

# Computational Analysis of Vibrational Spectra and Structure of Aqueous Cytosine

Sergey A. Katsyuba,\* Timur I. Burganov

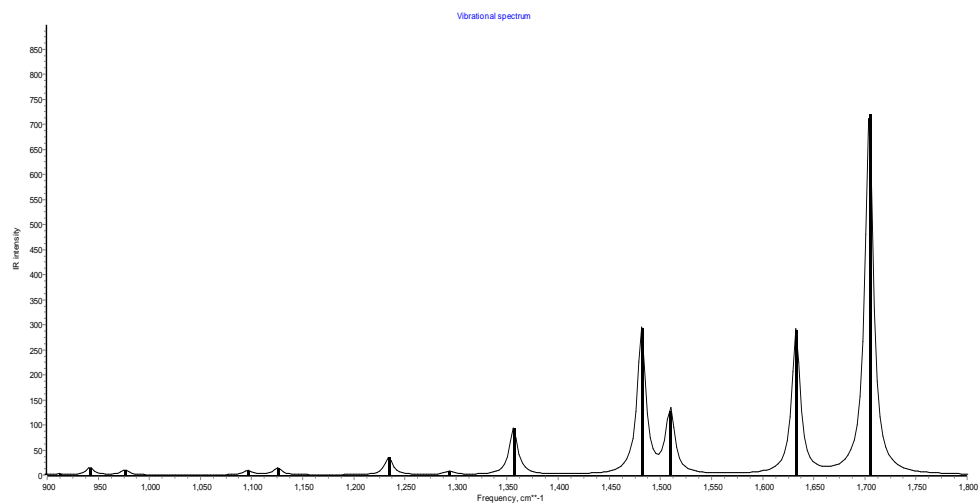
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Kazan, Russia.*

## Supporting information

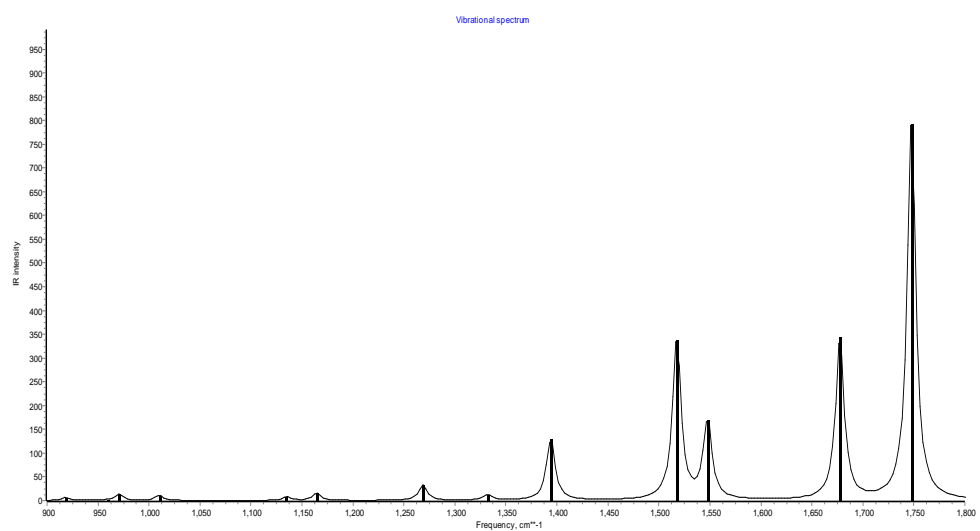
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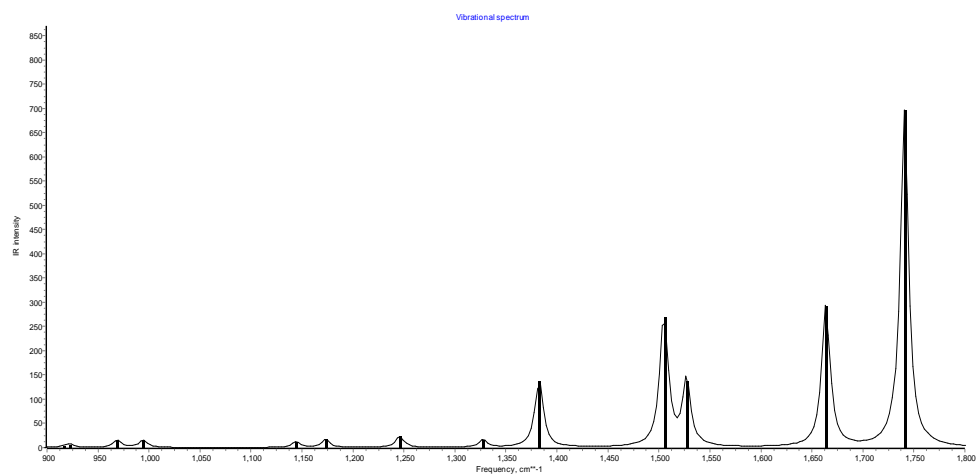
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PBE/aug-cc-pVDZ



B3LYP/aug-cc-pVDZ



B97-3c

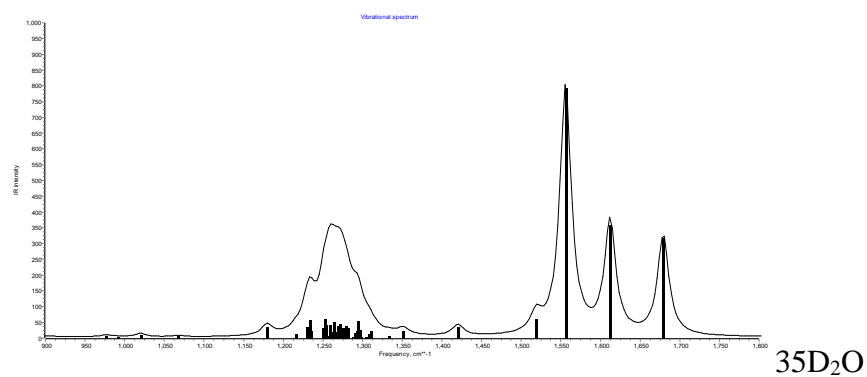
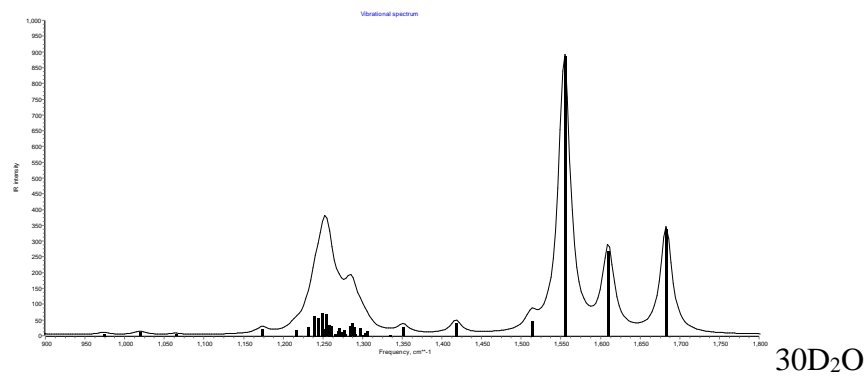
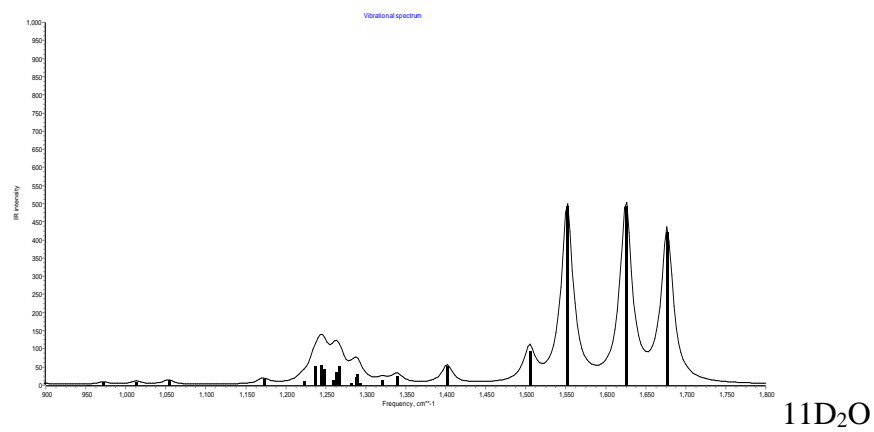
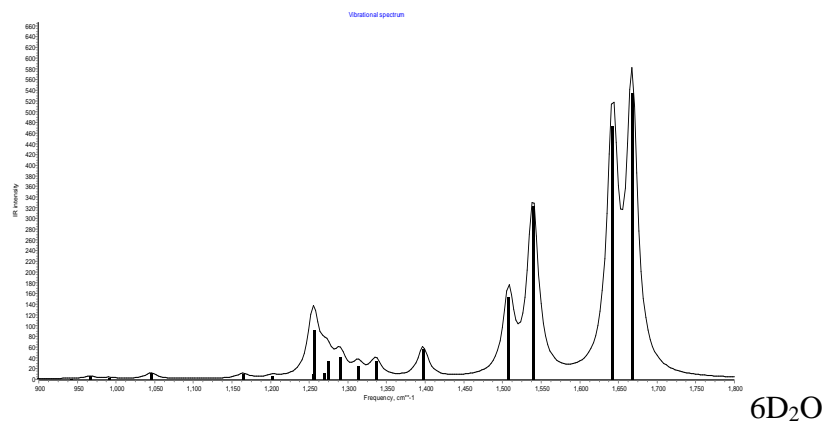
**Figure S1.** IR spectra of cytosine- $\text{d}_3$  simulated with the use of three different DFT methods.

**Table S1.** Frequencies ( $\nu/\text{cm}^{-1}$ ) and relative IR intensities ( $I_{\text{rel}}$ ) of the strongest bands in the spectra of cytosine (spectral region  $1100\text{-}1800\text{ cm}^{-1}$ ).

