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# Intramolecular Mode Coupling of the Isotopomers of Water: A Non-Scalar Charge Density-Derived Perspective

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#### 1. Supplementary Materials S1.

**I(i)** *QTAIM* and stress tensor bond critical point (BCP) properties; ellipticity  $\varepsilon$ , total local energy density  $H(\mathbf{r}_b)$ , stress tensor eigenvalue  $\lambda_{3\sigma}$  and the stress tensor trajectory  $T_{\sigma}(s)$ :

The four types of QTAIM critical points are labeled using the notation  $(R, \omega)$  where *R* is the rank of the Hessian matrix, i.e., the number of distinct non-zero eigenvalues and  $\omega$  is the signature (the algebraic sum of the signs of the eigenvalues); the (3, -3) [nuclear critical point (*NCP*), a local maximum], (3, -1) and (3, 1) [saddle points, referred to as bond critical points (*BCP*) and ring critical points (*RCP*), respectively] and (3, 3) [the cage critical points (*CCP*)]. In the limit that the forces on the nuclei are zero, an atomic interaction line<sup>33</sup>, the line passing through a *BCP* and terminating on two nuclear attractors along which the charge density  $\rho(\mathbf{r})$  is locally maximal with respect to nearby lines, becomes a bond-path<sup>34</sup>. The full set of critical points with the bond-paths of a molecule or cluster is referred to as the molecular graph.



The figure shows the cross section through a bond at the bond critical point (*BCP*). The  $\lambda_1$  and  $\lambda_2$  eigenvalues with associated eigenvectors  $\underline{\mathbf{e}}_1$  and  $\underline{\mathbf{e}}_2$  respectively, define the axes of the ellipse and indicate the magnitudes of the least and greatest extents of the distribution of  $\rho(\mathbf{r})$ .

• Total local energy density 
$$H(\mathbf{r}_{\mathbf{b}}) = G(\mathbf{r}_{\mathbf{b}}) + V(\mathbf{r}_{\mathbf{b}}).$$
 (1)

Where  $G(\mathbf{r}_b)$  and  $V(\mathbf{r}_b)$  from equation (1) are the local kinetic and potential energy densities at a *BCP*, respectively. The possession of a degree of covalent character, determined from the total local energy density  $H(\mathbf{r}_b)$  [*J. Mol. Struct. THEOCHEM* **255**, 189–206 (1992)], [*Chem. Phys. Lett.* **317**, 97–102 (2000)]. A value of  $H(\mathbf{r}_b) < 0$  for the closed-shell interaction,  $\nabla^2 \rho(\mathbf{r}_b) > 0$ , indicates a *BCP* with a degree of covalent character and conversely  $H(\mathbf{r}_b) > 0$  reveals a lack of covalent character for the closed-shell *BCP*.

• Stress tensor eigenvalue  $\lambda_{3\sigma}$ 

This is used as a measure of bond-path instability, for values of  $\lambda_{3\sigma} < 0$  and is calculated within the QTAIM partitioning.

The quantum stress tensor  $\sigma(\mathbf{r})$  is directly related to the Ehrenfest force by the virial theorem and therefore provides a physical explanation of the low frequency normal modes that accompany structural rearrangements [*Int. J. Quantum Chem.* **115**, 1678–1690 (2015).]. In this work we use the definition of the stress tensor proposed by Bader to investigate the stress tensor properties within QTAIM. [*J. Chem. Phys.* **73**, 2871–2883 (1980).]. The quantum stress tensor  $\sigma(\mathbf{r})$  is used to characterize the mechanics of the forces acting on the electron density distribution in open systems, defined as:

$$\sigma(r) = -\frac{1}{4} \left[ \left( \frac{\partial^2}{\partial r_i \partial r'_j} + \frac{\partial^2}{\partial r'_i \partial r_j} - \frac{\partial^2}{\partial r_i \partial r_j} - \frac{\partial^2}{\partial r'_i \partial r'_j} \right) \cdot \gamma(r, r') \right]_{r=r'}$$
(2)

Where  $\gamma(\mathbf{r}, \mathbf{r'})$  is the one-body density matrix,

$$\gamma(r,r') = N \int \Psi(r,r_2,...,r_N) \Psi^*(r',r_2,...,r_N) dr_2 \cdots dr_N$$
(3)

The stress tensor is then any quantity  $\sigma(\mathbf{r})$ , that satisfies equation (2) since one can add any divergence free tensor to the stress tensor without violating this definition [*J. Phys. Chem. A*, 2010, **114**, 8884–8895.], [*J. Phys. Chem. A*, 2011, **115**, 13001–13006.] [*J. Chem. Phys.*, 1980, **73**, 2871–2883.].

Earlier, it was found that the stress tensor trajectories  $T_{\sigma}(s)$  were in line with physical intuition [*Chem. Phys. Lett.* **667**, 25–31 (2017)].

