of experimental and computational investigations have been carried out to determine its properties (for excellent summaries, see Refs [1] and [2]).[3–9] Sensitive tools for studying H-bonded complexes are rotational and vibrational spectroscopy where, in particular, far infrared spectroscopy has significantly improved the possibility of directly describing H-bonds via their stretching and bending motions. This has led to a full account of the 12 fundamentals of the vibrational spectrum of the **WD**.[10–12] Rotational spectroscopy has focused more on the dynamic processes, which the **WD** can undergo in the form of low energy tunnelling exchange of donor and acceptor hydrogen atoms. These rearrangements lead to a distinct splitting of the rotational levels of the **WD**, thus providing insight into the nature of the H-bond.[13] Recently, this research has been highlighted by the first observation of the rotationally resolved millimetre-wave spectrum of the **WD** at room temperature and reduced pressure.[14]

A number of studies have been carried out for deuterated isotopomers of the **WD**.[13,15–18] Fraser and co-workers[16] studied the rotation-tunnelling spectra of 8 of the 11 possible D-substituted **WD**s (see Fig. 1). However, there is little information on the changes in the vibrational spectra of the **WD** upon D-substitution.

In previous work, we have demonstrated how the vibrational properties of a molecule can be used to obtain a reliable insight into its electronic structure and bonding features.[19–23] This approach is especially attractive when applied to H-bonded complexes[24] and when measured vibrational frequencies, rather than calculated vibrational frequencies, are available.[25,26] In this work, we will extend the description of

molecular properties based on measured vibrational frequencies to determine the vibrational properties of isotopomers of a given target molecule. The target of our investigation will be the **WD**, for which a complete set of measured vibrational frequencies is available. We will use these frequencies to obtain a vibrational description of the 11 deuterium isotopomers of the **WD** shown in Fig. 1. Our investigation is meant to fulfil three different objectives: i) By determining the vibrational frequencies of the isotopomers shown in Fig. 1 we will facilitate the spectroscopic identification of deuterated **WD**s with the help of infrared or Raman spectroscopy. ii) Once these frequencies are available, the calculation of binding energies and enthalpies of the **WD** isotopomers at finite temperatures becomes possible. Accordingly, the stability of an isotopomer under given environmental conditions can be predicted. iii) Finally, there is the possibility of using the vibrational frequencies for the characterization of D-bonding as opposed to H-bonding. For this purpose, the local (localized) rather than normal (delocalized) vibrational modes have to be determined because only these modes can provide a reliable measure for the strength of a bond.[27]

For more than five decades, spectroscopists and theoreticians have attempted to determine local vibrational modes, which can be assigned to a specific structural unit such as a bond length, a bond angle, or a dihedral angle. Limited success leading, for example, to the spectroscopic description of chemical bonds is associated with the names of Decius, McKean, Henry, and many others.[28–35] Recently, we proved[36,37] that the local counterparts of the normal modes are the adiabatic modes of Konkoli and Cremer.[38,39] These authors solved the mass-decoupled Euler–Lagrange equations and obtained adiabatic (relaxed) vibrational modes, each of which is associated with a specific
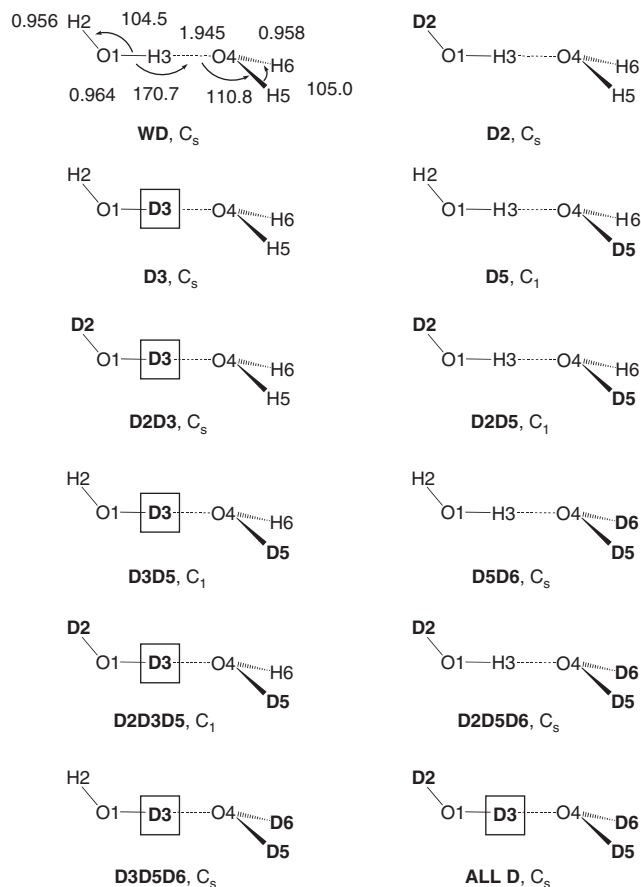
Fig. 1. The water dimer and its 11 deuterium isotopomers. CCSD(T)/CBS geometry of the water dimer. Bond lengths in Å and angles in degrees. The numbering of atoms is used throughout this work. Those isotopomers with a D-bond are indicated.

internal coordinate used to describe the molecule in question.[38] Larsson and Cremer showed that the adiabatic local modes verify the local character of McKean's isolated stretching modes and that of Henry's overtone modes.[20,40]

Zou and co-workers[36,37] proved that the adiabatic modes of Konkoli and Cremer directly relate to vibrational normal modes, explain the compliance constants of Decius, and provide an analytic description of mode-mode coupling via an adiabatic connection scheme (ACS). The Konkoli–Cremer adiabatic local modes for the isotopomers of the **WD** will be used in this work for the purpose of analyzing and explaining trends in their frequencies.

Results of this work will be presented in the following three sections. In the next section, the computational procedures used in this work are shortly described. In the third section, the isotopomer frequencies of the **WD** will be analyzed and their impact on the stability of the 11 D-substituted isotopomers discussed.