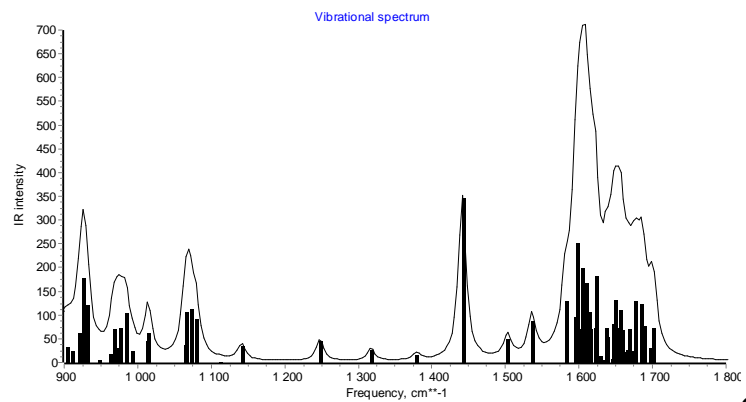
Ar matrixОшибка! Закладка не определена.		B3LYP/def2- TZVP	
$\nu$	$I_{\text{rel}}$	$\nu$	$I_{\text{rel}}$
1124	0.04	1109	0.01
1192	0.08	1195	0.07
1244	0.04	1236	0.04
1337	0.05	1337	0.07
1422	0.06	1417	0.12
1475	0.22	1481	0.21
1539	0.11	1538	0.23
1595	0.08	1604	0.22
1656	0.49	1658	0.68
1720	1	1740	1

**Table S2.** Frequencies ( $\nu/\text{cm}^{-1}$ ) and relative IR intensities ( $I_{\text{rel}}$ ) of the strongest bands in the spectra of cytosine- $\text{d}_3$  (spectral region  $1300\text{-}1800\text{ cm}^{-1}$ ).

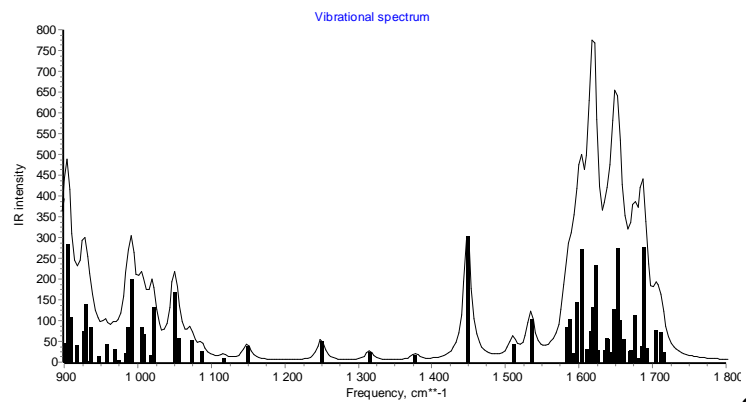
Ar matrixОшибка! Закладка не определена.		B3LYP/def2- TZVP	
$\nu$	$I_{\text{rel}}$	$\nu$	$I_{\text{rel}}$
1318	0.11	1307	0.03
1371	0.24	1366	0.21
1492	0.28	1485	0.42
1495	0.22	1509	0.25
1645	0.66	1642	0.50
1706	1	1722	1



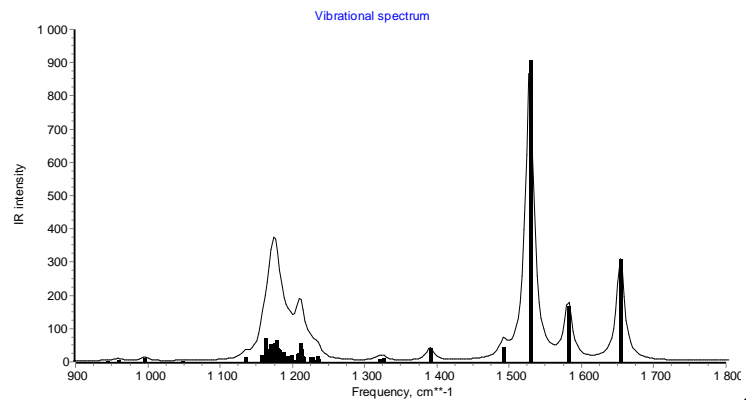
**Figure S2.** IR spectra of cytosine-d<sub>3</sub>, explicitly solvated with D<sub>2</sub>O molecules, simulated with the use of B97-3c method.



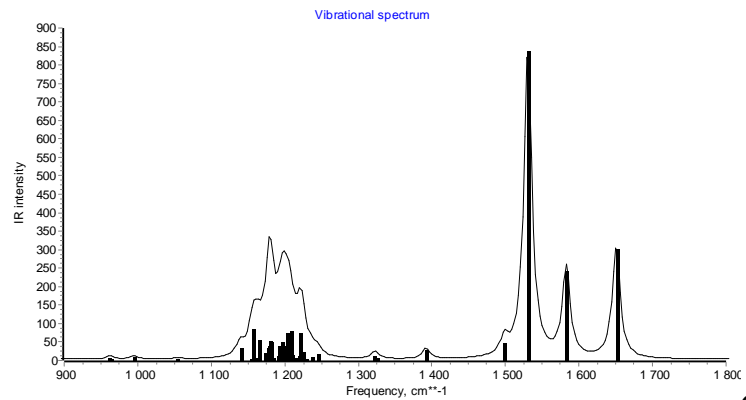
Cytosine-30H<sub>2</sub>O



Cytosine-35H<sub>2</sub>O

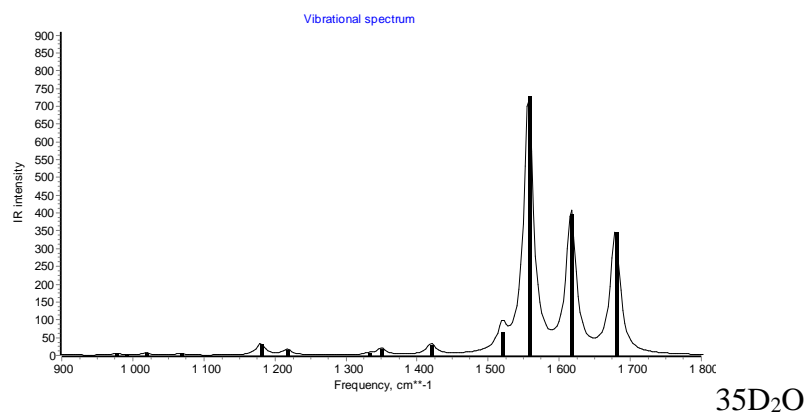
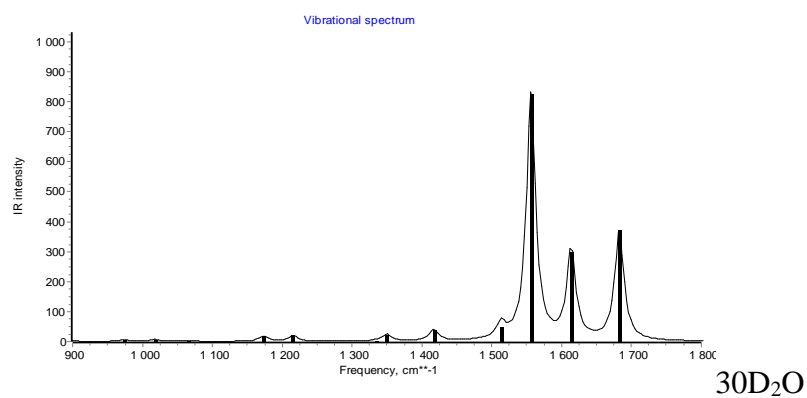
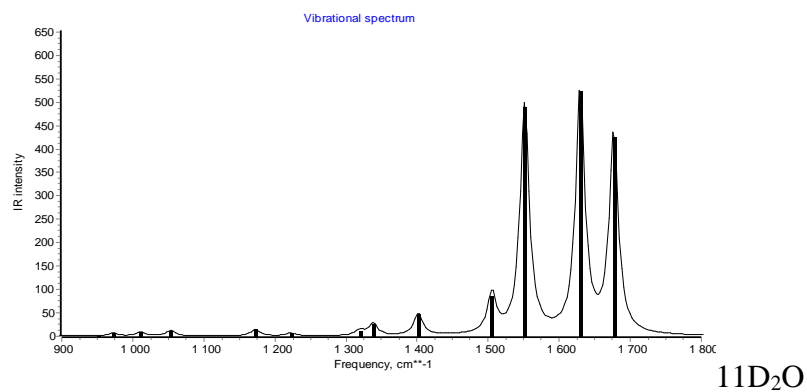
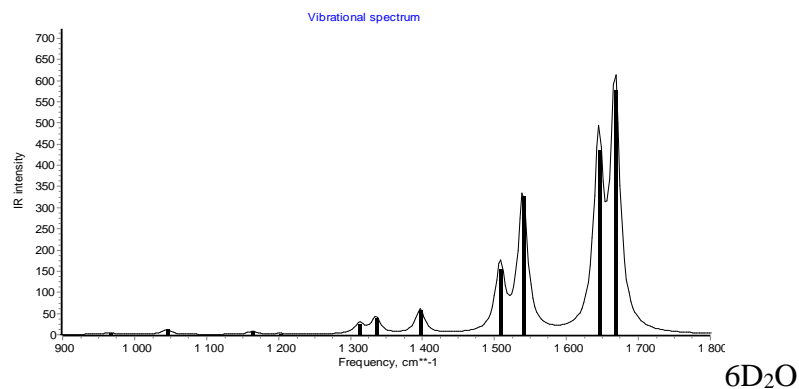