If we first consider a tiny cube of fluid flowing in 3-D space the stress  $\Pi(x, y, z, t)$ , a rank-3 tensor field, has nine components [*Interdiscip. Appl. Math.* xxii,405 (2006).] of these the three diagonal components  $\Pi_{xx}$ ,  $\Pi_{yy}$ , and  $\Pi_{zz}$  correspond to normal stress. A negative value for these normal components signifies a compression of the cube, conversely a positive value refers to pulling or tension, where more negative/positive values correspond to increased compression/tension of the cube. Diagonalization of the stress tensor  $\sigma(\mathbf{r})$ , returns the principal electronic stresses  $\Pi_{xx}$ ,  $\Pi_{yy}$ , and  $\Pi_{zz}$  that are realized as the stress tensor eigenvalues  $\lambda_{1\sigma}$ ,  $\lambda_{2\sigma}$ ,  $\lambda_{3\sigma}$ , with corresponding eigenvectors  $\mathbf{e}_{1\sigma}$ ,  $\mathbf{e}_{2\sigma}$ ,  $\mathbf{e}_{3\sigma}$  are calculated within the QTAIM partitioning.

Previously,  $\lambda_{3\sigma}$  was used to detect the lowering of the symmetry, caused by a torsion about the central C-C bond in biphenyl, inducing a phase transition [*Int. J. Quantum Chem.* **115,** 1678–1690 (2015)]. The *BCP*s calculated with QTAIM and stress tensor partitionings will not always coincide, particularly under the application of external force, such as an applied torsion.

Stress tensor trajectory T<sub>σ</sub>(s)

The changing orientation and characteristics corresponding to the normal modes, bending (Q1), anti-symmetric stretch (Q2) and symmetric stretch (Q3) of the H<sub>2</sub>O/D<sub>2</sub>O/HDO isotopomers will be undertaken using the stress tensor trajectory space formalism of the bond critical points (BCPs), instead of the Cartesian coordinate frame, see Scheme 1 of the main text. The stress tensor trajectory  $T_{\sigma}(s)$  space  $U_{\sigma}$  has been previously used to track changing orientation and characteristics of the series of rotational isomers of the S and R stereoisomers of the lactic acid [Journal of the American Chemical Society, 141(13), 5497-5503 (2019)], the prediction of torquoselectivity in competitive ring-opening reactions [J. Comput. Chem. 37, 2722–2733 (2016)], elucidating the mechanism of photochromism and fatigue switches [Int. J. Quantum Chem. 118(13), e25565 (2018)], the functioning of doped azophenine switches [Intl. J. Quantum. Chem. 118(16), e25676 (2018)] as well as for the reaction pathways of (H<sub>2</sub>O)<sub>5</sub> [*Chem. Phys. Lett.* 667, 25–31 (2017)]. The stress tensor trajectory  $T_{\sigma}(s)$  is intended for use in applications where there will be a finite, i.e. non-zero translation of a given BCP, either in real space or the stress tensor trajectory  $T_{\sigma}(s)$  space  $U_{\sigma}$ . For instance, previously, we examined torsion about the BCP located at the fixed 'pivot' of the torsion of the C-C bond linking the two phenyl rings in biphenyl where, as expected, was no significant translation of the central BCP [Int. J. Quantum Chem. 115, 1678–1690 (2015)]. For a given *BCP*, the stress tensor eigenvectors  $\{\underline{e}_{1\sigma}, \underline{e}_{2\sigma}, \underline{e}_{3\sigma}\}$  for that *BCP* at the step of the normal mode displacement are used as the projection set for the entire trajectory  $T_{\sigma}(s)$ . The location in the stress tensor  $U_{\sigma}$ space  $d\mathbf{r}'(s)$  corresponding to the direction vector  $d\mathbf{r}(s)$  in real space is given by  $\{(\underline{\mathbf{e}}_{1\sigma}\cdot\mathbf{dr}), (\underline{\mathbf{e}}_{2\sigma}\cdot\mathbf{dr}), (\underline{\mathbf{e}}_{3\sigma}\cdot\mathbf{dr})\}$ . The location in the U-space  $d\mathbf{r}'(s)$  corresponding to the direction vector  $d\mathbf{r}(s)$  in real space is given by  $\{(\mathbf{e}_{\mathbf{l}}\cdot d\mathbf{r}),$  $(e_2 \cdot dr), (e_3 \cdot dr)$ . The corresponding trajectory length  $L_{\sigma}$  (or L for the QTAIM eigenvector projection U-space) in the stress tensor eigenvector projection  $U_{\sigma}$ -space, are calculated as the sums:

$$\sum_{\sigma=s=0}^{\infty} |dr'(s+1) - dr'(s)|.$$

$$\sum_{L=s=0}^{\infty} |dr'(s+1) - dr'(s)|.$$
(4)

A greater trajectory length  $L_{\sigma}$  (or L) for a trajectory  $T_{\sigma}(s)$  implies a greater variation of a given *BCP*'s movement both in terms of direction in the stress tensor eigenvector projection  $U_{\sigma}$ -space (U-space) and the magnitude of the *BCP* shift,  $d\mathbf{r}'(s)$ . If the magnitude of the *BCP* shift,  $d\mathbf{r}'(s)$  and the direction of  $d\mathbf{r}'(s)$  are constant, then  $L_{\sigma} = 0$  (or L = 0). The procedure to generate the  $L_{\sigma}$  (or L) is provided in the **Supplementary** Materials S2 along with further explanations.

