

Electronic Supplementary Information:

Roles of the scalar and vector components of the solvation effects on the vibrational properties of hydrogen- or halogen-bond accepting stretching modes

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Supplementary figures

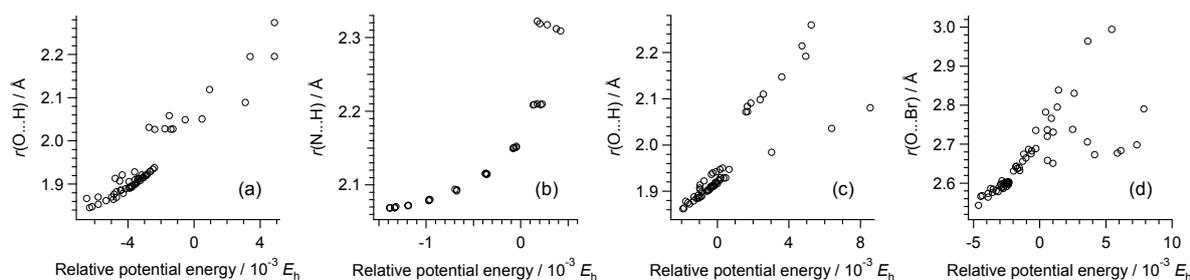


Fig. S1. Hydrogen- or halogen-bond distances [$r(O...H)$, $r(N...H)$, or $r(O...Br)$] plotted against the relative potential energies (obtained by adding 629.68 E_h , 209.217 E_h , 325.01 E_h , and 2913.13 E_h , respectively) for (a) the DMSO- $^{13}C_2...H_2O$ 1:1 complex, (b) the $CH_3CN...H_2O$ 1:1 complex, (c) the *N*-methylacetamide- $d_1...^2H_2O$ 1:1 complex, and (d) the *N*-methylacetamide- $d_1...BrNC$ 1:1 complex optimized with fixed angular positions (θ and φ) of the hydrogen- or halogen-bond donating atom.

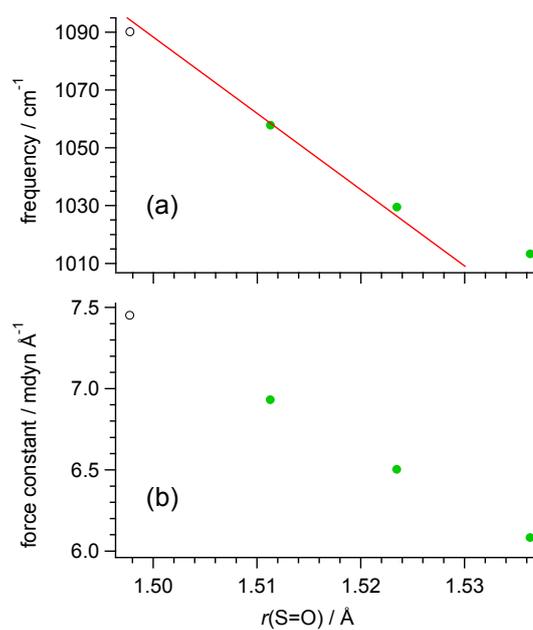


Fig. S2. (a) Vibrational frequency of the S=O stretching normal mode and (b) the force constant of the S=O stretching internal coordinate calculated for the fully optimized structures of the DMSO- $^{13}\text{C}_2 \dots n\text{H}_2\text{O}$ complexes ($n = 1-3$, shown with green filled circles) and an isolated DMSO- $^{13}\text{C}_2$ molecule (black open circle). The red solid line in part a shows the result of the linear regression obtained for the DMSO- $^{13}\text{C}_2 \dots \text{H}_2\text{O}$ 1:1 complex optimized with fixed angular positions (θ and φ) of the hydrogen atom of the water molecule shown in Fig. 2a.