Cytosine-d<sub>3</sub>-30D<sub>2</sub>O

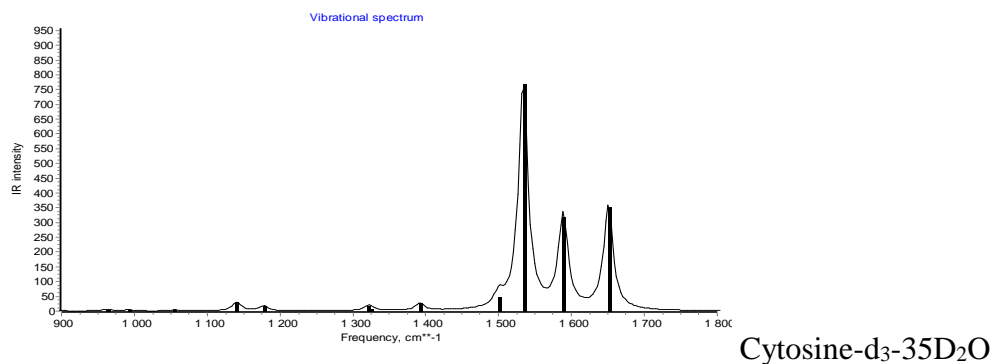
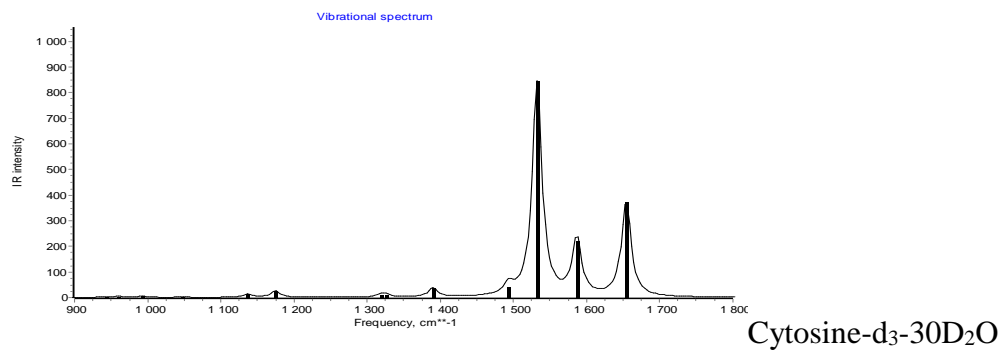
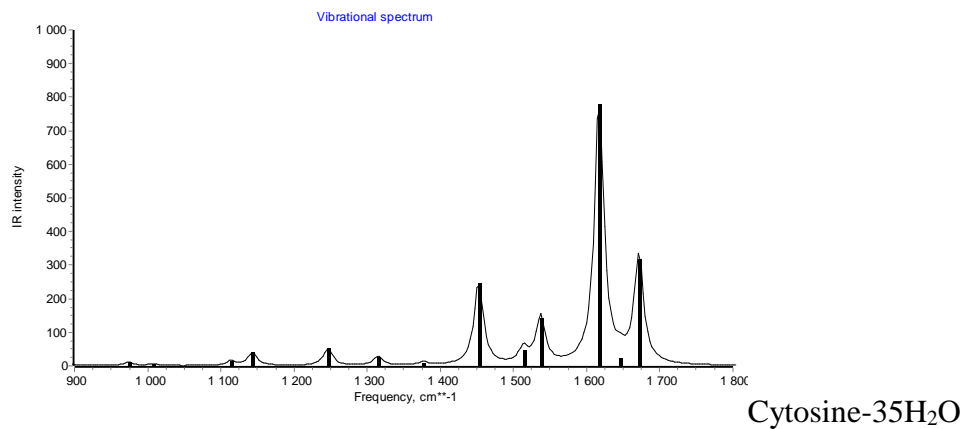
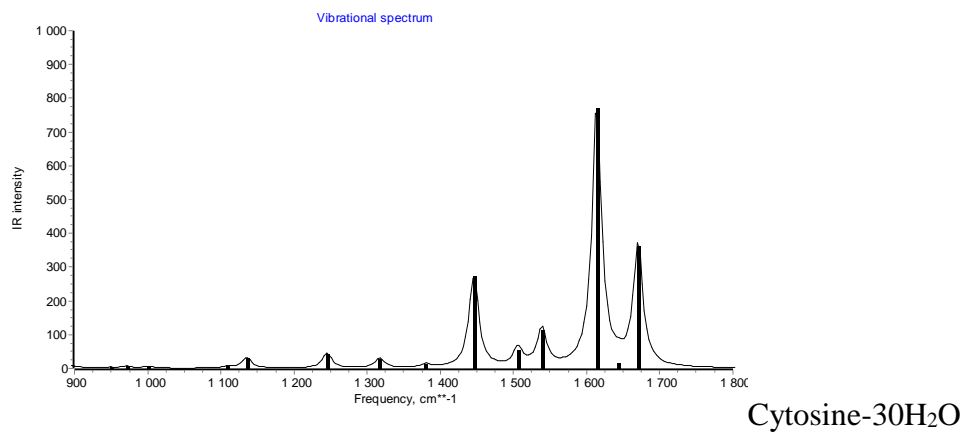


Cytosine-d<sub>3</sub>-35D<sub>2</sub>O

**Figure S3.** IR spectra of cytosine and cytosine-d<sub>3</sub>, explicitly solvated with H<sub>2</sub>O and D<sub>2</sub>O molecules, respectively, simulated with the use of PBE/def2-TZVP method.

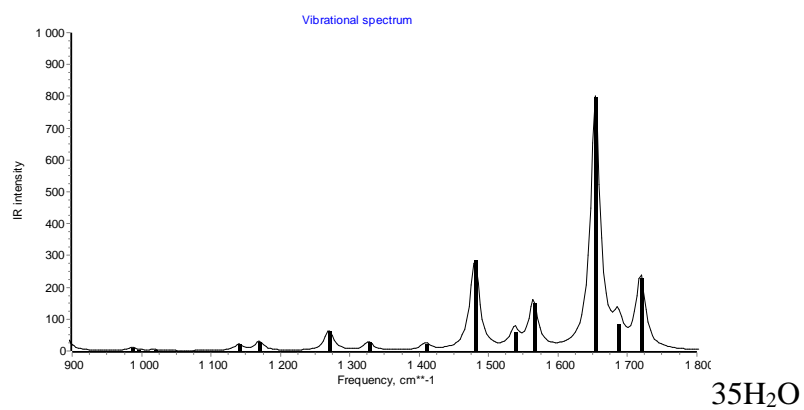
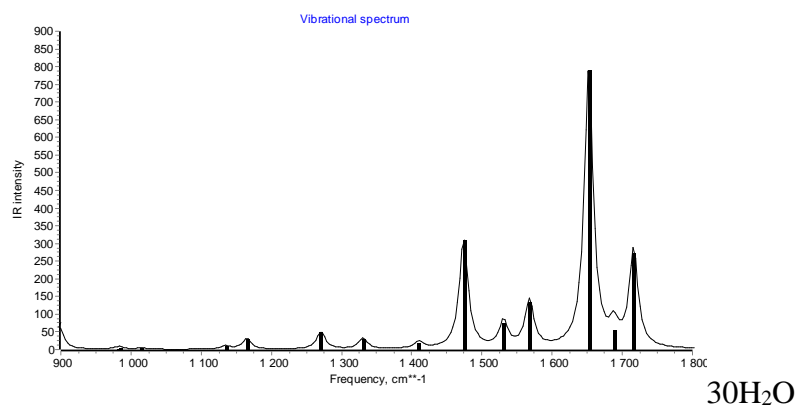
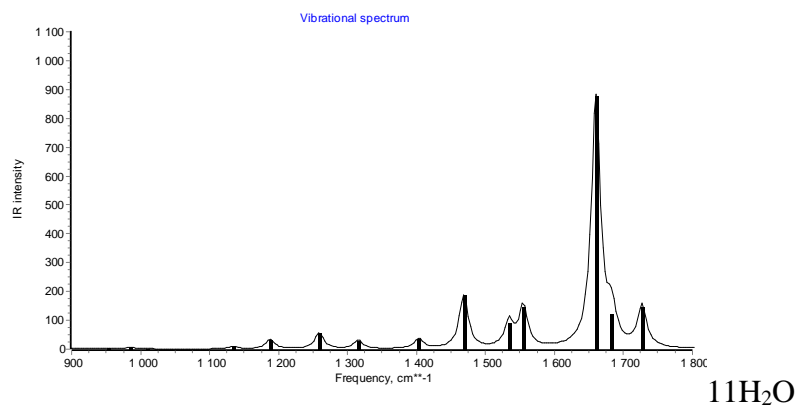
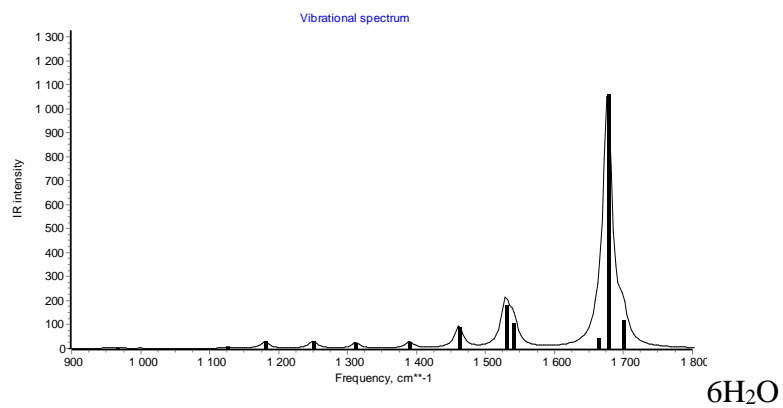


**Figure S2a.** IR spectra of cytosine-d<sub>3</sub>, explicitly solvated with heavy water molecules ( $m_H = m_O = 400$  aem, see main text), simulated with the use of B97-3c method. Comparison with Fig. S2 shows that the bands of cytosine that do not overlap with the bands of D<sub>2</sub>O (spectral region  $\sim 1300$ - $1800$  cm<sup>-1</sup>) do not change when D<sub>2</sub>O molecules are replaced by “heavy water”.