The corresponding real space lengths l(s) of the  $T_{\sigma}(s)$  are calculated as the sum:

$$\sum_{l = s} |dr(s)|$$

#### **I(ii).** *QTAIM bond-path properties; bond-path length (BPL), bond-path curvature :*

The bond-path length (BPL) is defined as the length of the path traced out by the  $\underline{e}_3$  eigenvector of the Hessian of the total charge density  $\rho(\mathbf{r})$ , passing through the *BCP*, along which  $\rho(\mathbf{r})$  is locally maximal with respect to any neighboring paths. The bond-path curvature separating two bonded nuclei is defined as the dimensionless ratio:

$$(BPL - GBL)/GBL$$
 (6)

Where the BPL is defined to be the bond-path length associated and GBL is the inter-nuclear separation. The BPL often exceeds the GBL particularly in strained bonding environments [*J. Phys. Condens. Matter* **12**, 10325 (2000)]. Earlier, one of the current authors hypothesized that a bond-path may possess 1-D, 2-D or a 3-D morphology [*Chem. Phys. Lett.* **317**, 97–102 (2000)], with 2-D or a 3-D bond-paths associated with a *BCP* with ellipticity  $\varepsilon > 0$ , being due to the differing degrees of charge density accumulation, of the  $\lambda_2$  and  $\lambda_1$  eigenvalues respectively. Bond-paths possessing zero and non-zero values of the bond-path curvature defined by equation (6) can be considered to possess 1-D and 2-D topologies respectively. We start by choosing the length traced out in 3-D by the path swept by the tips of the scaled  $\underline{e}_2$  eigenvectors of the  $\lambda_2$  eigenvalue, the scaling factor being chosen as the ellipticity  $\varepsilon$ .

# BCP sliding

The *BCP* sliding is evident in the change in *BCP* position relative to the O1 atom denoted by the unfilled (equilibrium geometry) and filled green circle (final *BCP* position) indicated on the bottom insert of **Scheme S2**. The *BCP* sliding is observed from differences in the gradients (slopes) of the *BCP*-O1 separation vs. normal mode displacement and the bond-path length (BPL) vs. normal mode displacement plots, see **Figure 3** of the main text.



Scheme S2. A sketch, (not to scale) of the QTAIM *BCP* trajectory T(s) for the P branch of the Q2 normal mode of the O1-H2 *BCP* for H<sub>2</sub>O, note each *BCP* displacement step **dr** defines a T(s) point. The  $\pm \mathbf{e_1}$  and  $\pm \mathbf{e_2}$  correspond to the least and most preferred directions of charge density accumulation respectively,  $\pm \mathbf{e_3}$  is defined along the bond-path, see Figure **3(b)**, Figure 4.

**2.** Supplementary Materials S2. The explanation and numerical procedures for the QTAIM T(s) and stress tensor  $T_{\sigma}(s)$  trajectories. Note in the main text we use the QTAIM trajectory T(s) and the U-space length L.

### The QTAIM bond critical point (BCP) trajectory T(s)

The QTAIM *BCP* trajectory T(s) is constructed exclusively using the frame of reference defined by the eigenvectors  $\{\pm \underline{e}_1, \pm \underline{e}_2, \pm \underline{e}_3\}$  of the Hessian of the total charge density  $\rho(\mathbf{r}_b)$  evaluated at the *BCP*, corresponding to the *equilibrium geometry* and is used to construct *all* subsequent points along the T(*s*), see the annotated H<sub>2</sub>O (top insert of **Scheme S2**). Note that  $\underline{e}_1 \equiv -\underline{e}_1$ ,  $\underline{e}_2 \equiv -\underline{e}_2$  and  $\underline{e}_3 \equiv -\underline{e}_3$  due to the symmetrical nature of the Hessian of  $\rho(\mathbf{r}_b)$ . This real space frame of reference has been referred to as U-space [*J. Am. Chem. Soc.* 141, 5497–5503 (2019)] [*Journal of Computational Chemistry* 410(21), 1881-1891 (2019)] [*Chemical Physics Letters* 722, 110–118, (2019)] [*Int J Quantum Chem* 118(16) e25676 (2018).] [*Int J Quantum Chem* 118(13), e25565 (2017)] [*Chem. Phys. Lett.* 667, 25–31 (2017)] however, this nomenclature is unnecessarily complex and so we won't use it in the main text, the interested reader may see the Supplementary Materials S2 for details of the procedure to obtain the T(*s*). The T(*s*) is constructed using the change in position of the *BCP*, referred to a d**r**, indicated on the axis of Scheme S2, for all displacement steps d**r** of the calculation of the normal modes. Each *BCP* shift vector d**r** is mapped to a point {( $\underline{e}_1 \cdot \mathbf{d}r$ ), ( $\underline{e}_2 \cdot \mathbf{d}r$ ), ( $\underline{e}_3 \cdot \mathbf{d}r$ )} in sequence, forming the T(*s*). This mapping is sufficiently symmetry breaking to distinguish stereo-isomers and isotopomers with degenerate relative energies.

In contrast, conventional QTAIM is confined to the use of scalar measures and therefore can only magnify differences that may exist in relative energies associated with different structures. Conventional QTAIM cannot therefore distinguish stereo-isomers and isotopomers that have degenerate, i.e. equal, relative energies.

