Infrared spectrum and structure of the homochiral serine octamer - dichloride complex

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SUPPLEMENTARY INFORMATION

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1. Experimental collision cross sections of serine cluster chloride complexes

Table 1. Measured CCS values of several serine cluster-dichloride complexes

Ser	Cl^-	*m*/*z*	CCS (Å^2)	
			L-Ser only	L/D-Ser
8	2	455	189	189, 201
9	2	508		211
10	2	560	221	223
11	2	612	236	237
12	2	665	248	251
13	2	717	258	262
14	2	770	273	273

2. IR spectra of serine octamer-dichloride complexes with isotopic substitutions

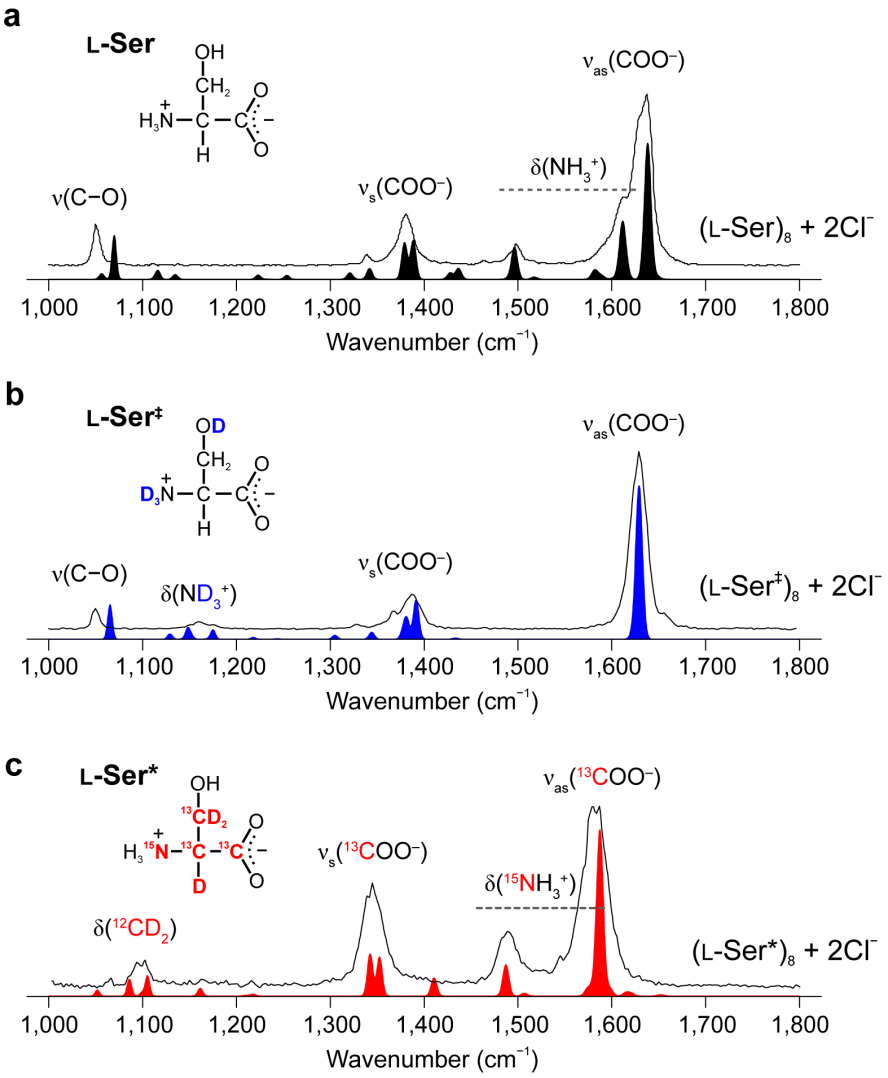

Figure 1. Experimental and theoretical IR spectra of octamer-dichloride complexes of L-Ser (**a**), L-Ser‡ (L-Ser after H/D exchange reaction, **b**), and L-Ser* (L-Ser-$^{13}C_3$,$^{15}N_1$,-2,3,3-D_3, **c**). Theoretical IR spectra (black, blue, and red shades) are obtained at the PBE0-D3 level using the cc-pVTZ basis set. Vibrational frequencies are scaled by 0.957.