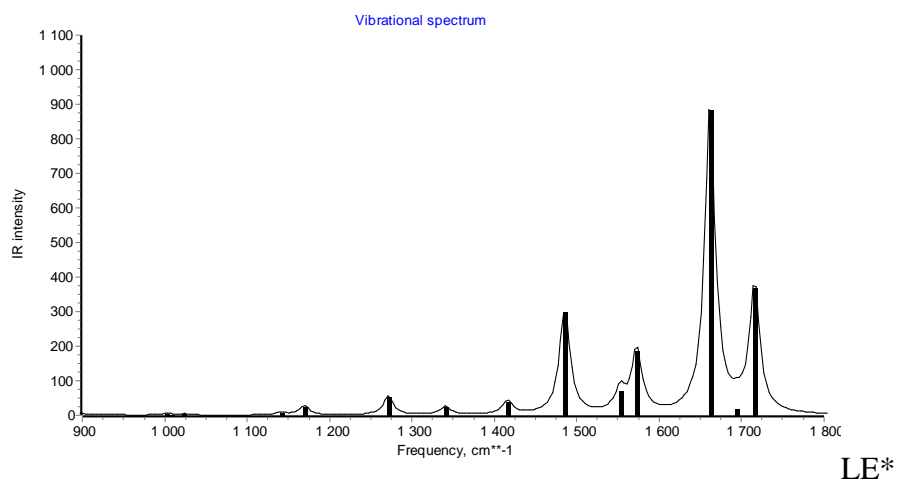
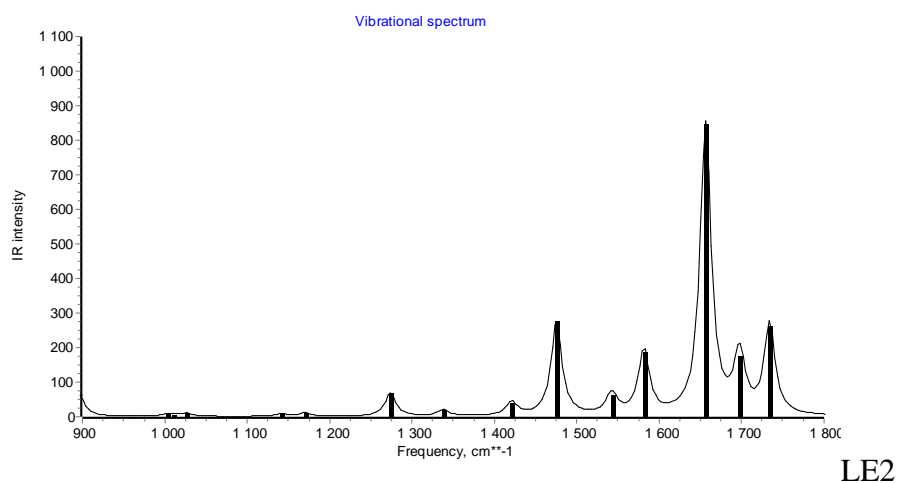
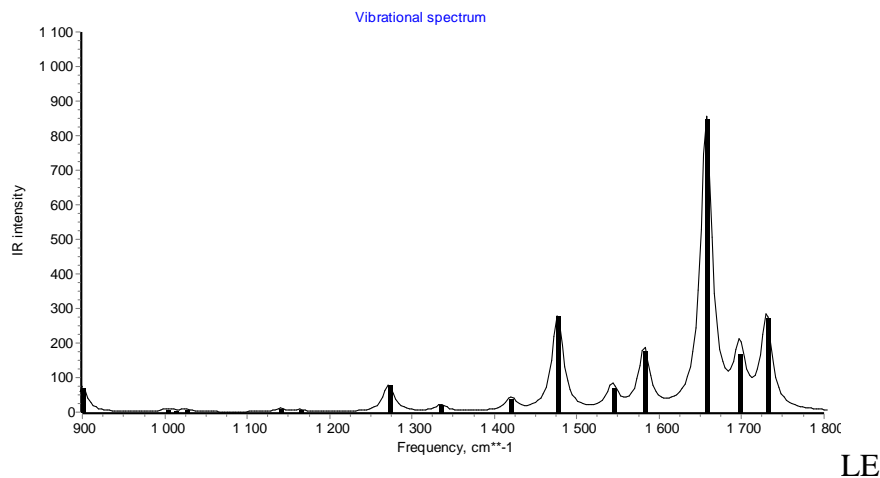


**Figure S3a.** IR spectra of cytosine and cytosine-d<sub>3</sub>, explicitly solvated with heavy water molecules ( $m_H = m_D = m_O = 400$  aem, see main text), simulated with the use of PBE/def2-TZVP method. Comparison with Fig. S3 shows that the bands of cytosine that do not overlap with the bands of H<sub>2</sub>O (spectral region  $\sim 1100-1550$  cm<sup>-1</sup>) or D<sub>2</sub>O (spectral region  $\sim 1300-1800$  cm<sup>-1</sup>) do not change when H<sub>2</sub>O or D<sub>2</sub>O are replaced by “heavy water”.

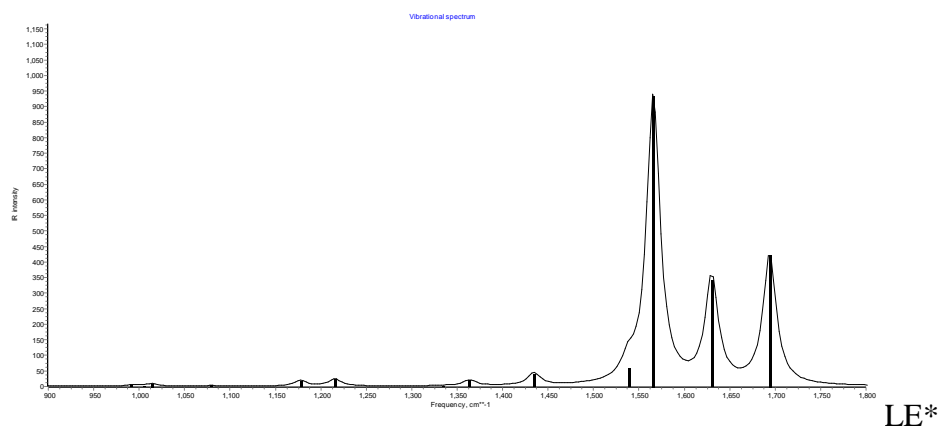
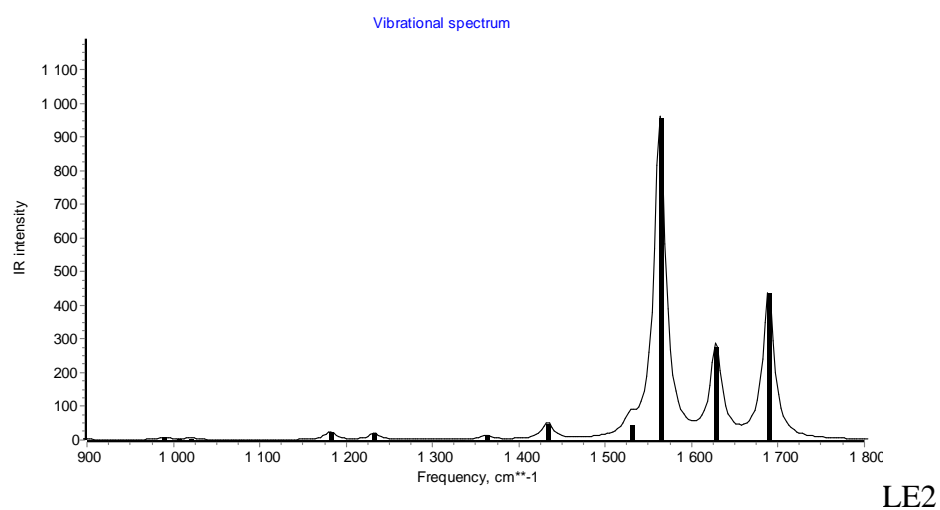
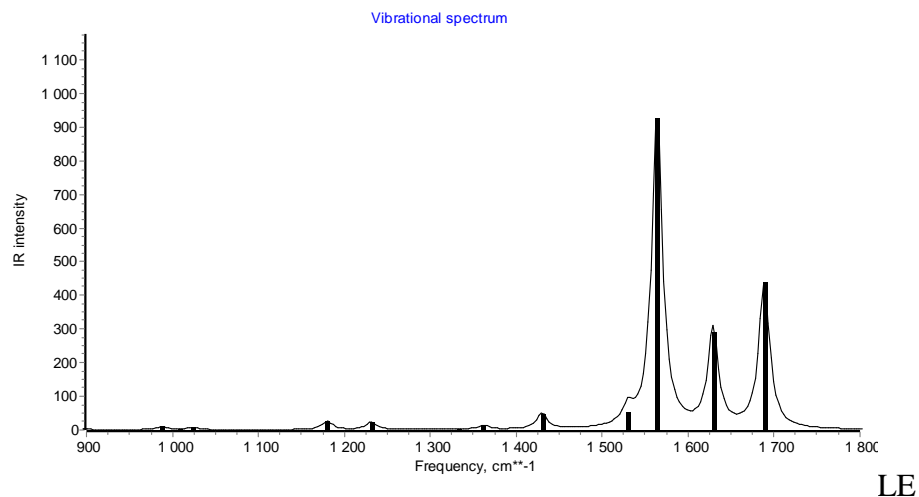




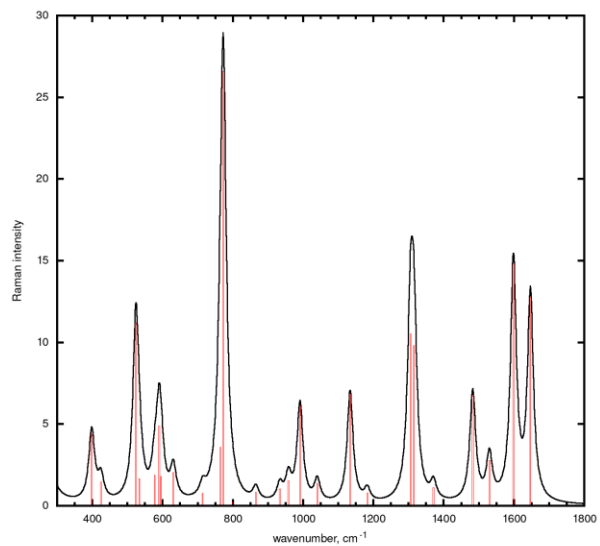
**Figure S4.** IR spectra of cytosine, explicitly solvated with heavy water molecules ( $m_H = m_O = 400$  aem, see main text), simulated with the use of B97-3c method.



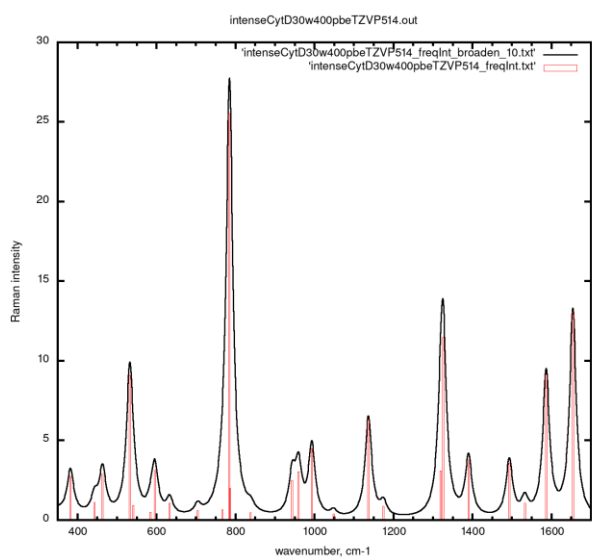
**Figure S5.** IR spectra of cytosine, explicitly solvated with 30 heavy water molecules ( $m_H = m_O = 400$  aem, see main text), simulated with the use of B3LYP-D3/def2-TZVP method for the lowest-energy (LE) and the second lowest energy (LE2) clusters from the generated ensemble of four clusters. The energy difference between LE and LE2 clusters = 2.4 cal/mol, and the corresponding Boltzmann weights of the clusters = 0.438 and 0.436, respectively. LE\* is the spectrum of the lowest-energy cluster generated in the different QCG run (see main text).