Computational Methods

The binding energy D_e of the **WD** was calculated by carrying out a set of CCSD(T) calculations[41] with aug-cc-pVXZ basis sets of increasing size, i.e. for X = D, T, Q, 5[42,43] for both the H-bonded dimer and the monomer. For each basis set, the equilibrium geometry of the complex was determined so that via extrapolation of calculated geometry parameters a reliable

CCSD(T)/CBS (complete basis set) limit geometry could be obtained.[44–46] In the same way, CCSD(T)/CBS values for D_e and the 12 vibrational frequencies of the **WD** were determined. For both energy and geometry, we used a 3-point and a 2-point extrapolation procedure always including the CCSD(T)/aug-cc-pV5Z results. Both procedures led to results differing by less than 0.01 kcal mol^{-1} (1 kcal mol^{-1} = 4.186 kJ mol^{-1}), 0.001 Å, and 0.1°.

The normal mode frequencies obtained in this way suffer from the harmonic approximation used in the CCSD(T) calculations. Even when calculating anharmonicity corrections[47,48] or applying efficient scaling procedures,[23,26] there is no guarantee that *ab initio* frequencies accurately reproduce the exact fundamental frequencies measured for a given target molecule. Therefore, we base the calculation of the isotopomer frequencies of the **WD** on the experimental frequencies rather than the CCSD(T)/CBS frequencies of the harmonic approximation. From the latter, we use only the (harmonic) normal mode vectors, which are needed for the analysis as described below.

For this purpose of determining the isotopomer frequencies, we start from the Wilson equation of vibrational spectroscopy:[49]

$$\mathbf{F}^q \mathbf{D} = \mathbf{G}^{-1} \mathbf{D} \boldsymbol{\Lambda} \tag{1}$$

where $\mathbf{F}^q$ is the calculated force constant matrix expressed in internal coordinates q_n, $\mathbf{D}$ collects the vibrational eigenvectors $\mathbf{d}_\mu$ in form of column vectors ($\mu = 1, \cdots, N_{vib}$ with $N_{vib} = 3N - L$; N: number of atoms; L: number of translations and rotations), $\mathbf{G}$ is the Wilson G-matrix,[49] and $\boldsymbol{\Lambda}$ is a diagonal matrix containing the vibrational eigenvalues $\lambda_\mu = 4\pi^2 c^2 \omega_\mu^2$ where ω_μ represents the harmonic vibrational frequency of mode $\mathbf{d}_\mu$ as calculated at the CCSD(T)/aug-cc-pVXZ level of theory.

One can assume that the calculated normal mode vectors $\mathbf{d}_\mu$ represent a reasonable approximation to the true normal mode vectors $\mathbf{d}'_\mu$ so that $\mathbf{D} \approx \mathbf{D}'$. This assumption is in line with the fact that reasonable approximations to the experimental frequencies can be obtained by simple scaling procedures of the calculated harmonic frequencies. As a matter of fact, all scaling procedures are based on the assumption that $\mathbf{D}$ is close to the true $\mathbf{D}'$. One can improve the CCSD(T) force constants utilizing the known experimental frequencies and applying first order perturbation theory:

$$(\mathbf{F}^q + \Delta\mathbf{F}^q)\mathbf{D}' = \mathbf{G}^{-1}\mathbf{D}'(\boldsymbol{\Lambda} + \Delta\boldsymbol{\Lambda}) \tag{2}$$

where $\mathbf{F}^q$ and $\boldsymbol{\Lambda}$ are based on the CCSD(T) calculations. The diagonal matrix $\Delta\boldsymbol{\Lambda}$ can be derived from the differences $\omega_\mu^{cal} - \omega_\mu^{exp}$. Hence, the unknown perturbation matrix $\Delta\mathbf{F}^q$ can be obtained from Eqn 3:

$$\Delta\mathbf{F}^q \mathbf{D} = \mathbf{G}^{-1}\mathbf{D}\Delta\boldsymbol{\Lambda} \tag{3}$$

where $\mathbf{D}'$ is replaced by $\mathbf{D}$. Using standard procedures, $\Delta\mathbf{F}^q$ and by this $\mathbf{F}^{q'} = \mathbf{F}^q + \Delta\mathbf{F}^q$ can be calculated.

Once Eqn 3 has been solved, the frequencies of any isotopomer can be calculated by inserting the appropriate masses into the $\mathbf{G}$ matrix and solving the Wilson equation (Eqn 1) again for the new $\mathbf{G}$ matrix and the known matrix $\mathbf{F}^{q'}$. Both the normal mode frequencies and the normal mode vectors depend on the mass distribution in an isotopomer of the **WD** whereas the force constant matrix does not change since it depends just on the electronic structure. There is a secondary

Table 1. **The normal mode frequencies of the water dimer and its 11 isotopomers based on the experimental frequencies of the former and an perturbational approach as described in the text**

Normal mode frequencies of H_2O are 1649, 3832, and 3943; HDO, 1445, 2824, and 3890; D_2O, 1207, 2762, and 2889

	WD	D2	D3	D5	D2D3	D2D5	D3D5	D5D6	D2D3D5	D2D5D6	D3D5D6	ALL D
12	3745(A″)	3745(A″)	3745(A″)	3704(A)	3745(A″)	3704(A)	3704(A)	2745(A″)	3704(A)	2745(A″)	2745(A″)	2745(A″)
11	3735(A′)	2708(A′)	3727(A′)	3735(A)	2729(A′)	2708(A)	3727(A)	3735(A′)	2729(A)	2708(A′)	3727(A′)	2729(A′)
10	3660(A′)	3660(A′)	3660(A′)	2690(A)	3660(A′)	2690(A)	2690(A)	2638(A′)	2690(A)	2638(A′)	2638(A′)	2638(A′)
9	3601(A′)	3610(A′)	2624(A′)	3601(A)	2605(A′)	3610(A)	2624(A)	3601(A′)	2605(A)	3611(A′)	2624(A′)	2605(A′)
8	1616(A′)	1444(A′)	1389(A′)	1615(A)	1180(A′)	1444(A)	1388(A)	1615(A′)	1180(A)	1444(A′)	1388(A′)	1180(A′)
7	1599(A′)	1600(A′)	1600(A′)	1403(A)	1600(A′)	1402(A)	1403(A)	1171(A′)	1403(A)	1171(A′)	1171(A′)	1171(A′)
6	523(A″)	523(A″)	404(A″)	512(A)	404(A″)	512(A)	390(A)	503(A″)	390(A)	503(A″)	376(A″)	376(A″)
5	311(A′)	104(A′)	102(A′)	300(A)	98(A′)	263(A)	265(A)	290(A′)	244(A)	86(A′)	253(A′)	82(A′)
4	143(A′)	135(A′)	138(A′)	141(A)	132(A′)	135(A)	137(A)	139(A′)	132(A)	134(A′)	136(A′)	131(A′)
3	108(A′)	276(A′)	280(A′)	106(A)	260(A′)	104(A)	100(A)	88(A′)	97(A)	250(A′)	85(A′)	229(A′)
2	103(A″)	103(A″)	96(A″)	81(A)	96(A″)	81(A)	79(A)	77(A″)	78(A)	77(A″)	74(A″)	74(A″)
1	88(A″)	68(A″)	88(A″)	86(A)	68(A″)	65(A)	86(A)	85(A″)	65(A)	64(A″)	85(A″)	64(A″)