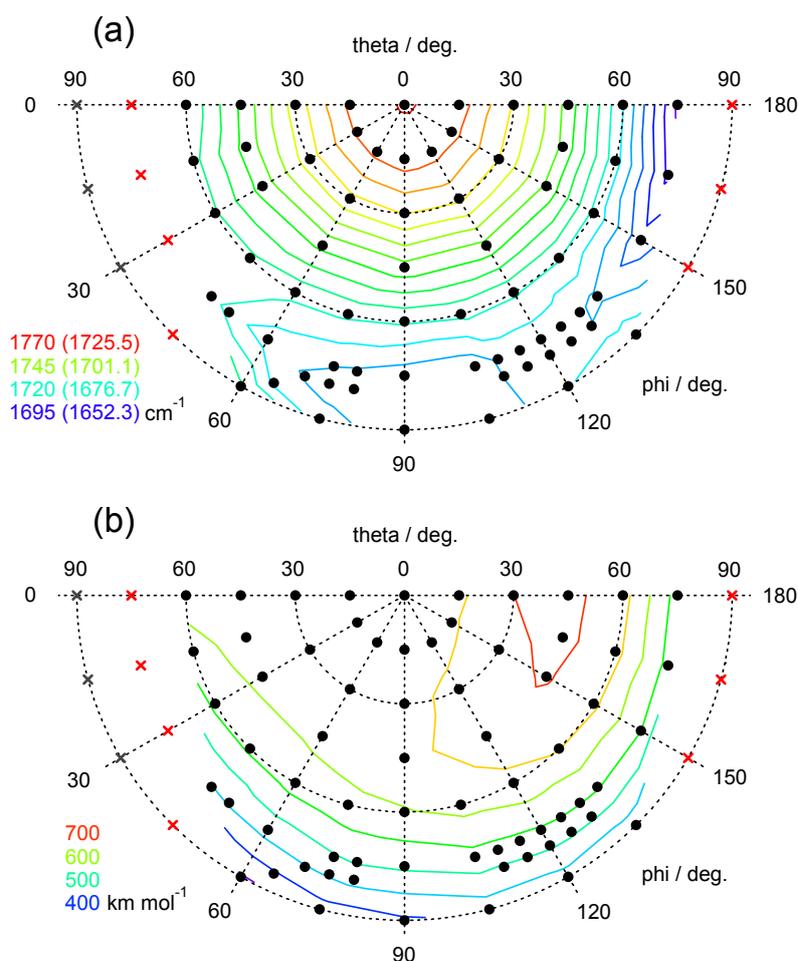


Fig. S3. Two-dimensional contour plots of the (a) vibrational frequency and (b) IR intensity of the amide I' mode calculated at the ω B97XD/6-31+G(2df,p) level for the *N*-methylacetamide-*d*₁...BrF 1:1 complex optimized with fixed angular positions (θ and φ) of the Br atom of the BrF molecule which is halogen-bonded to the C=O bond. The spherical polar coordinate system (r , θ , φ) is defined by taking the carbonyl oxygen atom as the origin, the C→O direction as the z axis, and the N–C=O...Br dihedral angle as φ . The calculated configurations of the complex are indicated with black filled circles. The red crosses indicate the angular positions where halogen-bonded optimized structures could not be obtained, and the gray crosses indicate those where the absence of halogen-bonded optimized structures is assumed on the basis of the calculations indicated by red crosses. The contours are drawn with the interval of 5 cm⁻¹ (for part a) and 50 km mol⁻¹ (for part b), with the color code shown on the left-hand side. The values in parentheses in part a are the scaled (by 0.9748) frequencies.