The interpretation of the trajectories T(s) for the normal modes Q1, Q2, Q3, see **Figures 4-6** and **Table 1** in the main text:

We have renamed each of the  $\{\underline{e_1}.dr, \underline{e_2}.dr, \underline{e_3}.dr\}$  coordinate axes to express their physical interpretation:

(i)  $\underline{\mathbf{e}}_1.\mathbf{dr} \rightarrow \mathbf{bond}$ -flexing. The  $\underline{\mathbf{e}}_1$  corresponds to the least  $(\pm \underline{\mathbf{e}}_1)$  preferred direction of charge density  $\rho(\mathbf{r})$  accumulation, i.e. the *least* (facile) readily distorted direction in the plane perpendicular to the bond-path. This is because bond-flexing requires an increase in bond-path length from the straight-line bonded separation. A value  $\{\underline{\mathbf{e}}_1.\mathbf{dr}\}_{max} = 0.0$  in U-space corresponds to constant (unchanging) bond-flexing in real space.

(ii)  $\underline{\mathbf{e}}_2 \cdot \mathbf{dr} \to \mathbf{bond} \cdot \mathbf{twist}$ . The  $\underline{\mathbf{e}}_2$  corresponds to the most  $(\pm \underline{\mathbf{e}}_2)$  preferred direction of charge density  $\rho(\mathbf{r})$  accumulation and therefore the most facile direction in the plane perpendicular to the bond-path. It does not involve a change in the bond-path length. A value  $\{\underline{\mathbf{e}}_2 \cdot \mathbf{dr}\}_{max} = 0.0$  in U-space corresponds to constant

(unchanging) orientation of the  $(\pm \underline{e}_2)$  eigenvector in real space and therefore constant bond-path torsion (bond twist). A value  $\{\underline{e}_2.dr\}_{max} > 0.0$  indicates the disruption of the coupling between the bond-paths of sigma O-H *BCP* and hydrogen-bond *BCP*s. This is because hydrogen bonds can couple with the sigma O-H bonds that share an H atom: this coupling requires a high degree of bond-path collinearity. The coupling of hydrogen-bonds and sigma O-H bonds yields stronger than expected hydrogen bonds as quantified by the presence of values of the total local energy density  $H(\mathbf{r}_b) < 0$  [*Chemical Physics Letters* 317, no. 1–2 (2000): 97–102.].

A twisted O-H sigma bond will inhibit the interaction with hydrogen bonding since coupling is facilitated by the presence of co-linear i.e. untwisted hydrogen bonding. Earlier, we found using the Ehrenfest Force  $\mathbf{F}(\mathbf{r})$  partitioning that when a degree of covalent coupling is present as indicated by the total local energy density  $H(\mathbf{r}_b) < 0$  for a hydrogen bond *BCP* that the  $\underline{\mathbf{e}}_{2F}$  eigenvectors, that denote the orientation of the bond-path, are parallel for the hydrogen bond and O-H sigma bond, that donates the covalent character. For cases where the hydrogen bonds were twisted relative to the O-H sigma bonds then  $H(\mathbf{r}_b) > 0$ , i.e. for an absence of covalent character and coupling, the O-H and hydrogen bond  $\underline{\mathbf{e}}_{2F}$  eigenvectors were twisted relative to one another. The fact that the O-H bond and hydrogen bond  $\underline{\mathbf{e}}_{2F}$  eigenvectors are parallel indicates that the corresponding bond-paths are also parallel. [The Ehrenfest force topology: a physically intuitive approach for analyzing chemical interactions," *Phys. Chem. Chem. Phys.* **15**(41), 17823–17836 (2013).] The relevance for this work being to show that twisted O-H bonds will not couple with hydrogen bonds.

(iii)  $\underline{\mathbf{e}}_{3}.\mathbf{dr} \rightarrow \mathbf{bond}$ -anharmonicity. A value  $\{\underline{\mathbf{e}}_{3}.\mathbf{dr}\}_{\max} = 0.0$  in U-space corresponds to constant (unchanging) *BCP* shift  $\mathbf{dr}$  in real space relative to the bond-path and therefore an absence of bond anharmonicity. Conversely, a changing *BCP* shift  $\mathbf{dr}$  in real space relative to the bond-path implies a change in chemical character due to the change of the charge density  $\rho(\mathbf{r})$  distribution. The lack of overlap of the T(s), in particular, corresponding to the H<sub>2</sub>O and D<sub>2</sub>O isotopomers, is due to the lifting of the degeneracy with respect to the  $\underline{\mathbf{e}}_{3}$  eigenvectors, which is visible as the separation parallel to the bond-anharmonicity =  $\underline{\mathbf{e}}_{3} \cdot \underline{\mathbf{dr}}$  axis of the T(*s*). The presence of  $\{\underline{\mathbf{e}}_{3}.\mathbf{dr}\}_{\max} > 0$  is favorable to sigma O-H and hydrogen bond coupling and hence mode coupling if  $\{\underline{\mathbf{e}}_{2}.\mathbf{dr}\}_{\max} = 0.0$ , i.e. an absence of bond-path twist.

Note: for the stress tensor trajectory we have  $\{\underline{e_{1\sigma}}.\mathbf{dr} \rightarrow \text{bond-twist}, \underline{e_{2\sigma}}.\mathbf{dr} \rightarrow \text{bond-flexing}, \underline{e_{3\sigma}}.\mathbf{dr} \rightarrow \text{bond-anharmonicity}\}$ , since the interpretation of the stress tensor  $\underline{e_{1\sigma}}$  and  $\underline{e_{2\sigma}}$  eigenvectors map onto the QTAIM  $\underline{e_2}$  and  $\underline{e_1}$  eigenvectors respectively.