3. Comparison between two different interaction patterns which form D4 structure

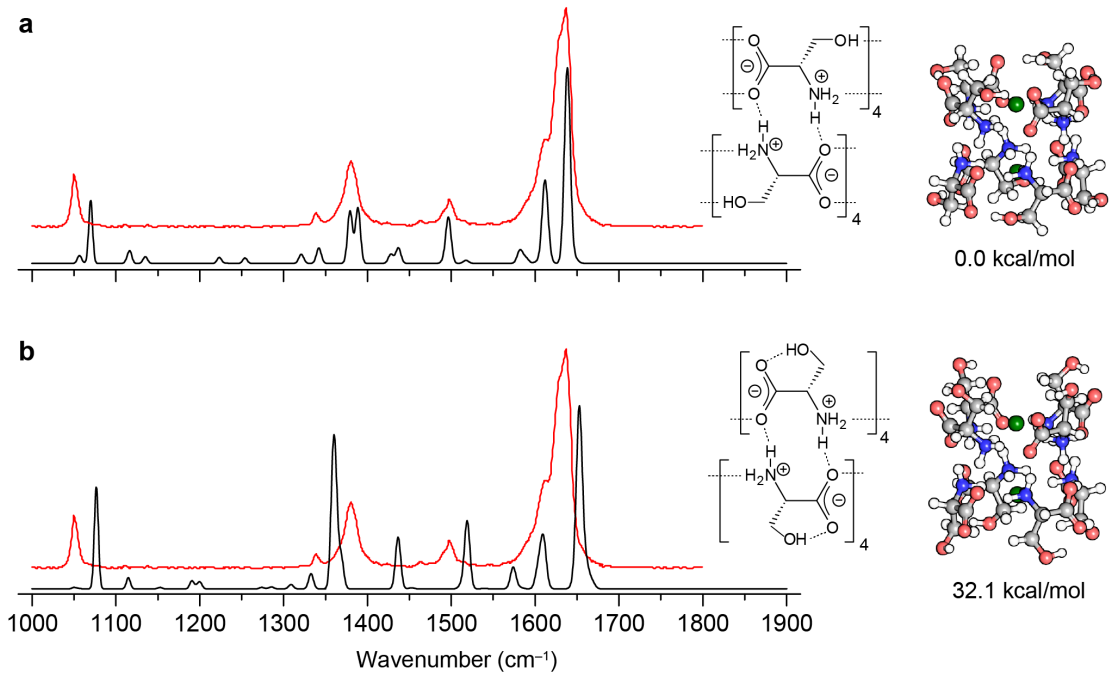

Figure 2. Comparison between two different structures, both of D4 symmetry, however with different interaction patterns. Predicted IR spectra of the present structure (a) and the less stable structure with intramolecular H-bonds between OH and COO^- (b). The red line is the experimental IRMPD spectrum of $Ser_8Cl_2^{2-}$. The observed IR band positions are diagnostic for the proposed lower energy structure.