dependence of the isotopomer frequencies on the approximation used when calculating matrix **D** in the perturbation approach. By varying the normal mode calculation from coupled cluster to density functional theory (DFT) (B3LYP[50,51] and ωB97X-D[52,53]), the largest variation ($\leq 10\,cm^{-1}$) was found for the stretching frequencies, which still guarantees a sufficient accuracy for the spectroscopic identification of the isotopomers of the **WD** with the help of the normal mode frequencies presented in this work.

If $\mathbf{K}'$ is the diagonal matrix, which is obtained by diagonalizing $\mathbf{F}^{q'}$, then the local vibrational modes are obtained according to Konkoli and Cremer[37,38] as

$$\mathbf{a}_n = \frac{(\mathbf{K}')^{-1}\mathbf{d}_n^\dagger}{\mathbf{d}_n(\mathbf{K}')^{-1}\mathbf{d}_n^\dagger} \qquad (4)$$

where $\mathbf{d}_n$ is now a row vector of matrix **D**. The local mode force constant k_n^a is given by Eqn 5:

$$k_n^a = \mathbf{a}_n^\dagger \mathbf{K}' \mathbf{a}_n \qquad (5)$$

The compliance constants Γ_n of Decius[28] are nothing else but the inverse of the local mode force constants k_n^a:[36,37]

$$k_n^a = \frac{1}{\Gamma_n^q} \qquad (6)$$

i.e. the constants Γ_n obtain their physical meaning via the local vibrational modes of Konkoli and Cremer.[38]

One can re-write the Wilson equation (Eqn 1) with the help of the compliance matrix $\mathbf{\Gamma}^q$ as:[36,37]

$$\mathbf{G}(\mathbf{\Gamma}^q)^{-1}\mathbf{D} = \mathbf{D}\,\mathbf{\Lambda}$$

$$\mathbf{G}\,\mathbf{R} = \mathbf{\Gamma}^q\mathbf{R}\mathbf{\Lambda} \qquad (7)$$

where the new eigenvector matrix **R** is given by $(\mathbf{\Gamma}^q)^{-1}\mathbf{D}$. Zou and co-workers[36,37] partitioned matrices $\mathbf{\Gamma}^q$ and **G** into diagonal ($\mathbf{\Gamma}_d^q$ and $\mathbf{G}_d$) and off-diagonal ($\mathbf{\Gamma}_o^q$ and $\mathbf{G}_o$) parts:

$$(\mathbf{G}_d + \lambda\,\mathbf{G}_o)\,\mathbf{R}_\lambda = (\mathbf{\Gamma}_d^q + \lambda\,\mathbf{\Gamma}_o^q)\,\mathbf{R}_\lambda\mathbf{\Lambda}_\lambda \qquad (8)$$

where the scaling factor λ varies from 0 to 1. For $\lambda = 0$, the local vibrational modes are obtained whereas $\lambda = 1$ defines the normal vibrational modes. Eqn 8 is the basis for the ACS, which, by increasing parameter λ stepwise from 0 to 1, relates local vibrational modes to normal vibrational modes in terms of their eigenvalues (frequencies) and eigenvectors (mode vectors).[36,37] In this way, each normal mode frequency ω_μ can be expressed by a local mode frequency ω_a and a coupling frequency ω_c, i.e. $\omega_\mu = \omega_a + \omega_c$. The zero-point energy (ZPE) is split up in two parts where one results from the local mode frequencies and one from the coupling frequencies.[36]

The experimental frequencies of the **WD** were taken from the literature.[10–12] The normal vibrational modes are characterized in terms of local vibrational modes using the CNM (characterizing normal modes) approach by Konkoli and Cremer[39] as integrated in the quantum chemical program package *COLOGNE2013*.[54] For the calculation of the CCSD(T) energies, geometries, and harmonic vibrational modes, the program *CFOUR*[55] was used.

Results and Discussion

In Fig. 1, the CCSD(T)/CBS geometry of the **WD** is given. The corresponding binding energy D_e is $5.00\,kcal\,mol^{-1}$. These properties are the same for all 12 isotopomers shown in Fig. 1. Differences are found for those molecular properties, which depend directly or indirectly (via the vibrational frequencies) on the mass distribution in the complex. In Table 1, the vibrational frequencies of the eleven isotopomers of the **WD**, correctly ordered according to symmetry and mode character, are compared with those measured for the parent complex. Table 2 contains binding energies $D^0 = \Delta E_0$, enthalpies $\Delta H(T)$, and free energies $\Delta G(T)$ for various temperature (T) values. Local OH and OD stretching frequencies ω_n^a based on the normal mode frequencies ω_μ of Table 1 are given in Table 3.

Replacement of one H atom by deuterium leads, on the average, to a lowering of the ZPE from $27.49\,kcal\,mol^{-1}$ by about $1.85\,kcal\,mol^{-1}$ to $25.65\,kcal\,mol^{-1}$ (Table 2). This energy change is predominantly caused by the O–H/O–D stretching frequency change (for **D2** from 3735 to $2708\,cm^{-1}$), which is complemented by smaller changes in bending and out-of-plane frequencies (see Table 1). Each D/H-exchange leads to decrease of the ZPE by about $1.8 – 1.9\,kcal\,mol^{-1}$ so that for the **ALL D** isotopomer a ZPE of $20.0\,kcal\,mol^{-1}$ is the result (Table 2).