#### *The U-space length L of the trajectory T(s), see Table S7(b):*

This quantity defines the total shift in U-space for the duration of the normal mode. When the *BCP* moves with equal sized steps (**dr**) *and* in a constant direction the U-space length L = 0. This is because, in this special case, all the *BCP* shifts **dr** in real space map to the same point in U-space. For example, a trajectory that is linear

would indicate no variation in the direction of the *BCP* motion from the start (the equilibrium geometry) to the maximum extent of the normal mode motion. Therefore, for two linear T(s) with different lengths, e.g. for the Q1 modes of H<sub>2</sub>O and D<sub>2</sub>O, we can say that the greater T(s) U-space length L is caused by greater variability in the **dr** shifts compared to the smaller T(s).

## Interpretation of the real space length l of the trajectory T(s), see **Table S7(c)**:

Defined as the sum of the *BCP* shifts (**dr**) for the duration of the normal mode, i.e. the total distance moved in real space by a *BCP*, e.g. for the Q1 modes of H<sub>2</sub>O and D<sub>2</sub>O differences in the *l* are explained by different distributions of mass associated with the H and D isotopes that causes different redistributions of electronic charge density as a response to the normal mode Q1.

# Reasons for using the trajectories T(s) for the analysis of normal modes Q1, Q2, Q3:

We wish to understand the changes in the electronic charge density at the bond critical point (*BCP*) throughout the complete vibrational motion associated with the normal modes Q1, Q2, Q3, starting at the equilibrium geometry. We do not consider the motions of the atomic nuclei associated with these normal modes sufficient: instead we choose to use the motion of the *BCP* itself. The conventional sole use of nuclear motions to describe normal modes incorrectly assumes that the bonds do not deviate from straight lines joining the nuclei and also assume linear dependence of chemical properties of the bond on the conventional bond-length (i.e. the geometric distance between bonded nuclei). Additionally, this conventional description does not provide any information about changes to the electron density distribution. To address these shortcomings we quantify the *BCP* motion by choosing the reference coordinate frame defined by the orthogonal unit eigenvectors  $\underline{e_1}$ ,  $\underline{e_2}$ ,  $\underline{e_3}$ respectively associated with the ordered eigenvalues of the appropriate matrix evaluated at the *BCP*. These seemingly complicated reference vectors are returned as a matter of course by any QTAIM software package as they are used to locate any given *BCP*. This choice is motivated by the fact that for the QTAIM Hessian of the charge density, the eigenvectors  $\underline{e_1}$  and  $\underline{e_2}$  are the directions associated with the bond ellipticity  $\varepsilon = |\lambda_1|/|\lambda_2| - 1$ and the eigenvector  $\underline{e_3}$  is the direction associated with the bond path.

The 3-D vector-based trajectories can quantify the full 3-D character of the normal modes as well as distinguishing the  $H_2O$  and  $D_2O$  isotopomers: this is not possible with any scalar-based measures that are 2-D.

# Numerical considerations for calculations of the trajectories for the normal modes Q1, Q2, Q3:

Central to the concept of the trajectories T(s) is the concept of a monotonically increasing sequence parameter *s*, which may take the form of an increasing integer sequence (0, 1, 2, 3,...) in applications where a set of discrete numbered steps are involved, or a continuous real number. The 3-D trajectory T(s) is then defined as an ordered set of points, whose sequence is described by the parameter *s*. In this application, we used an integer step

number for *s*. We first choose to associate s = 0 with a specific reference molecular graph, in this case, the energy minimum structure. For a specific *BCP*, the coordinates associated with each of the points are calculated by evaluating the components of the shift vector  $\mathbf{dr} = \mathbf{r}_{\mathbf{b}}(s) - \mathbf{r}_{\mathbf{b}}(s-1)$  where  $\mathbf{r}_{\mathbf{b}}$  indicates the location of the *BCP*, from the previous step to the current step in the reference coordinate frame defined by the eigenvectors  $\mathbf{e}_1$ ,  $\mathbf{e}_2$ ,  $\mathbf{e}_3$ .

Note: for <u>displaying</u> the QTAIM T(s) and stress tensor trajectories  $T_{\sigma}(s)$ , large steps that can occur at the beginning or end of a trajectory (or T(s))  $T_{\sigma}(s)$  may swamp the appearance of the trajectory T(s). To solve this we temporarily filter these steps before including them back in to correctly calculate the (or U)  $U_{\sigma}$ -space trajectory  $T_{\sigma}(s)$  length  $L_{\sigma}$  (or L).

The calculation of the T(*s*) is made easier if the code which produces the list of structures corresponding to points along each of the Q1, Q2, Q3 normal modes generates these structures at regularly-spaced points along the normal mode vibration. The consequence of this desirable characteristic is that there are few or no large changes or 'spikes' in the magnitude of the *BCP* shift vector **dr** i.e.  $\Delta$ **dr**, between path step *s* and *s* + 1. Such anomalies occur because some path-following algorithms may employ occasional small predictor-corrector steps that are at least an order of magnitude smaller than standard steps. In this analysis it is observed that such intermittent relatively small steps in turn cause very small shifts **dr** to be interspersed between longer runs of larger changes, causing 'spike' noise in the otherwise smooth trajectories T(*s*). Such 'spikes', which usually only consist of a single spurious point deviating from the locally smooth trajectory, can make potentially large spurious contributions to the trajectory T(*s*) lengths L and may be safely filtered. This filtering process was carried out manually in the current work.