4. Theoretical predictions for the possible chiral substitutions

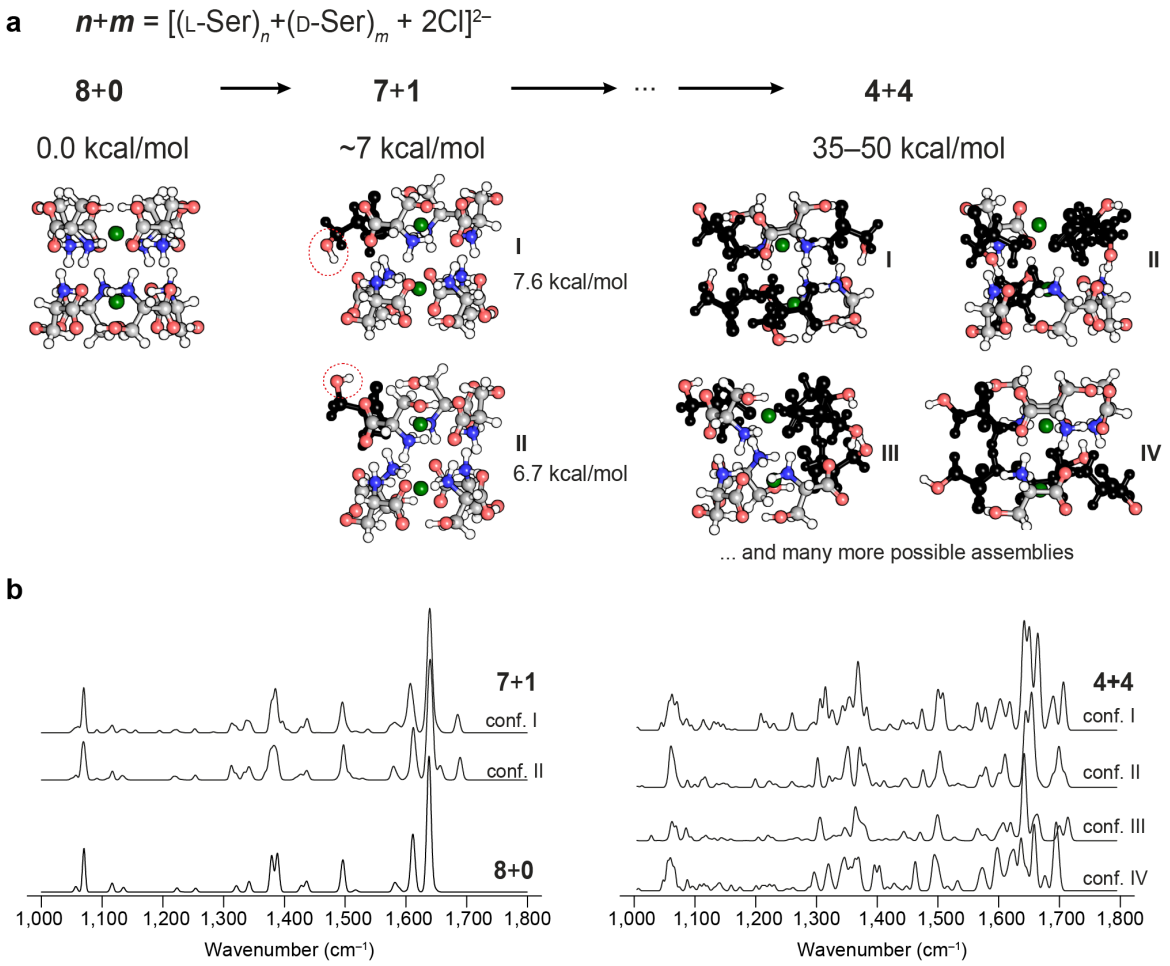

Figure 3. Comparisons of the predicted energetics (a) and IR spectra (b) between homochiral (**8+0**) and non-homochiral (**7+1** and **4+4**)octamers. PBE0/cc-pVTZ level of density functional theory was used for the all calculations.