For the water molecule, the changes in the ZPE value of $12.88\,kcal\,mol^{-1}$ are 1.81 and $1.86\,kcal\,mol^{-1}$ for the replacement of the two H atoms by D. Because of the loss of six

Table 2.   Calculated binding energies of the isotopomers of the water dimer

ZPE: zero point energy of isotopomer; ΔZPE: ZPE contribution to $D_0 = D_e + ZPE$, which is the binding energy at 0 K; ΔH(298K): binding enthalpy at 298 K; S: entropy of the isotopomer; ΔS: entropy contribution to the free binding energy; ΔG(298 K): free binding energy at 298 K and 1 atm; ΔG(80 K): free binding energy at 80 K and 110 Pa, at which spectroscopic measurements are carried out. For the notation of isotopomers, see Fig. 1. The ZPE values for H_2O, HDO, and D_2O are 12.88, 11.15, and 9.37 kcal mol^{-1}; those for the entropy 45.1, 46.2, and 47.3 cal K^{-1} mol^{-1}, respectively

Molecule	ZPE [kcal mol^{-1}]	ΔZPE [kcal mol^{-1}]	D [kcal mol^{-1}]	ΔH(298) [kcal mol^{-1}]	S [cal K^{-1} mol^{-1}]	ΔS [cal K^{-1} mol^{-1}]	ΔG(298) [kcal mol^{-1}]	ΔG(80) [kcal mol^{-1}]
WD	27.49	−1.74	3.28	3.47	72.9	17.2	−1.66	2.58
D2	25.70	−1.67	3.34	3.47	74.2	17.1	−1.63	2.51
D3	25.52	−1.49	3.52	3.60	73.8	17.4	−1.60	2.65
D5	25.70	−1.67	3.35	3.49	74.0	17.3	−1.67	2.51
D2D3	23.70	−1.45	3.57	3.60	75.1	17.3	−1.57	2.57
D2D5	23.90	−1.60	3.41	3.49	75.3	17.2	−1.64	2.44
D3D5	23.72	−1.42	3.59	3.63	74.9	17.5	−1.60	2.58
D5D6	23.85	−1.60	3.41	3.51	75.0	17.4	−1.67	2.44
D2D3D5	21.90	−1.37	3.64	3.62	76.1	17.4	−1.58	2.50
D2D5D6	22.06	−1.54	3.48	3.51	76.3	17.3	−1.64	2.37
D3D5D6	21.87	−1.35	3.66	3.65	76.0	17.6	−1.60	2.52
ALL D	20.05	−1.30	3.71	3.64	77.2	17.5	−1.58	2.43

Table 3.   Local OH and OD stretching frequencies based on the normal mode frequencies of the isotopomers of the water dimer

Local mode frequencies of H_2O are 3690 and 1595; HDO, 3690, 2687, and 1398; D_2O, 2687 and 1169 cm^{-1}

Parameter	WD	D2	D3	D5	D2D3	D2D5	D3D5	D5D6	D2D3D5	D2D5D6	D3D5D6	ALL D
H(D)2-O1	3709	2700	3709	3709	2700	2700	3709	3709	2700	2700	3709	2700
H(D)3-O1	3597	3597	2619	3597	2619	3597	2619	3597	2619	3597	2619	2619
H(D)3-O4	398	398	290	398	290	398	290	398	290	398	290	290
H(D)5-O4	3680	3680	3680	2679	3680	2679	2679	2679	2679	2679	2679	2679
H(D)6-O4	3680	3680	3680	3680	3680	3680	3680	2679	3680	2679	2679	2679

vibrational modes upon dissociation of the complex, the ZPE contribution to the binding energy is negative. Therefore, the D_e value of the **WD** is reduced from 5.01 kcal mol^{-1} (CCSD(T)/CBS result) to a D_0 value of 3.28 kcal mol^{-1} (ΔH(298) = 3.47 kcal mol^{-1}, Table 2).

The influence of $ΔZPE = 2 \times ZPE(monomer) - ZPE(dimer)$ is reduced from −1.74 to −1.67 kcal mol^{-1} when H2 is substituted by D2, which is negligible. A somewhat larger reduction of 0.25 kcal mol^{-1} is obtained for **D3**, which has a D_0 value of 3.52 kcal mol^{-1} (0.24 kcal mol^{-1} higher than that of the parent molecule, Table 2). As expected, the substitution of H3 by D3 leads to a larger change in the vibrational frequencies due to the involvement of H3/D3 in H-bonding. Similar observations can be made for all other D3-isotopomers: The binding energy D_0 increases by 0.25 − 0.43 kcal mol^{-1} relative to that of the **WD** (**ALL D**: 3.71 kcal mol^{-1}, Table 2). For all other isotopomers, changes are relatively small ranging from 0.07 to 0.20 kcal mol^{-1}, which reflects the fact that the ZPE contributions for the **WD** and two water molecules largely cancel each other. The changes in the binding enthalpies ΔH(298) are even smaller (slight increase from 3.47 to 3.64 kcal mol^{-1}).

Interesting observations are the changes in entropy S upon D-substitution of the **WD**. It is well-known that an increase of the atomic mass leads to a closer packing of the discrete rotational and vibrational levels because the mass is inversely proportional to the magnitude of the energy splittings. Hence, the number of possibilities of distributing a certain energy amount over the various rotational and vibrational energy levels increases and consequently so does entropy. For water, there is a an increase by 1 entropy unit (eu) per D-substitution from 45.1 to 46.2 and

47.3 eu (Table 2). A similar increase in S is obtained for the **WD**: For each additional D/H-exchange, S increases by about 1 eu so that the largest value (77.1 eu) is found for the **ALL D** isotopomer compared to 72.9 eu for the parent dimer.

The changes in the entropy are largely cancelled by the corresponding changes for two water molecules. Furthermore, changes in enthalpy and entropy largely cancel each other when calculating free binding energies ΔG(298). According to the calculated free energy values ΔG(298) of −1.63 ± 0.05 kcal mol^{-1} (Table 2), none of the 12 water dimer isotopomers can be observed at room temperature. However, ΔG(80) adopts a value of 2.6 kcal mol^{-1}, which was obtained for a reduced pressure of 110 Pa (0.001 atm, Table 2). Under these conditions, all isotopomers are spectroscopically observable.