In future to avoid the need to manually filter out these 'spikes', a combination of criteria are recommended for automated rejection of inclusion of a specific point into the trajectories T(s):

1. If the magnitude of the **dr** associated with any current trajectory point is less than 50% of the average of the corresponding **dr** values associated with the immediately preceding point and the immediately following point, the current point is filtered out as a 'spike'.

2. Abrupt changes in direction in the trajectory T(s), e.g. turning by more than  $60^{\circ}$  from one trajectory T(s) step to the next cause the current point to be labelled as a 'spike'.

These two rules taken together are referred to as the 'turn' filter. These rules can be repeatedly applied across multiple 'passes' through the trajectory data as necessary.

It has been observed that the magnitudes of the steps **dr** naturally tend to slowly decrease toward the end of paths, corresponding to a slowed approach to an end minimum, and the corresponding part of the trajectory T(s)

turns toward the U-space origin. A combination of the criteria mentioned above may be deployed to retain these parts of the trajectory T(s) and their inclusion in the calculation of the trajectory T(s) length L.

An alternative Kolmogorov-Zurbenko (W. Yang and I. Zurbenko, *WIREs Comp Stat*, 2010, **2**, 340–351) data smoothing filter may also be applied.

1. Percentage deviation  $\Delta d\mathbf{r}$  of the magnitude of the  $d\mathbf{r}$  from a moving average calculated along the trajectory T(s) exceeding a specific value should be 10% or less.

2. Abrupt changes in direction in the trajectory T(s), e.g. turning by more than 60<sup>0</sup> from one trajectory T(s) step to the next.

It has been observed that the magnitudes of the steps **dr** naturally tend to slowly decrease toward the end of paths, corresponding to a slowed approach to an end minimum, and the corresponding part of the trajectory T(s) turns toward the U-space origin. A combination of the criteria mentioned above may be deployed to retain these parts of the trajectory T(s) and their inclusion in the calculation of the trajectory T(s) length L. A range of alternative traditional 'denoising' algorithms may also conceivably be usefully deployed.

#### 3. Supplementary Materials S3.

Table S3(a). Harmonic frequencies of isotopomers of water computed at the B3LYP/aug-cc-pVQZ level, in cm<sup>-1</sup>.

Vibrational mode	H <sub>2</sub> O	D <sub>2</sub> O	HDO
Bending (Q1)	1629.36	1192.78	1428.35
Symmetric stretch (Q2)	3804.19	2741.76	2800.47
Anti-symmetric stretch (Q3)	3905.99	2862.74	3857.05

Table S3(b). Classical turning points in dimensionless normal mode coordinates.

	H <sub>2</sub> O	$D_2O$	HDO
Q1	-0.14603 0.13552	-0.11533 0.10960	-0.13347 0.12953
Q2	-0.08485 0.09989	-0.08088 0.07072	-0.08808 0.06776
Q3	-0.08153 0.08847	-0.07924 0.07076	0.08196 0.10229



**Figure S3**. The variation of the relative energy  $\Delta E$  for the H<sub>2</sub>O, HDO and D<sub>2</sub>O isotopomers corresponding to the bend (Q1), symmetric stretch (Q2) and asymmetric stretch (Q3) normal modes respectively, are presented in the sub-figure (**a-c**) respectively, the harmonic range of amplitudes (± 0.1) is indicated by the vertical dashed lines, also see **Scheme 1** of the main document for the atom labelling scheme and sketch of the normal modes.



Figure S4. The variation of the bond-path length (BPL) for  $H_2O$  (red), HDO (blue) and  $D_2O(dark-yellow)$  isotopomers of the *BCP*s corresponding to the Q1, Q2 and Q3 normal modes are presented in sub-figures (a-c) respectively, also see the caption of Figure S3.

**Table S4.** The BPL separation for the positive *BCP* displacement (P) and negative *BCP* displacement (N) of the Q1, Q2 and Q3 normal modes, see **Scheme 1** and refer to theory section 2.2. Note, all values have been multiplied by a factor of 100.

BCP	$H_2O$	Ν	$D_2O$	01	$\mathrm{H}_{2}\mathrm{O}$	Р	$D_2O$
O1-H2/O1-D2	0.0537		0.0754	QI	0.0132		0.0134
O1-H3/O1-D3	0.0537		0.0754		0.0132		0.0134
				$\Omega^{2}$			
01 112/01 D2	0.0570		0.0601	Q2	0.0570		0.0502
01 - 112/01 - D2	0.0579		0.0001		0.0570		0.0592
01-113/01-D3	0.0379		0.0001		0.0370		0.0392
				03			
O1-H2/O1-D2	0.0589		0.0599	<b>X</b> -	0.0633		0.0641
O1-H3/O1-D3	0.0599		0.0589		0.0641		0.0633
	•	UD	~	n			
	Ν	HD	0	Р			
01 D2	0.0002	QI		0.000	h		
01-D2 01-U2	0.0095			0.0825	,		
01 <b>-</b> H3	0.1127			0.1804	ł		
		02	,				
01-D2	0 8642	×-		0.8513	5		
O1 H3	0.0012			0.0010			
	0.0500			0 0508	2		
01-115	0.0500			0.0508	\$		
01-115	0.0500	Q3	5	0.0508	\$		
01-D2	0.0500	Q3	;	0.0508	3		



**Figure S5**. The variation of the stress tensor ellipticity  $\varepsilon_{\sigma} = |\lambda_{2\sigma}|/|\lambda_{1\sigma}| - 1$ , for H<sub>2</sub>O (red), HDO (blue) and D<sub>2</sub>O (dark-yellow) isotopomers of the *BCP*s corresponding to the Q1, Q2 and Q3 normal modes are presented in sub-figures (a-c) respectively, see the caption of **Figure S3** for further details.