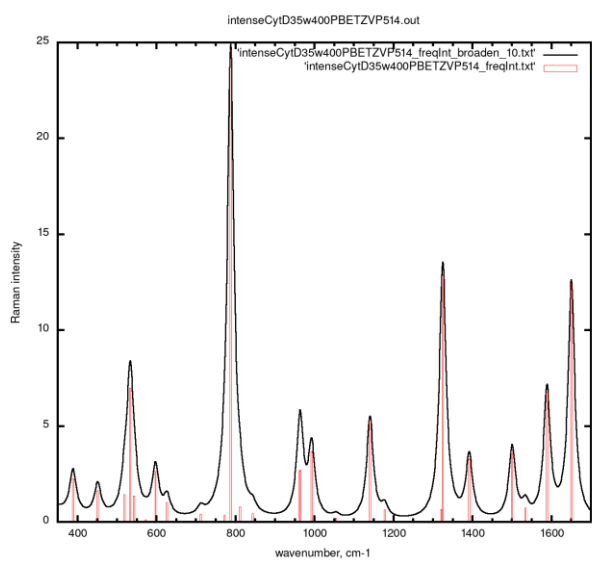
**Figure S6.** IR spectra of cytosine-d<sub>3</sub>, explicitly solvated with 30 heavy water molecules ( $m_D = m_O = 400$  aem, see main text), simulated with the use of B3LYP-D3/def2-TZVP method for the lowest-energy (LE) and the second lowest energy (LE2) clusters from the generated ensemble of four clusters. The energy difference between LE and LE2 clusters = 2.4 cal/mol, and the corresponding Boltzmann weights of the clusters = 0.438 and 0.436, respectively. LE\* is the spectrum of the lowest-energy cluster generated in the different QCG run (see main text).



11D<sub>2</sub>O

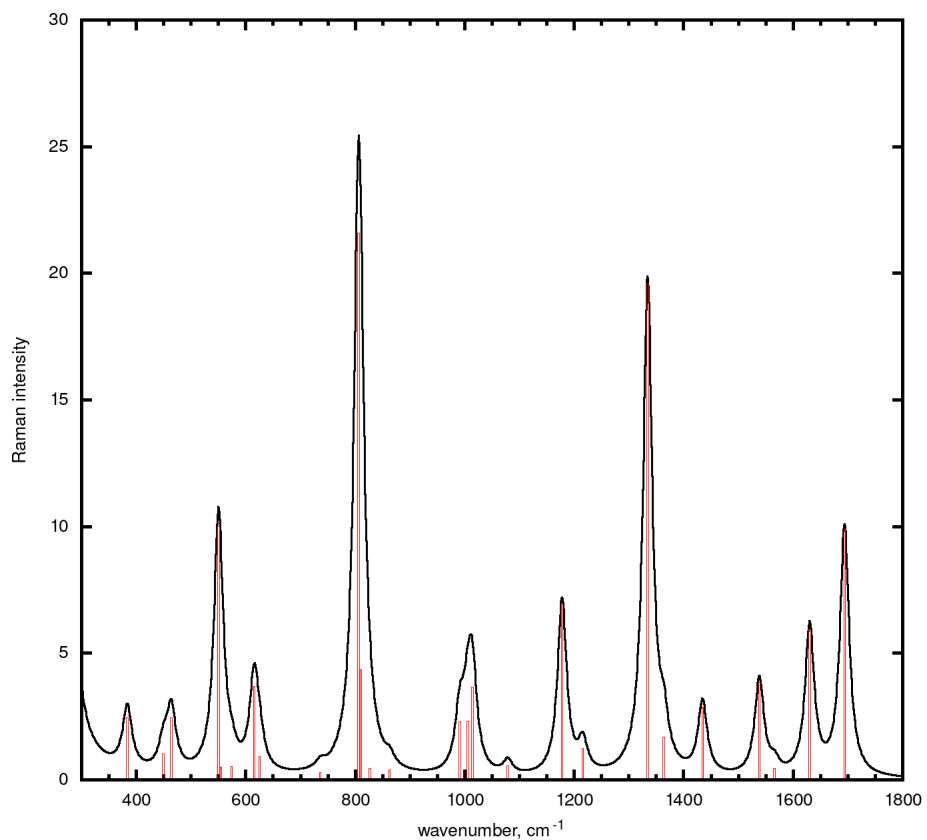


30D<sub>2</sub>O

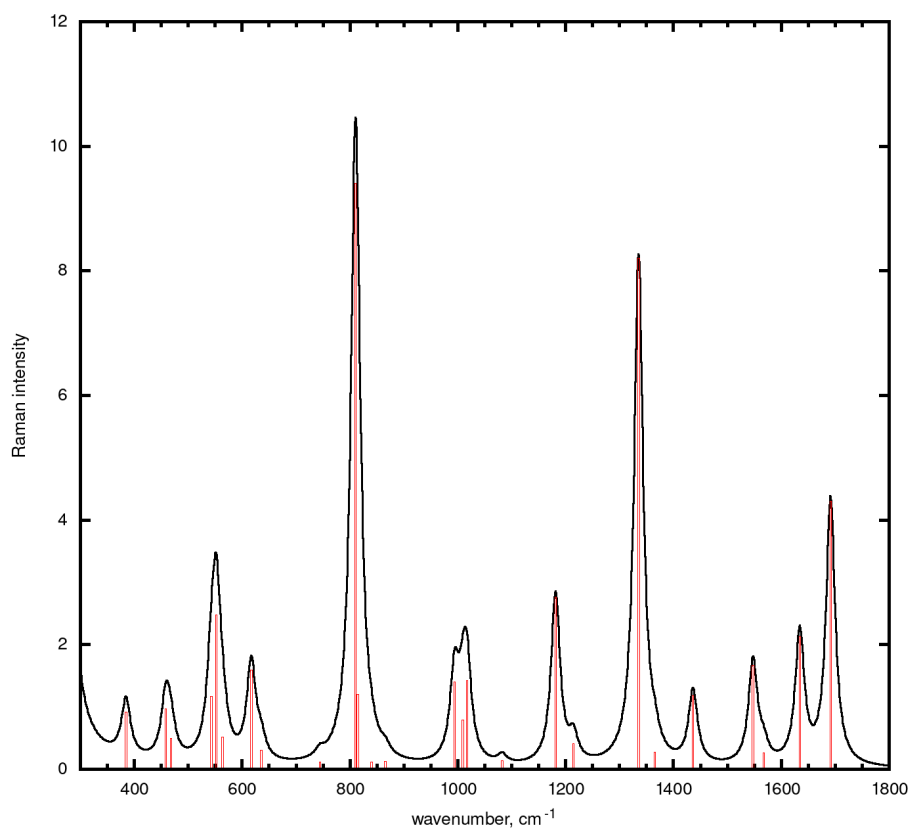


35D<sub>2</sub>O

**Figure S7.** Raman spectra of cytosine-d<sub>3</sub>, explicitly solvated with heavy water molecules ( $m_D = m_O = 400$  aem, see main text), simulated with the use of PBE/def2-TZVP method.