5. Fragmentation pattern of $Ser_8Cl_2^{2-}$.

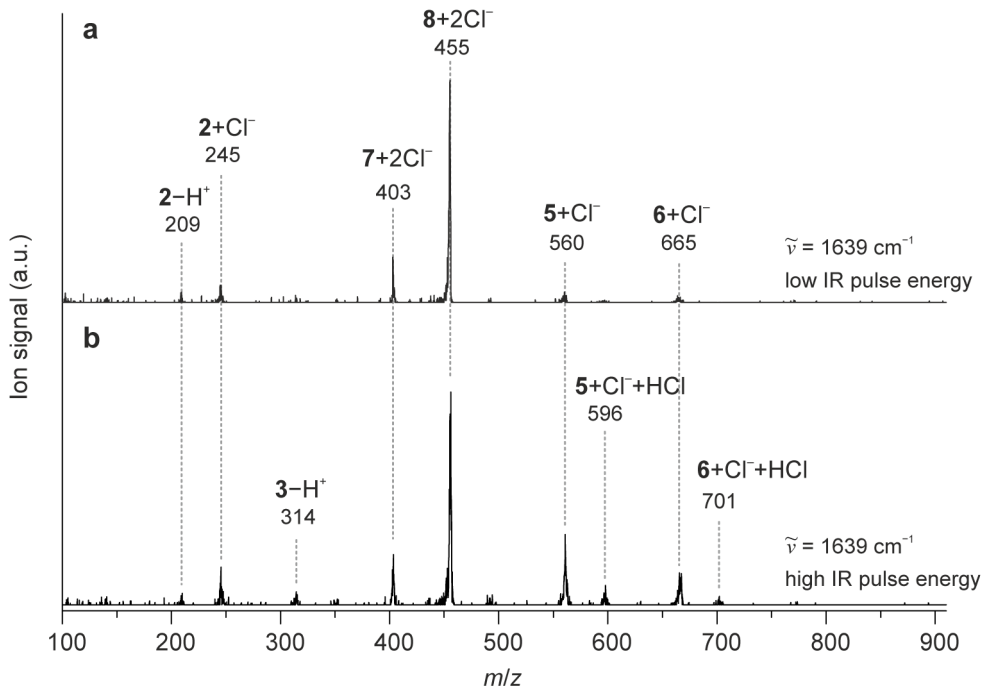

Figure 4. Fragment mass spectra of $Ser_8Cl_2^{2-}$ obtained by IR irradiations with low (a) and high (b) pulse energies. The notations ***n***+***z***Cl^-, ***n***+***z***Cl^-+HCl, and ***n***–H^+ stand for $Ser_nCl_z^{z-}$, $Ser_nCl_z^{z-}$ with HCl adduct, and $(Ser_n–H)^-$, respectively.

6. Optimized geometry of the serine octamer-dichloride complex

Table 2. An *xyz*-coordinate of optimized $[(\text{L-Ser})_8 + 2\text{Cl}]^{2-}$

atoms	coordinate (Å)		
	x	*y*	*z*
C	–0.785444	3.819411	2.363353
C	0.747160	3.760286	2.407251
O	1.323823	3.524819	1.307527
O	1.295569	3.939601	3.501349
N	–1.279457	2.882751	1.331698
H	–2.288516	2.677644	1.448326
H	–0.807749	1.968162	1.438344
H	–1.126560	3.218440	0.359388
C	–1.472683	3.513540	3.685034
H	–1.257981	2.476150	3.969971
H	–1.026240	4.158147	4.444722
O	–2.850124	3.753069	3.578390
H	–3.325880	2.892409	3.564110
H	–1.083167	4.824097	2.051058
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Cl	0.000000	0.000000	–1.980078

7. Energetics of the serine octamer in the gas phase at the PBE0+D3/cc-pVTZ level

Table 3. Energetics

	Cl^-	Ser[a]	Ser_8 [b]	Ser_8Cl^- [b]	$(Ser_8Cl_2)^{2-}$
E_0[c]	–460.1259	–398.6894	–3189.6828	–3650.0078	–4110.2273
ZPE[d]	—	0.1150	—	—	0.9443
G_{corr}[e]	–0.0150	0.0834	—	—	0.8453

a) Non-zwitterionic conformer from ref. [1].

b) Calculated at the optimized geometry of $(Ser_8Cl_2)^{2-}$ by removing one or two chloride ions.

c) Electronic energy in Hartree

d) Zero-point energy in Hartree

e) Correction to the Gibbs free energy at 298 K in Hartree

Table 4. Thermodynamics

	$(Ser_8Cl_2)^{2-}$	Ser_8Cl^- [a]	Ser_8 [a]
ΔE_0[b]	–237 (289)[e]	–52 (59)[e]	–169 (184)[e]
ΔE[c]	–221 (273)[e]	—	—
$\Delta G^0(298K)$[d]	–106 (158)[e]	—	—

a) Calculated at the optimized geometry of $(Ser_8Cl_2)^{2-}$ by removing one or two chloride ions.

b) Difference in electronic energy for the reactions: 8 Ser + 2 Cl^-, Ser_8Cl^- + Cl^- and Ser_8 + 2Cl^- in kcal/mol. Basis-set superposition error (BSSE) is taken into account.

c) as b), including zero point correction and BSSE.

d) Gibbs free energy for the reaction 8 Ser + 2 $Cl^- \rightarrow (Ser_8Cl_2)^{2-}$ at 298 K in kcal/mol. BSSE is taken into account.

e) Values in parentheses stand for those without BSSE corrections.

8. References

1 K. He & W. D. Allen. Conformers of Gaseous Serine. *J. Chem. Theory Comput.* **12**, 3571-3582 (2016).