**Figure S6**. The variation of the stress tensor eigenvalue  $\lambda_{3\sigma}$  for H<sub>2</sub>O (red), HDO (blue) and D<sub>2</sub>O(dark-yellow) isotopomers of the O1-H2 *BCP* and O1-H3 *BCP* corresponding to the Q1, Q2 and Q3 normal modes are presented in sub-figures (**a-c**) respectively, see the caption of **Figure S3** for further details.

### 7. Supplementary Materials S7.

**Table S7(a)**. The stress tensor projection space  $U_{\sigma}$  trajectory lengths  $L_{\sigma}$  in a.u., for H<sub>2</sub>O, D<sub>2</sub>O and HDO isotopomers for (N,P) negative *BCP* and positive *BCP* displacements of the Q1, Q2 and Q3 normal modes, see **Scheme 1 of the main text**: note that all values have been multiplied by a factor of 100.

		$L_{\sigma}$	
BCP	$H_2O$	$D_2O$	HDO
		Q1	
O1-H2/O1-D2/O1-D2	(0.0816,0.1099)	(0.0899, 0.1336)	(0.7821,0.2015)
O1-H3/O1-D3/O1-H3	(0.0816, 0.1099)	(0.0899, 0.1336)	(0.6996, 0.1509)
		Q2	
O1-H2/O1-D2/O1-D2	(0.6449, 0.2324)	(0.6939, 0.2418)	(0.5214,1.7381)
O1-H3/O1-D3/O1-H3	(0.6449,0.2324)	(0.6939, 0.2418)	(0.3677,0.6513)
		Q3	
O1-H2/O1-D2/O1-D2	(0.8996,1.3322)	(1.5451,1.0433)	(0.6155, 0.4297)
O1-H3/O1-D3/O1-H3	(1.3084,0.9257)	(1.0433,1.5451)	(1.6022,0.5431)

**Table S7(b)**. The QTAIM projection U-space trajectory lengths L in a.u., for  $H_2O$ ,  $D_2O$  and HDO isotopomers for the (N,P) negative *BCP* and positive *BCP* displacements of the Q1, Q2 and Q3 normal modes, see **Scheme 1** of the main text: note that all values have been multiplied by a factor of 100.

		L	
BCP	$H_2O$	$D_2O$	HDO
		Q1	
O1-H2/O1-D2/O1-D2	(0.0816,0.1099)	(0.0899,0.1336)	(0.7821,0.2015)
O1-H3/O1-D3/O1-H3	(0.0816,0.1099)	(0.0899,0.1336)	(0.6996,0.1509)
		Q2	
O1-H2/O1-D2/O1-D2	(0.6449, 0.2324)	(0.6939,0.2418)	(0.5214,1.7381)
O1-H3/O1-D3/O1-H3	(0.6449, 0.2324)	(0.6939,0.2418)	(0.3677,0.6513)
		Q3	
O1-H2/O1-D2/O1-D2	(0.8996,1.3320)	(1.5455,1.0429)	(0.6155,0.4297)
O1-H3/O1-D3/O1-H3	(1.3082,0.9257)	(1.0429, 1.5455)	(1.6016,0.5431)
			,

**Table S7(c)**. The real space trajectory lengths *l* in atomic units (a.u.), see the caption of **Table S7(a)** of the stress tensor trajectories  $T_{\sigma}(s)$  and QTAIM T(s), for further details, all values have been multiplied by a factor of 10.

		l	
	Ν		Р
BCP	H <sub>2</sub> O D <sub>2</sub> O HDO		H <sub>2</sub> O D <sub>2</sub> O HDO
		01	
O1-H2/O1-D2/O1-D2	(3.539, 3.773, 4.402)		(3.532, 3.799, 3.154)
O1-H3/O1-D3/O1-H3	(3.539, 3.773, 2.712)		(3.532, 3.799, 3.743)
		02	
O1-H2/O1-D2/O1-D2	(3.039, 3.197, 4.561)	<b>x</b> -	(2.302, 2.288, 6.935)
О1-Н3/О1-D3/О1-Н3	(3.039, 3.197, 3.419)		(2.302, 2.288, 5.244)
		02	
01 42/01 02/01 02	(6 111 6 607 1 877)	Q3	(6.240, 7.060, 2.815)
01-H2/01-D2/01-D2	(0.441, 0.007, 4.877)		(0.240, 7.000, 3.813)
O1-H3/O1-D3/O1-H3	(6.070, 7.060, 6.050)		(6.614, 6.607, 4.869)