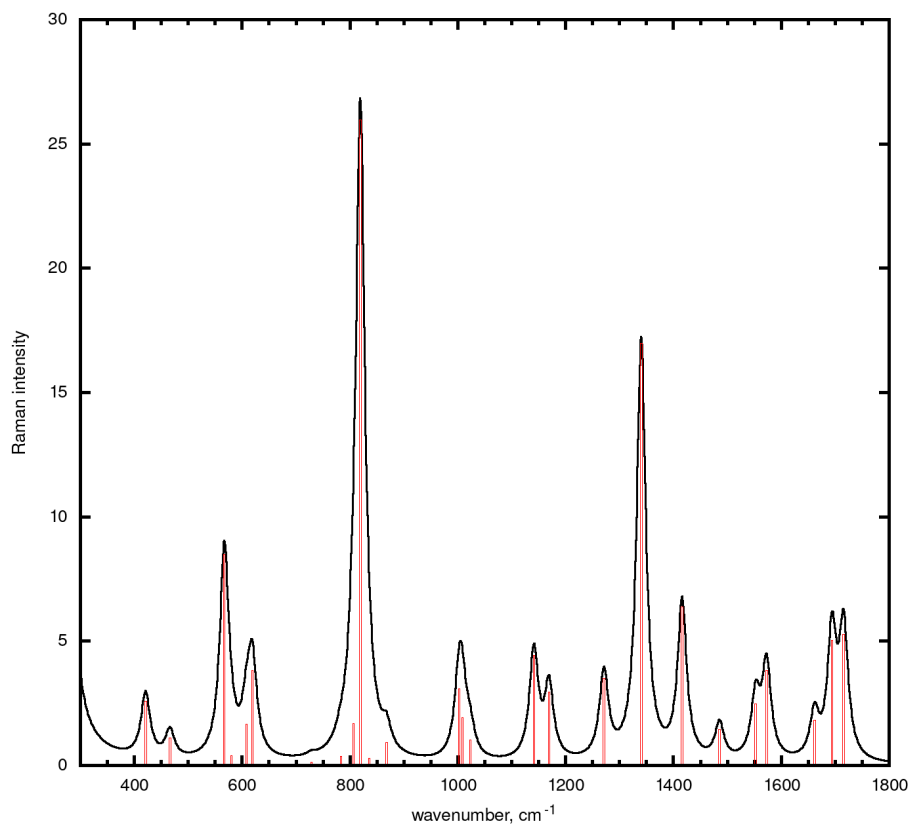


30D<sub>2</sub>O

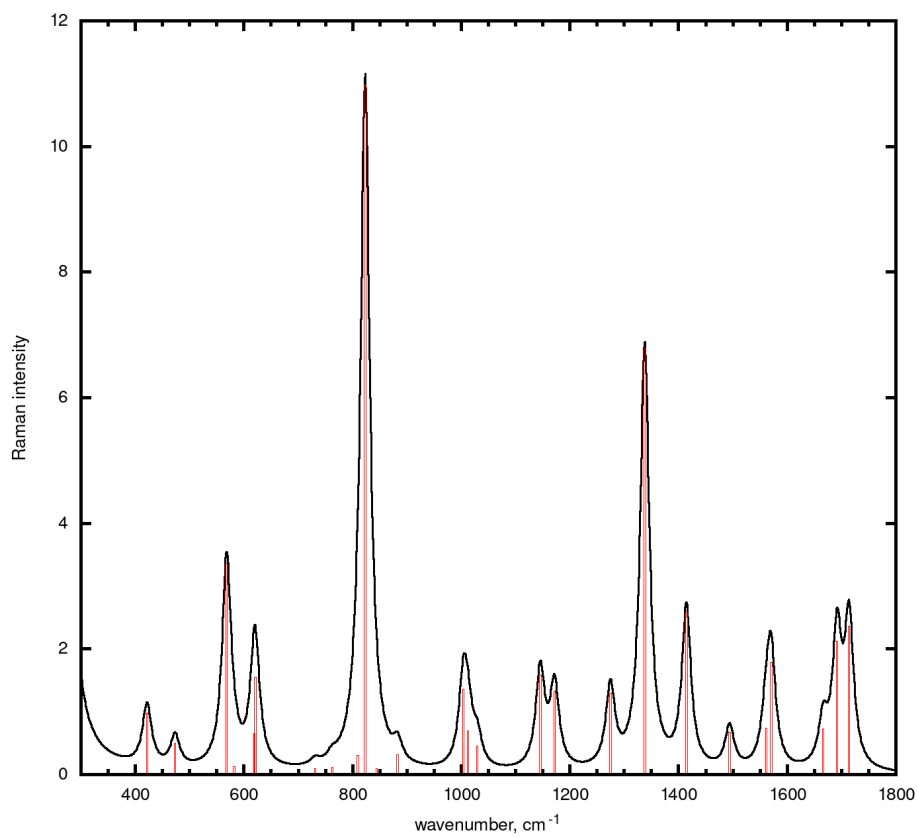


33D<sub>2</sub>O

**Figure S8.** Raman spectra of cytosine-d<sub>3</sub>, explicitly solvated with heavy water molecules ( $m_D = m_O = 400$  aem, see main text), simulated with the use of B3LYP/def2-TZVP method.



30H<sub>2</sub>O

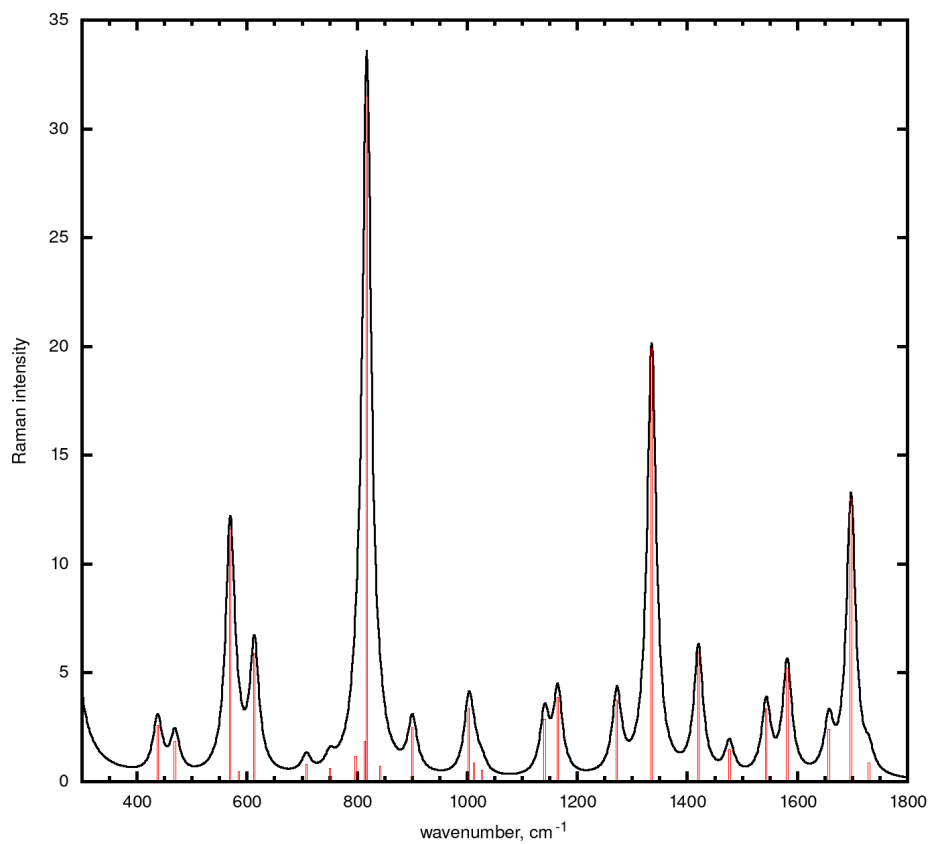


33H<sub>2</sub>O

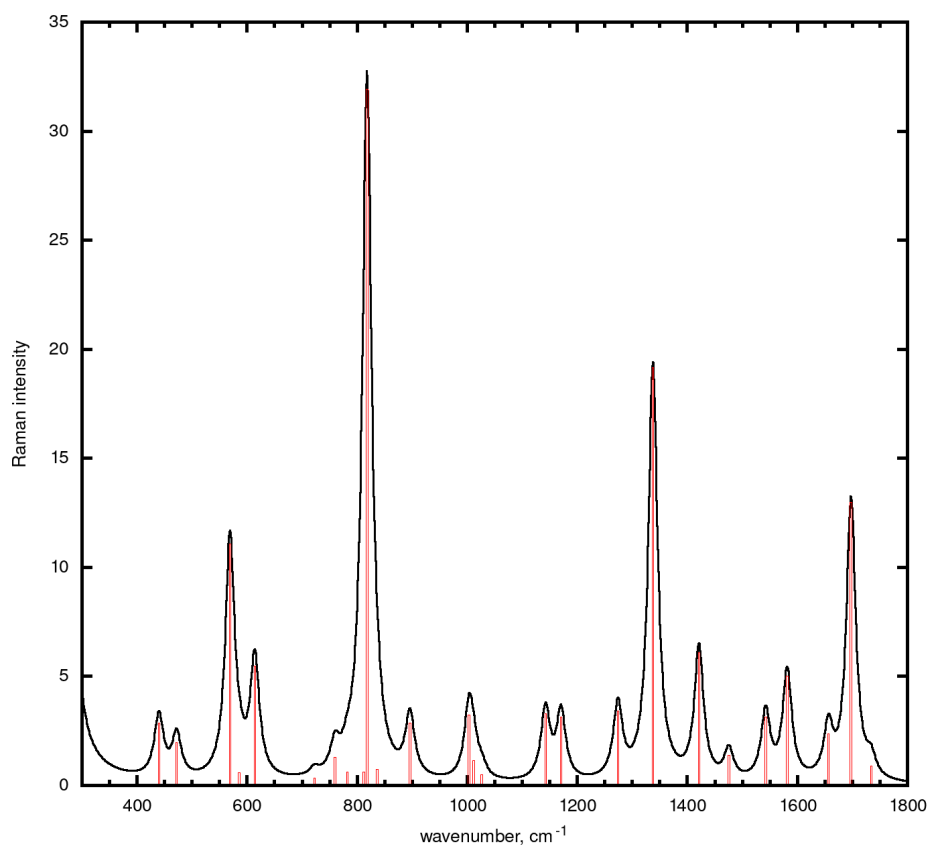
**Figure S9.** Raman spectra of cytosine, explicitly solvated with heavy water molecules ( $m_H = m_O = 400$  aem, see main text), simulated with the use of B3LYP/def2-TZVP method.

**Table S3.** Non-scaled frequencies ( $\nu/\text{cm}^{-1}$ ) and relative Raman intensities ( $I_{\text{rel}}$ ) of the strongest bands in the spectra of cytosine- $\text{d}_3$  computed for various clusters cytosine- $\text{d}_3$ - $6\text{D}_2\text{O}$  with the use of PBE-D3/def2-TZVP method (spectral region  $700\text{-}1800\text{ cm}^{-1}$ ). 25 clusters were generated with relative energies (E) up to 0.6 kcal/mol.

The lowest-energy cluster		The fourth lowest-energy cluster (E = 0.1 kcal/mol)		The highest-energy cluster (E = 0.6 kcal/mol)	
$\nu$	$I_{\text{rel}}$	$\nu$	$I_{\text{rel}}$	$\nu$	$I_{\text{rel}}$
1613	0.68	1613	0.68	1583	0.89
1522	0.27	1522	0.27	1522	0.31
1289	0.50	1289	0.50	1293	0.87
1124	0.26	1124	0.27	1132	0.21
945	0.24	945	0.24	935	0.20
770	1.00	770	1.00	772	1.00