Description of the H-bond

Contrary to the strong changes in the normal mode O–H stretching frequencies upon D substitution (1000 − 1027 cm^{-1}, Table 1), the changes in the O4···H3 H-bond stretching frequency are marginal (≤ 12 cm^{-1}, Table 1) and vary between 143 and 131 cm^{-1}. The first value was obtained for the parent dimer with the help of far infrared spectroscopy and is verified by our CCSD(T)/CBS calculations. To the best of our knowledge, no spectroscopic H(D)-bonding stretching frequencies have been published for the 11 D-isotopomers. They are given now in Table 1 and do not seem to follow a specific pattern. This is surprising as it suggests that D-substitution has only a slightly reducing effect on the H-bond stretching frequency.
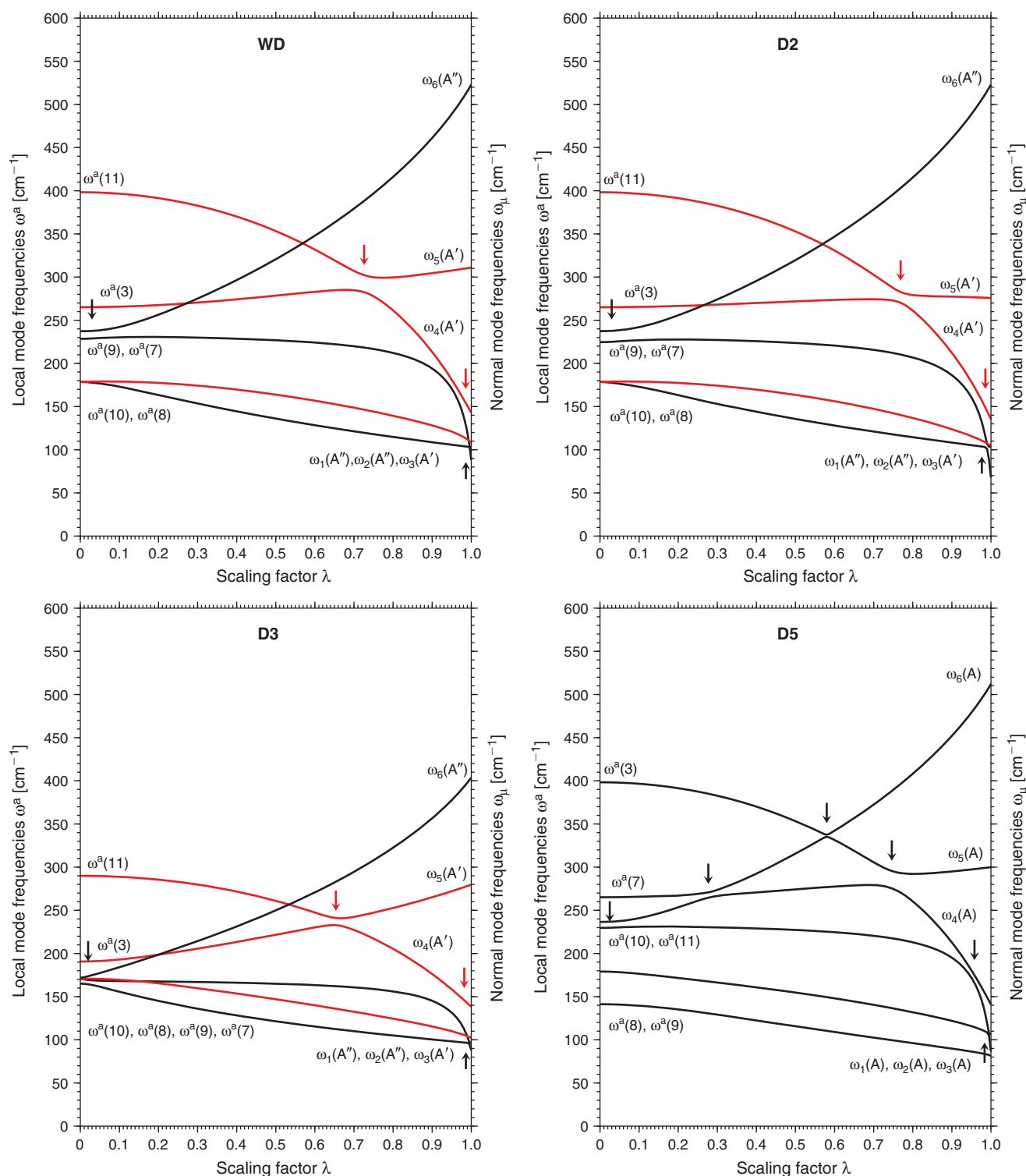
Fig. 2. Adiabatic connection schemes (ACS) for the frequency range of 0–600 cm^{-1} are given for the 12 isotopomers of the water dimer with deuterium substitutions denoted in by bold labels and avoided crossings indicated with arrows coloured by symmetry. The local mode frequency ω^a (on the left) and normal mode frequencies ω_n (on the right) are given. For normal mode symmetries and local mode numbering, see Supplementary Material.

The local stretching frequencies given in Table 3 underline the uniqueness of the local vibrational modes. An OH stretching frequency does not change when a D atom is incorporated at some other position in the dimer. Furthermore, the stretching frequencies reflect the strength of the different OH bonds, which is reliable in this case as the masses involved are the same for all