Examination of the real space length *l* of the T(*s*) for the bending mode (Q1) shows that for the H2-O1-H3 'closing' motion, i.e. the negative amplitude (N) then the O1-H2/O1-D2 *BCP* and O1-H3/O1-D3 *BCP* pair move  $\approx 6.2$  % further for the heavier D<sub>2</sub>O than the lighter H<sub>2</sub>O isotopomer, see **Table S7(c)**. The converse is true for the H2-O1-H3 closing motion, i.e. the positive amplitude (P) where the O1-D2/O1-D3 *BCP* pair for D<sub>2</sub>O only move  $\approx 7.0$  % of the distance moved by the lighter H<sub>2</sub>O isotopomer. These differences in the real space lengths *l* of the T(*s*) can be explained by the different distribution of mass associated with the heavier D<sub>2</sub>O isotopomer which causes a different redistribution of electronic charge density. This causes a different motion of the *BCP* for the H<sub>2</sub>O and D<sub>2</sub>O isotopomers in response to the normal mode. Consistent with the differences in masses, we see that for the Q1 mode of the (mixed) isotopomer HDO, the values of *l* for the heavier D2 are 38.4 % greater for the N branch and 15.7 % less for the P branch compared with the corresponding values of H3, see **Table S7(b)**. A similar effect occurs for the HDO symmetric stretch (Q2) mode, see **Table S7(b**). We observe that for the Q2 modes of the H<sub>2</sub>O and D<sub>2</sub>O isotopomers that the values of *l* are lower for the N than the P branches, see **Figure 5(a-b**). The differences between the O1-D2/O1-H3 for the H<sub>2</sub>O and O1-D2/O1-D3 D<sub>2</sub>O isotopomers due to the mass difference between the D2 and H3 atoms of the HDO isotopomer. **Table S7(d).** The maximum stress tensor  $U_{\sigma}$  space projections  $T(s)_{max} = \{\underline{e}_{1\sigma} \cdot d\mathbf{r} \rightarrow \text{bond-twist}, \underline{e}_{2\sigma} \cdot d\mathbf{r} \rightarrow \text{bond-flexing}, \underline{e}_{3\sigma} \cdot d\mathbf{r} \rightarrow \text{bond-anharmonicity}\}$ , see the caption of **Table S7(a)** for further details. Note that table entries indicated as 0.000 were effectively 0 to machine precision and all values have been multiplied by a factor of 100.

# {bond-twist, bond-flexing, bond-anharmonicity}

BCP	$H_2O$	N D <sub>2</sub> O		$H_2O$	<b>P</b> D <sub>2</sub> O
			Q1		
O1-H2/O1-D2	{0.000, 0.039, 0.069}	{0.000, 0.037, 0.080	}	{0.000, 0.016, 0.100}	{0.000, 0.119, 0.050}
O1-H3/O1-D3	{0.000, 0.039, 0.069}	{0.000, 0.037, 0.080	}	{0.000, 0.016, 0.100}	{0.000, 0.119, 0.050}
			Q2		
O1-H2/O1-D2	{0.000, 0.013, 0.517}	{0.000, 0.534, 0.161	}	$\{0.000, 0.002, 0.232\}$	$\{0.000, 0.234, 0.050\}$
O1-H3/O1-D3	{0.000, 0.013, 0.517}	{0.000, 0.534, 0.161	}	{0.000, 0.002, 0.232}	{0.000, 0.234, 0.050}
			Q3		
O1-H2/O1-D2	$\{0.000, 0.142, 0.857\}$	{0.798, 0.343, 0.453	}	{1.187, 0.243, 0.321}	$\{1.339, 0.335, 0.443\}$
O1-H3/O1-D3	{0.000, 1.012, 0.700}	{1.339, 0.335, 0.443	}	{0.738, 0.290, 0.383}	{0.798, 0.343, 0.453}
		Ν	HDO	Р	
			Q1		
O1-D2		{0.000, 0.608, 0.486	}	{0.031, 0.116, 0.153}	
O1-H3		{0.000, 0.631, 0.300	}	{0.091, 0.048, 0.063}	
			Q2		
O1-D2		{1.153, 0.174, 0.230	}	{0.000, 0.071, 0.488}	
О1-Н3		{0.635, 0.050, 0.067	}	{0.000, 0.339, 0.137}	
			Q3		
O1-D2		{0.591, 0.073, 0.097	}	{0.372, 0.125, 0.165}	
01-Н3		{1.392, 0.146, 0.193	}	{0.404, 0.203, 0.268}	



**Figure S7(a).** The stress tensor trajectories  $T_{\sigma}(s)$  for H<sub>2</sub>O, D<sub>2</sub>O and HDO isotopomers for the bending (Q1) normal mode are presented in sub-figures (**a-b**). The  $T_{\sigma}(s)$  correspond to the mappings  $\underline{\mathbf{e}}_{1\sigma}$ . **dr**  $\rightarrow$  bond-twist,  $\underline{\mathbf{e}}_{2\sigma}$ . **dr**  $\rightarrow$  bond-flexing,  $\underline{\mathbf{e}}_{3\sigma}$ . **dr**  $\rightarrow$  bond-anharmonicity, where **dr** is the *BCP* shift vector and is indicated by the larger symbols. The negative (N) and positive (P) *BCP* displacements are presented in sub-figures (**a**) and (**b**) respectively.



**(b)** 

Figure S7(b). The  $T_{\sigma}(s)$  for the symmetric stretch (Q2) normal mode are presented in sub-figures (a-b), see the caption of Figure S7(a) for further details.



Figure S7(c). The  $T_{\sigma}(s)$  for the anti-symmetric stretch (Q3) normal mode are presented in sub-figures (a-b), see the caption of Figure S7(a) for further details.