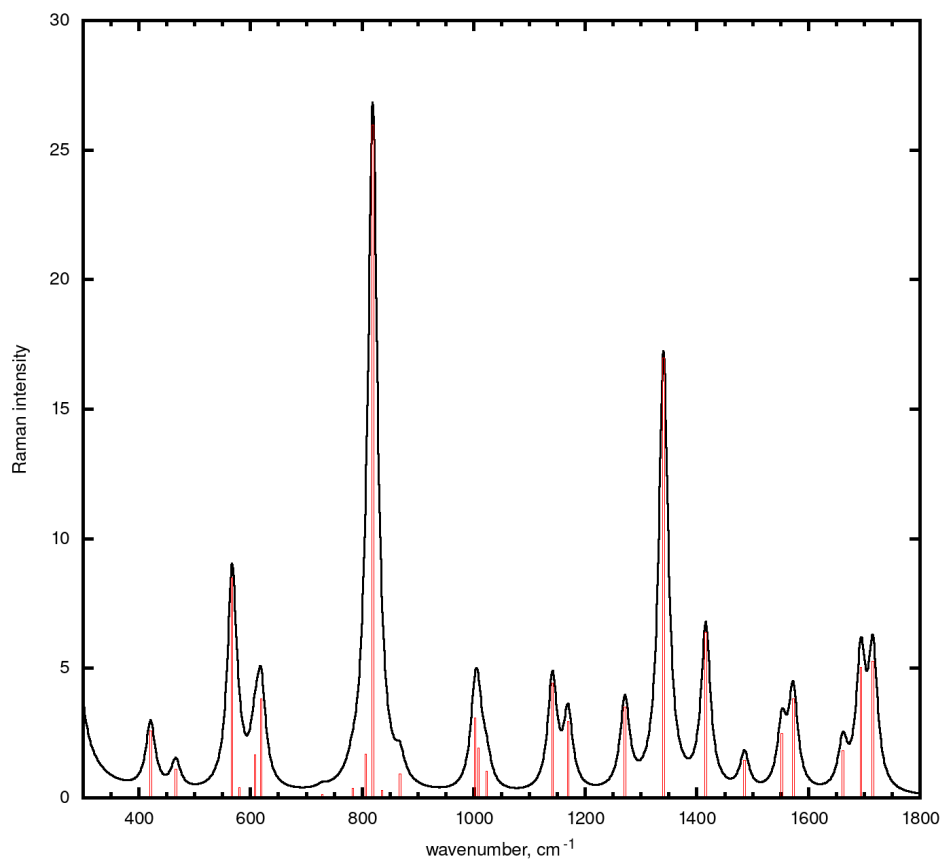


LE



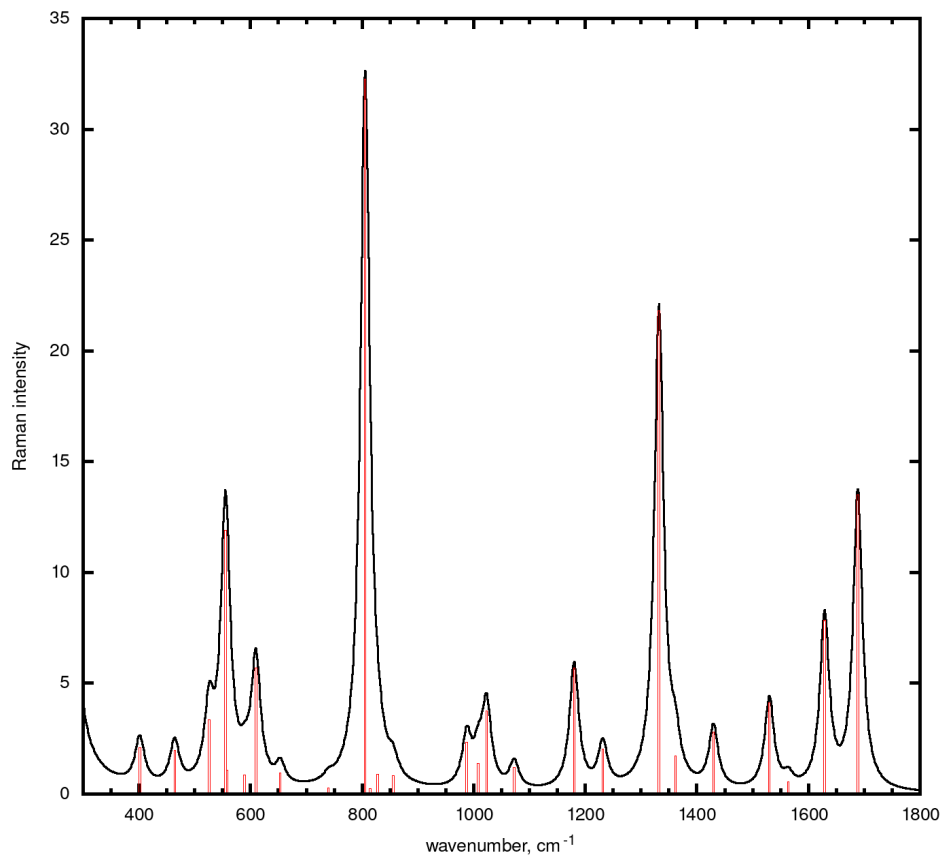
LE2



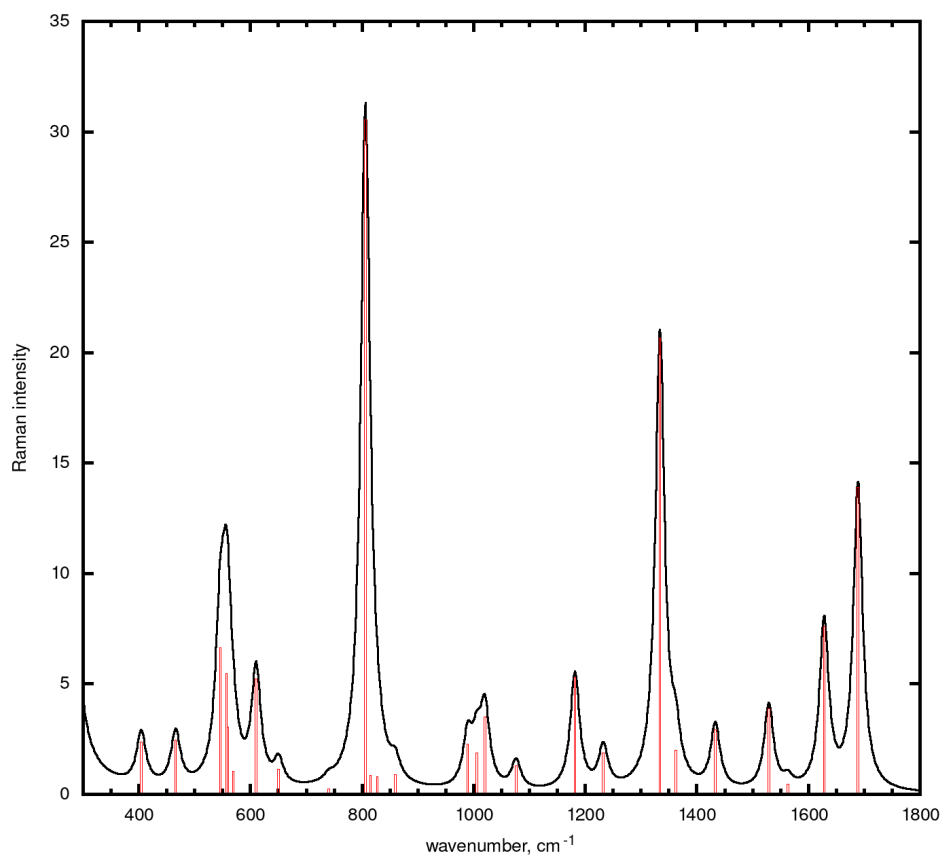


LE\*

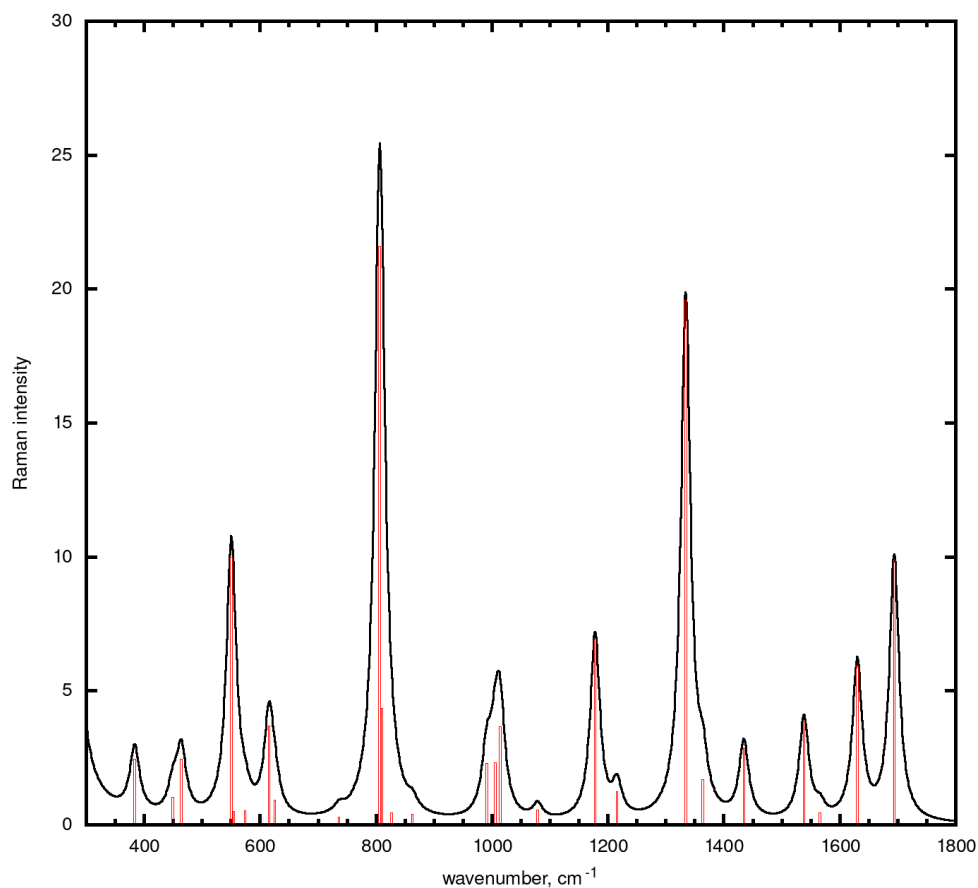
**Figure S10.** Raman spectra of cytosine, explicitly solvated with 30 heavy water molecules ( $m_H = m_O = 400$  aem, see main text), simulated with the use of B3LYP-D3/def2-TZVP method for the lowest-energy (LE) and the second lowest energy (LE2) clusters from the generated ensemble of four clusters. The energy difference between LE and LE2 clusters = 2.4 cal/mol, and the corresponding Boltzmann weights of the clusters = 0.438 and 0.436, respectively. LE\* is the spectrum of the lowest-energy cluster generated in the different QCG run (see main text).