bonds (actually, only the force constant can provide a reliable account of the bond strength).[24] For the acceptor molecule, the O4H5 and O4H6 frequencies establish a reference of 3680 cm^{-1}. The donor bond O1H3 frequency is red-shifted by 83 cm^{-1} to 3597 cm^{-1} because of the weakening of the donor bond when establishing the H-bond. This leads to increased bond polarity
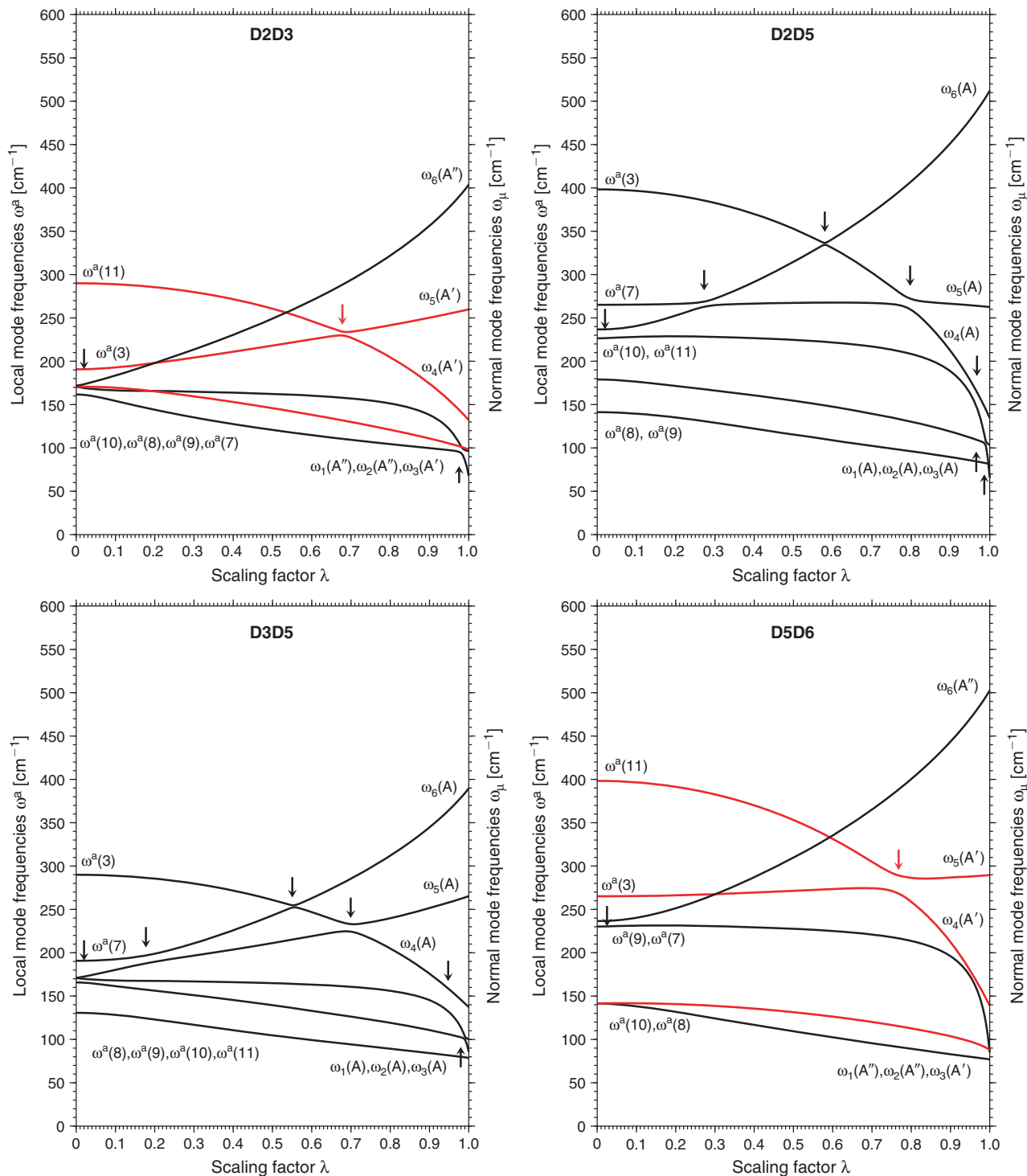
Fig. 2. (cont.)

and bond strengthening in the case of the O1–H2 bond as reflected by the frequency of 3709 cm^{-1} (increase by 29 cm^{-1}, Table 3).

The local H-bond stretching frequency is 398 cm^{-1} and this is significantly larger than the measured value of 143 cm^{-1}. The ACS diagrams in Fig. 2 reveal that mass coupling leads to a lowering of the local H-bond stretching frequency and subsequently to an avoided crossing (AC) at $\lambda = 0.75$ ($\sim$300 cm^{-1}) with the O1H3···O4 bending mode. At this AC, the mode character is exchanged with that of the lower frequency mode so that mode 4 gains the H-bond stretching character, with a strong

admixture of O1H3···O4 bending character. An additional AC with mode 3 for λ close to 1 leads to the admixture of H3···O4H5 and H3···O4H6 bending character. Although the H-bond stretching character of mode 4 still dominates (65 %, see Supplementary Material), one cannot draw any conclusions from the H-bond stretching frequency of 143 cm^{-1} on the strength of the H-bond in **WD**. This is only possible with the help of the local mode data.[36]

Exchanging H with D leads to a reduction of the local OH stretching frequency by about 1000 cm^{-1} to 2619 (O1–D3),
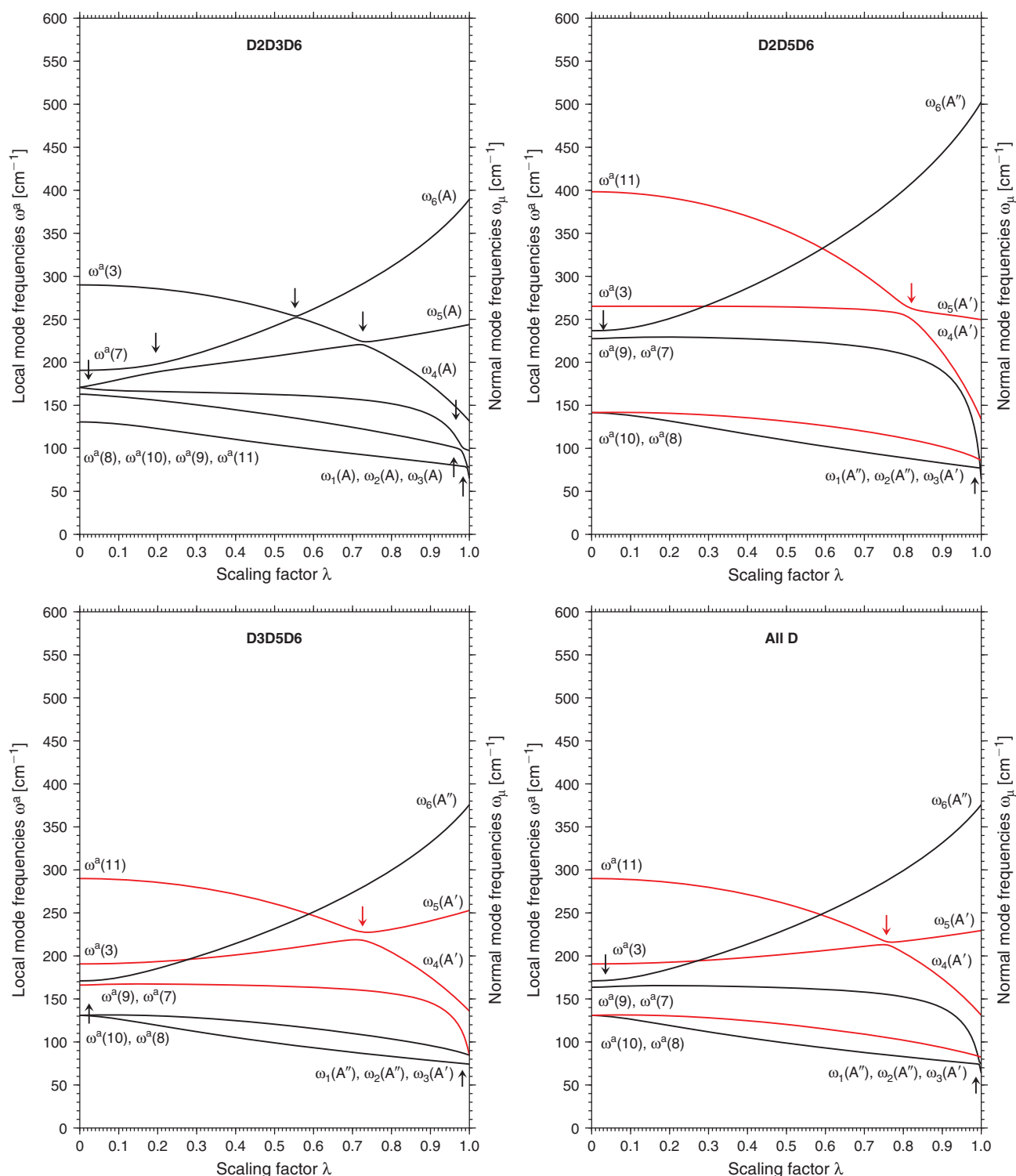
Fig. 2.   (cont.)