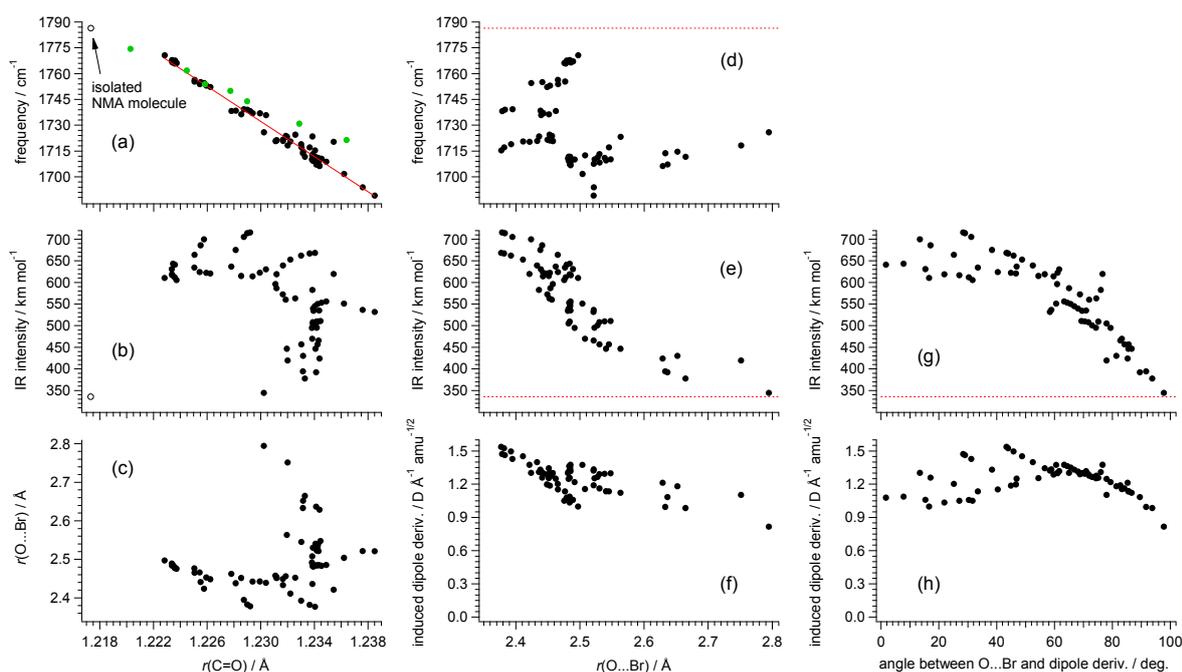


Fig. S4. (a,d) Vibrational frequency, (b,e,g) IR intensity, and (f,h) the magnitude of the induced dipole derivative $\delta(\partial\mu/\partial Q_{\text{ami}})$ of the amide I' mode, and (c) the O...Br distance, plotted against (a–c) the C=O bond length, (d–f) the O...Br distance, and (g,h) the angle between the O...Br halogen bond and the dipole derivative [of an isolated molecule ($\partial\mu/\partial Q_{\text{ami}}$)_{isolated}], calculated at the $\omega\text{B97XD}/6\text{-}31\text{+G}(2\text{df,p})$ level for the *N*-methylacetamide-*d*₁...BrF 1:1 complex optimized with fixed angular positions (θ and φ) of the Br atom of the BrF molecule which is halogen-bonded to the C=O bond (shown with black filled circles). The red solid line in part a shows the result of the linear regression. The open circles in part a and b and the red dotted line in part d, e, and g indicate the values calculated for an isolated *N*-methylacetamide-*d*₁ molecule. The green filled circles shown in part a indicate the values calculated for some fully optimized structures of the *N*-methylacetamide-*d*₁...*n*²H₂O complexes ($n = 1\text{--}3$), showing that the correlation between the frequency and the C=O bond length is quite similar.

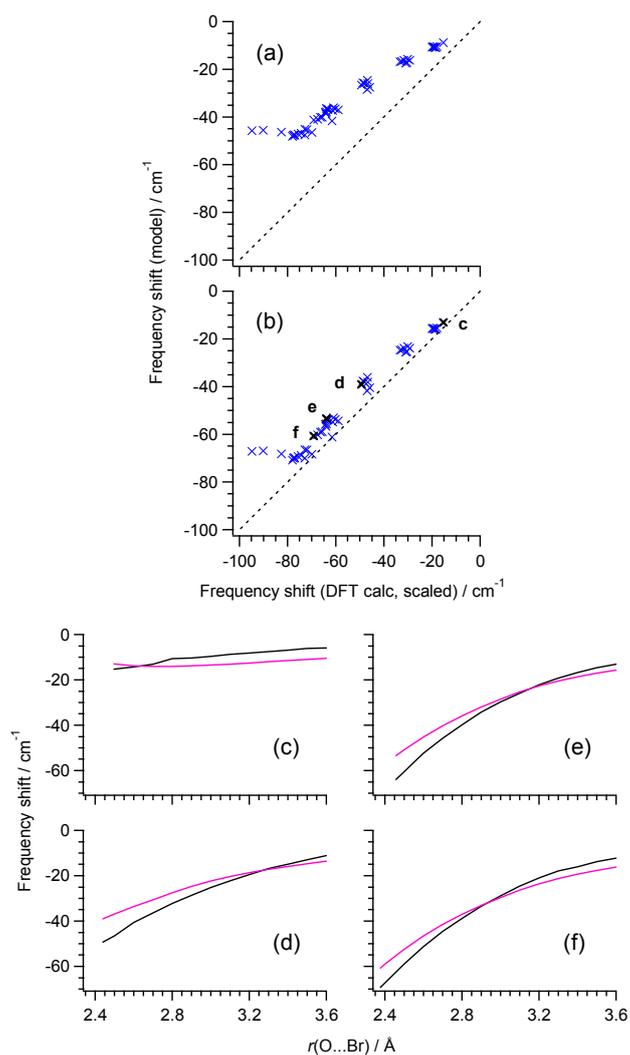


Fig. S5. (a) Frequency shifts of the amide I' mode predicted by the 2P3F electrostatic interaction model proposed (for *N*-methylacetamide-*d*₁...²H₂O) in the previous study³ plotted against the values directly calculated at the ω B97XD/6-31+G(2df,p) level (scaled by 0.9748) for the *N*-methylacetamide-*d*₁...BrF 1:1 complex optimized with fixed angular positions (θ and φ) of the Br atom of the BrF molecule which is halogen-bonded to the C=O bond. The black dotted line is the line of gradient unity passing through the origin. (b) Frequency shifts obtained by effectively taking into account the polarization effect of BrF by the enhancement factor of 1.470, which is estimated from the ratio to the molecular dipole moment of BrF in the electrostatic environment generated by the *N*-methylacetamide-*d*₁ molecule compared to that of an isolated BrF molecule. The four black bold crosses labeled as c–f indicate the angular positions where the distance dependence is also examined. (c–f) Dependence of the amide I' frequency shift on the O...Br distance, at the angular positions of $\theta = 0^\circ$ and $(\theta, \varphi) = (45^\circ, 0^\circ), (60^\circ, 90^\circ),$ and $(60^\circ, 180^\circ)$, respectively (marked with black bold crosses in part b). Pink solid line: predicted by the 2P3F model (with the enhancement factor), black solid line: directly calculated at the ω B97XD/6-31+G(2df,p) level (scaled by 0.9748).