LE

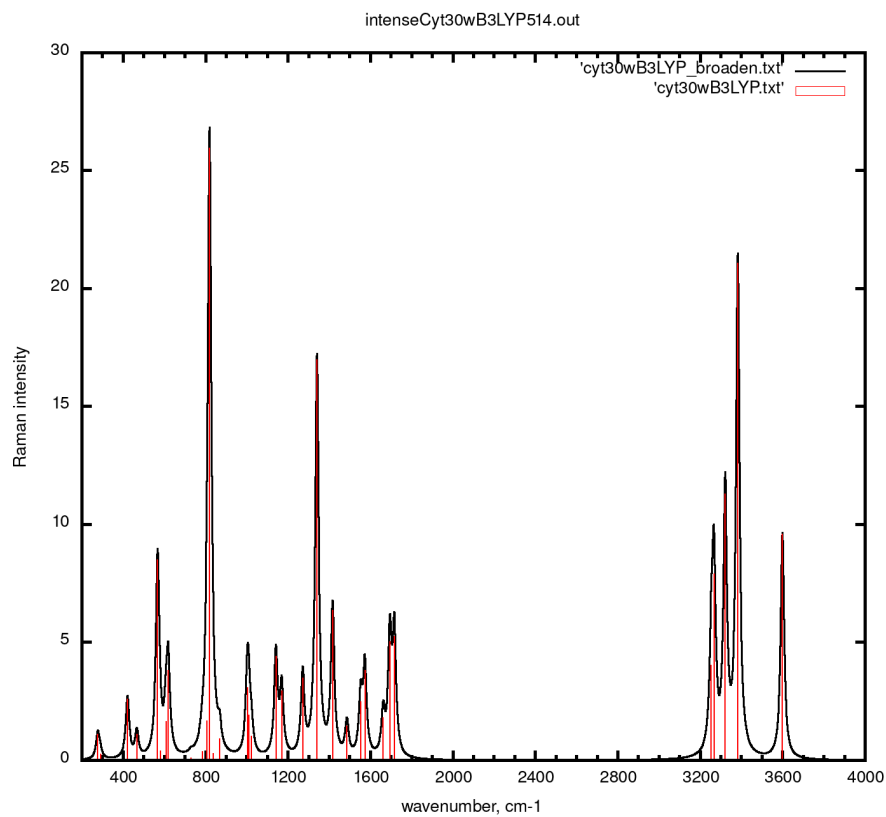


LE2

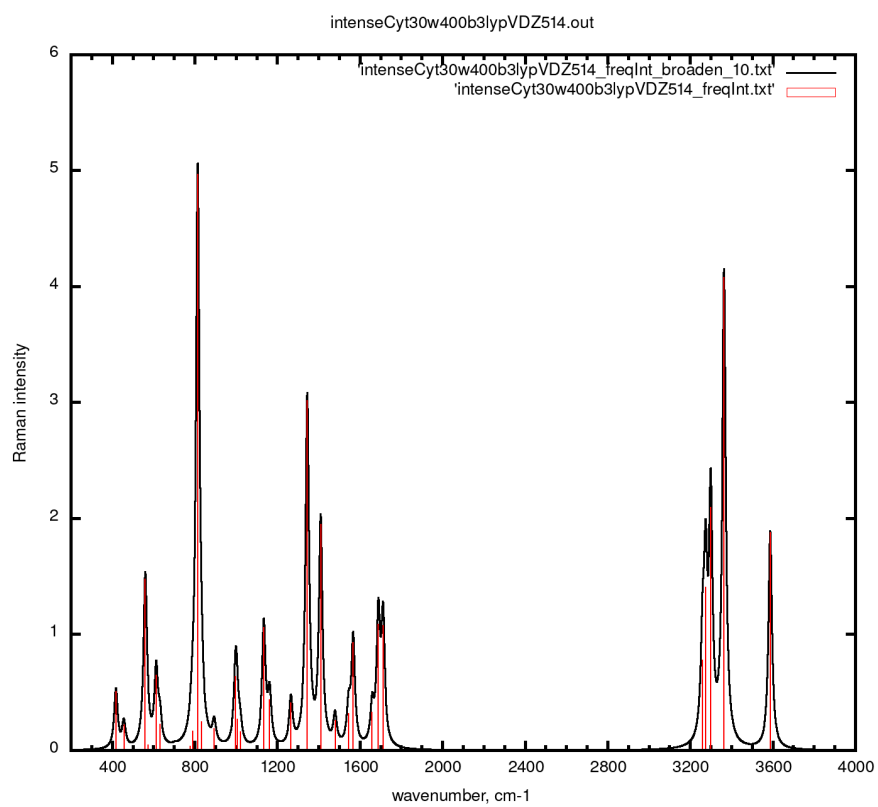


LE\*

**Figure S11.** Raman spectra of cytosine-d<sub>3</sub>, explicitly solvated with 30 heavy water molecules ( $m_D = m_O = 400$  aem, see main text), simulated with the use of B3LYP-D3/def2-TZVP method for the lowest-energy (LE) and the second lowest energy (LE2) clusters from the generated ensemble of four clusters. The energy difference between LE and LE2 clusters = 2.4 cal/mol, and the corresponding Boltzmann weights of the clusters = 0.438 and 0.436, respectively. LE\* is the spectrum of the lowest-energy cluster generated in the different QCG run (see main text).

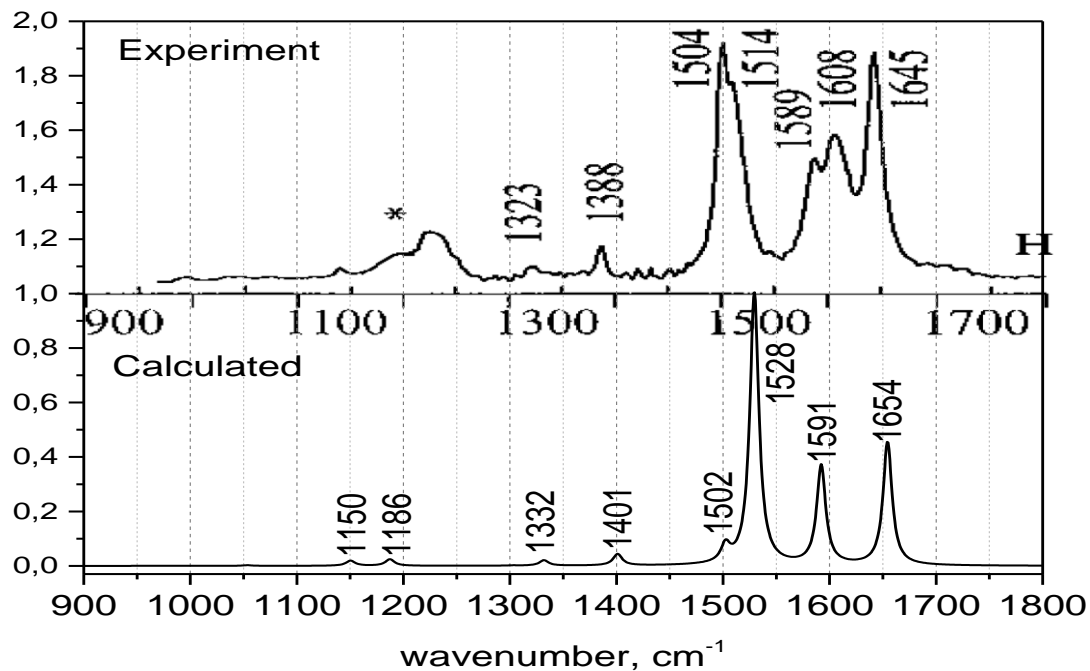
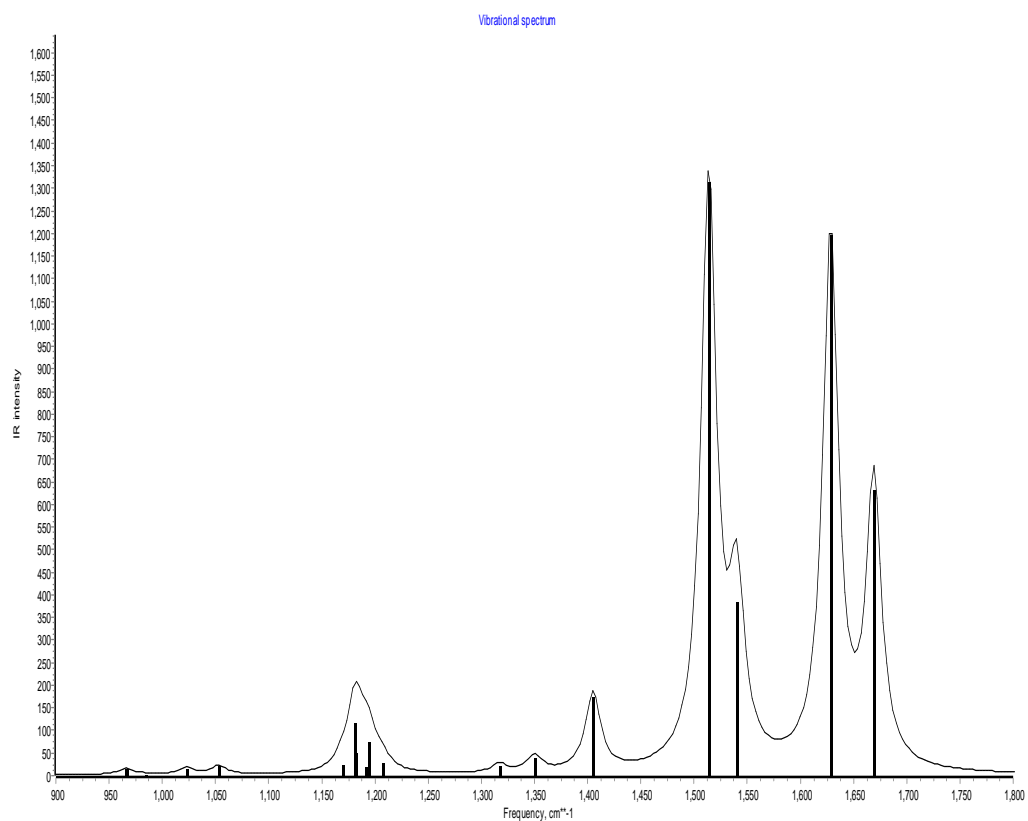


B3LYP/def2-TZVP



B3LYP/aug-cc-pVDZ

**Figure S12.** Raman spectra of cytosine, explicitly solvated with 30 heavy water molecules ( $m_H = m_O = 400$  aem, see main text), simulated with the use of B3LYP-D3/def2-TZVP and B3LYP-D3/aug-cc-pVDZ.



**Figure S13.** IR spectra simulated for clusters cytosine- $d_3$ : $4D_2O$  (top) and cytosine- $d_3$ : $30D_2O$  (bottom) with the use of protocols adopted in Ref. 3 and in present paper, respectively, in comparison to the experiment.