2679 (O4–D5), and 2700 cm^{-1} (O1–D2), respectively, but still reflecting the strength of the different bonds (the electronic structure does not change). For the H-bond, the local stretching frequency is lowered by 108 cm^{-1} to 290 cm^{-1}. Using the local OH/OD stretching modes, each isotopomer can be easily identified whereas an identification with the help of the normal mode frequencies is more difficult. The latter reveal how many H atoms are replaced by D atoms. However, without the normal

mode frequencies of the 12 isotopomers given in Table 1, it would be difficult to distinguish among all members of an n-D (n: number of D atoms) isotopomer set.

This holds true especially when investigating the H(D)-bond normal mode stretching frequency. Since the value of this frequency is bound by two ACs (see Fig. 2), it cannot change very much. If, by increasing deuteration, the frequency ω_2 is lowered and therefore the second AC less developed, then a

somewhat lower value for the H-bond stretching frequency becomes possible. The two ACs also influence the local character of the final normal mode dominated by H-bond stretching. At a diabatic AC, the two vibrational eigenstates (frequencies) approach each other closely, energy and mode characters are fully exchanged, and then the eigenstates depart. Such a diabatic AC is found for the completely deuterated species at $\lambda = 0.75$ between ω_4 and ω_5. The second AC for **ALL D** is less developed, due to a lowering of ω_2, and therefore mode 4 has the highest H-bond stretching character (89 %).

If the AC is more adiabatic (the gap between the two eigenstates at the AC is larger and the eigenstates are almost parallel for some λ-range) as for the **WD** itself (see Fig. 2), then a stronger mixing of the modes takes place and the resulting mode is more delocalized. The degree of diabatic or adiabatic AC depends on several factors where the mass ratios especially play a role.

Conclusions

The following conclusions can be drawn from this work:

1. The CCSD(T)/CBS geometry and binding energy D_e of the water dimer have been determined involving an aug-cc-pV5Z basis set. The binding energy is 5.00 kcal mol^{-1}, and is in good agreement with previous investigations.
2. Using a perturbational approach, the known experimental frequencies of the **WD**, and the calculated normal vibrational modes, the normal mode frequencies of its 11 deuterated isotopomers (see Fig. 1) have been determined (see Table 1). Tests reveal that these are accurate by ± 10 cm^{-1} or better.
3. Deuterium substitution increases the binding energy D_0 of the **WD** from 3.28 by maximally 0.43 kcal mol^{-1} to 3.71 kcal mol^{-1}. This is caused by a lowering of stretching and bending frequencies accompanying the mass doubling from H to D and a concomitant reduction of the (negative) ZPE contribution to the binding energy D_0. Somewhat smaller increases are also calculated for the binding enthalpy at 298 K, $\Delta H(298)$.
4. The entropies of the 11 isotopomers increase from 72.9 to maximally 77.2 eu (see Table 2) with an increase of the atomic masses, which is a result of the well-known denser spacing of rotational and vibrational energy levels.
5. Because of a cancellation of entropy and enthalpy changes, all isotopomers of the **WD** possess similar negative free binding energies $\Delta G(298)$, i.e. they are all unstable at room temperature.
6. Recalculation of the free binding energy for typical spectroscopic conditions (80 K and 110 Pa) leads to almost identical $\Delta G(80)$ values in the range 2.37 to 2.65 kcal mol^{-1}, which shows that all isotoomers are observable under these conditions.
7. The 12 isotopomers can be easily identified with the help of the normal mode frequencies given in this work, where the OH(D) stretching frequencies are especially helpful.
8. The variation in the H(D)-bond stretching frequency is less pronounced (143 – 131 cm^{-1}, Table 1) and does not even help to identify **D3**-isotopomers (isotopomers with D in position 3).
9. The easiest identification of the isotopomers is provided by their local mode frequencies. D3-substitution lowers the H-bond stretching frequency by about 198 cm^{-1} from 398 to 200 cm^{-1}. The relatively large change in the local

mode frequency is not reflected by the normal mode frequencies because of two avoided crossing with bending motions.
10. The procedure described in this work presents a general approach of obtaining and analyzing the normal mode frequencies of isotopomers once the frequencies of the parent molecule have been measured.

Supplementary Material

Tables of characterization of the normal modes in terms of the local mode contributions, bar diagrams of the decomposition of the normal modes into local modes, and adiabatic connection schemes for the water dimer isotopomers are available on the Journal's website.

Acknowledgements

References

[1] G. Gilli, P. Gilli, *The Nature of the Hydrogen Bond–IUCr Monographs on Crystallography 23* **2009** (Oxford University Press: New York, NY).
[2] *Hydrogen Bonding – New Insights* (Ed. S. J. Grabowski) **2006**, Challenges and Advances in Computational Chemistry and Physics Vol. 3 (Springer: New York, NY)
[3] K. Müller-Dethlefs, P. Hobza, *Chem. Rev.* **2000**, *100*, 143.
[4] T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48.
[5] N. Belkova, E. Shubina, L. M. Epstein, *Acc. Chem. Res.* **2005**, *38*, 624631.
[6] M. Meot-Ner, *Chem. Rev.* **2005**, *105*, 213.
[7] P. Munshi, T. Row, *Cryst. Rev.* **2005**, *11*, 199.
[8] P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, *Acc. Chem. Res.* **2009**, *42*, 33.
[9] S. Grabowski, *Chem. Rev.* **2011**, *111*, 2597.
[10] Y. Bouteiller, B. Tremblay, J. P. Perchard, *Chem. Phys.* **2011**, *386*, 29.
[11] A. Gutberlet, G. Schwaab, M. Havenith, *J. Phys. Chem. A* **2011**, *115*, 6297.
[12] K. Kuyanov-Prozument, M. Y. Choi, A. F. Vilesov, *J. Chem. Phys.* **2010**, *132*, 014304.
[13] F. N. Keutsch, R. J. Saykally, *PNAS* **2001**, *98*, 10533.
[14] M. Y. Tretyakov, E. A. Serov, M. A. Koshelev, V. V. Parshin, A. F. Krupnov, *Phys. Rev. Lett.* **2013**, *110*, 093001.
[15] J. A. Odutola, T. R. Dyke, *J. Chem. Phys.* **1980**, *72*, 5062.
[16] G. T. Fraser, F. J. Lovas, R. D. Suenram, E. N. Karyakin, A. Grushow, W. A. Burns, K. R. Leopold, *J. Mol. Spectrosc.* **1997**, *181*, 229.
[17] M. Kawasaki, A. Sugita, C. Ramos, Y. Matsumi, H. Tachikawa, *J. Phys. Chem. A* **2004**, *108*, 8119.
[18] J. Ceponkus, P. Uvdal, B. Nelander, *J. Phys. Chem. A* **2008**, *112*, 3921.
[19] D. Cremer, J. A. Larsson, E. Kraka, in *New Developments in the Analysis of Vibrational Spectra on the Use of Adiabatic Internal Vibrational Modes* (Ed. C. Parkanyi) **1998**, pp. 259–327 (Elsevier: Amsterdam)
[20] E. Kraka, J. A. Larsson, D. Cremer, in *Generalization of the Badger Rule Based on the Uses of Adiabatic Vibrational Modes* (Ed. J. Grunenberg) **2010**, pp. 105–149 (Wiley: New York, NY).
[21] E. Kraka, D. Cremer, *ChemPhysChem* **2009**, *10*, 686.
[22] E. Kraka, M. Freindorf, D. Cremer, *Chirality* **2013**, *25*, 185.
[23] R. Kalescky, E. Kraka, D. Cremer, *J. Phys. Chem. A* **2013**, *117*, 8981.
[24] M. Freindorf, E. Kraka, D. Cremer, *Int. J. Quantum Chem.* **2012**, *112*, 3174.
[25] R. Kalescky, E. Kraka, D. Cremer, *Mol. Phys.* **2013**, *111*, 1497.
[26] R. Kalescky, W. Zou, E. Kraka, D. Cremer, *Chem. Phys. Lett.* **2012**, *554*, 243.
[27] D. Cremer, E. Kraka, *Curr. Org. Chem.* **2010**, *14*, 1524.

[28] J. Decius, *J. Chem. Phys.* **1963**, *38*, 241.

[29] D. C. McKean, *Chem. Soc. Rev.* **1978**, *7*, 399.

[30] J. L. Duncan, J. L. Harvie, D. C. McKean, C. Cradock, *J. Mol. Struct.* **1986**, *145*, 225.

[31] D. C. McKean, *Int. J. Chem. Kinet.* **1989**, *21*, 445.

[32] W. F. Murphy, F. Zerbetto, J. L. Duncan, D. C. McKean, *J. Phys. Chem.* **1993**, *97*, 581.

[33] B. R. Henry, *Acc. Chem. Res.* **1987**, *20*, 429.

[34] M. Vijay Madhav, S. Manogaran, *J. Chem. Phys.* **2009**, *131*, 174112.

[35] A. Espinosa, R. Streubel, *Chem. - Eur. J.* **2011**, *17*, 3166.

[36] W. Zou, R. Kalescky, E. Kraka, D. Cremer, *J. Chem. Phys.* **2012**, *137*, 084114.

[37] W. Zou, R. Kalescky, E. Kraka, D. Cremer, *J. Mol. Model.* **2012**, 1.

[38] Z. Konkoli, D. Cremer, *Int. J. Quant. Chem.* **1998**, *67*, 1.

[39] Z. Konkoli, D. Cremer, *Int. J. Quant. Chem.* **1998**, *67*, 29.

[40] J. Larsson, D. Cremer, *J. Mol. Struct.* **1999**, *485*, 385.

[41] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479.

[42] T. J. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007.

[43] D. Woon, T. J. Dunning, *J. Chem. Phys.* **1993**, *98*, 1358.

[44] Y. He, D. Cremer, *J. Phys. Chem. A* **2000**, *104*, 7679.

[45] D. Cremer, E. Kraka, Y. He, *J. Mol. Struct.* **2001**, *567*, 275.

[46] A. Halkier, T. Helgaker, P. Jorgensen, W. Klopper, H. Koch, J. Olsen, A. K. Wilson, *Chem. Phys. Lett.* **1998**, *286*, 243.

[47] V. Barone, *J. Chem. Phys.* **2005**, *122*, 014108.

[48] H. G. Kjaergaard, A. L. Garden, G. M. Chaban, R. B. Gerber, D. A. Matthews, J. F. Stanton, *J Phys Chem A* **2008**, *112*, 4324.

[49] E. B. Wilson, J. C. Decius, P. C. Cross, *Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra* **1955** (McGraw-Hill: New York, NY).

[50] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[51] P. J. Stevens, F. J. Devlin, C. F. Chablowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[52] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615.

[53] J.-D. Chai, M. Head-Gordon, *J. Chem. Phys.* **2008**, *128*, 084106.

[54] E. Kraka, M. Filatov, W. Zou, J. Gräfenstein, H. Joo, D. Izotov, J. Gauss, Y. He, A. Wu, V. Polo, L. Olsson, Z. Konkoli, Z. He, D. Cremer, *COLOGNE2013* **2013** (Southern Methodist University: Dallas, TX).

[55] J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay, A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts, J. Almlöf, P. R. Taylor, T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, A. V. Mitin, C. van Wüllen, *CFOUR* **2010**. Available at http://www.cfour.de