

Supporting Information

Nonenzymatic Hydrolysis of Acetylthiocholine by Silver Nanoparticles

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Full Reference (40):

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.

Table S1. Conformational angles of geometry-optimized acetylthiocholine (AcSCh).^a

Conformer	Conformational angles				Relative energy
	τ_0	τ_1	τ_2	τ_3	ΔE
t g ⁺ tt/tg ⁻ tt	+179.9/-179.9	+83.9/-83.9	180.0/180.0	-177.2/+177.2	0.00
tttt/tttt	-178.8/+178.8	+179.3/-179.3	+179.8/-179.8	-179.9/+179.9	+1.22
tg ⁺ g ⁺ t/ tg ⁻ g ⁻ t	-179.9/+179.9	+82.9/-82.9	+85.7/-85.7	-179.5/+179.5	+2.18
g ⁺ g ⁺ tt/g ⁻ g ⁻ tt	+4.9/-4.9	+94.0/-94.0	+177.1/-177.1	-177.5/+177.5	+2.50
g ⁺ ttt/g ⁻ ttt	0.0/0.0	180.0/180.0	180.0/180.0	180.0/180.0	+5.59
g ⁺ g ⁺ g ⁺ t/g ⁻ g ⁻ g ⁻ t	+2.4/-2.4	+87.9/-87.9	+82.3/-82.3	-179.7/+179.7	+7.20

^aConformational angles are in degrees. For their definition see Figure 1B (main text) .

Relative energy (ΔE) of each conformer is expressed in kcal/mol.

Four letters notations, reflecting from left to right the relative orientations (g⁺, g⁻ and t) of the four skeletal torsion angles (τ_0 -to- τ_3), were used to designate the global conformation of the optimized structures. See main text for details.

Geometry optimization has been performed in a solvent continuum at the B3LYP/6-311++ G(d,p) level.

Table S2. Conformational angles of geometry-optimized thiocholine (SCh).^a

	τ_2	τ_3	ΔE
tt/tt	180.0/180.0	+179.6/-179.6	0.00
g ⁺ t/g ⁻ t	+64.4/-64.4	+175.1/-175.1	+2.65

^aConformational angles are in degrees. For their definition see Figure 1E (main text).

Relative energy (ΔE) of each conformer is expressed in kcal/mol.

Two letters notations, reflecting from left to right the relative orientations (g⁺, g⁻ and t) of the torsion angles (τ_2 and τ_3), were used to designate the global conformation of optimized structures. See main text for details.

Geometry optimization has been performed in a solvent continuum at the B3LYP/6-311++ G(d,p) level.

Table S3. Assignment of the observed Raman spectra from the aqueous samples of acetylthiocholine, thiocholine and acetate.^a

Acetylthiocholine (AcSCh)			Thiocholine (SCh)			Acetate		
Obs	Calc ^b	Assignment ^b	Obs	Calc	Assignment	Obs	Calc	Assignment
1685 (s)	1731	v(C2=O)						
1470 (sh)	1510	CH ₃ -asymm. bend.	1479 (sh)		CH ₃ -asymm. bend.			
1450 (s)	1485	CH ₂ -bend.	1452 (s)	1483	CH ₂ -sciss.; CH ₃ -asymm. bend.			
1422 (sh)	1460	CH ₂ -rock.; CH ₂ -bend.						
						1416 (s)	1475	CH ₃ -asymm. bend.
1346 (w)	1376	CH ₂ -twist.	1344 (w)	1371	CH ₂ -twist.	1348 (m)	1350	COO ⁻ -symm. st.; CH ₃ -symm. bend.
1278 (m)	1305	CH ₂ -rock.	1282 (m)	1311	CH ₂ -rock.			
1135 (m)	1148	CH ₃ -asymm. rock.	1135 (w)	1144	CH ₃ -asymm. rock.			
1085 (m)	1114	CH ₃ -asymm. rock.; v(C1-C2); δ(C1-C2=O)						
1052 (m)	1058	v(C4-C5)	1055 (m)	1055	v(C4-C5)			
972 (s)	967	CH ₃ -asymm. rock.	972 (s)	964	N ⁺ C ₃ -asymm. st.			
945 (m)	941	N ⁺ C ₃ -asymm. st.						
						928 (s)		v(C1-C2); δ(O-C-O)
911 (s)	894	v(C4-C5); N ⁺ C ₃ -asymm. st.	908 (s)	888	v(C5-N6); N ⁺ C ₃ -symm. st.			
790 (s)	778	v(C4-S3); N ⁺ C ₃ -symm. st.; CH ₂ -scissor.	780 (s)	776	v(C4-S3); N ⁺ C ₃ -symm. st.;			
743 (s)	730	v(C4-S3); N ⁺ C ₃ -symm. st.; v(C5-C6)	750 (sh)	743	CH ₂ -wagg.; N ⁺ C ₃ -symm. st.;			
			670 (w)		v(C4-S3); N ⁺ C ₃ -symm. st.; v(C5-N6)			
						653 (w)		δ(O-C-O)
637 (s)	609	v(C2-S3); δ(C1-C2=O); v(C1-C2); δ(S3-C2=O)						
514 (m)	512	N ⁺ C ₃ -symm. bend.; N ⁺ C ₃ -symm. rock.	507 (m)	504	N ⁺ C ₃ -symm. bend.; N ⁺ C ₃ -symm. rock.			
453 (m)	453	N ⁺ C ₃ -asymm. bend.; N ⁺ C ₃ -asymm. rock.	453 (w)	453	N ⁺ C ₃ -asymm. bend.; N ⁺ C ₃ -asymm. rock.			
370 (m)	362	N ⁺ C ₃ -asymm. rock.; N ⁺ C ₃ -asymm. bend.	372 (m)	366	N ⁺ C ₃ -asymm. bend.; N ⁺ C ₃ -asymm. rock.			
254 (s)	243	δ(C1-C2-S3); CH ₂ -bend.; v(C4-S3)	278 (s)	262	CH ₂ -bend.; v(C5-N6); v(C4-S3)			

^aSee Figure 1 (main text) for Observed spectra.^bTaken from Ref. 41.Wavenumbers are in cm⁻¹. (s) strong, (m) medium, (w) weak, (sh) shoulder.

Assignments are based on the potential energy distribution (PED) matrix as expressed in terms of internal coordinates. For atom numbering, see Figure 1 (main text).

Calculated wavenumbers correspond to the tg⁺tt/tg⁻tt (lowest energy) conformers of AcSCh (Table S1), to the tt conformer of SCh (Table S2), and to the geometry-optimized acetate.

Geometry optimization and vibrational calculations have been performed in a solvent continuum at the B3LYP/6-311++ G(d,p) level.

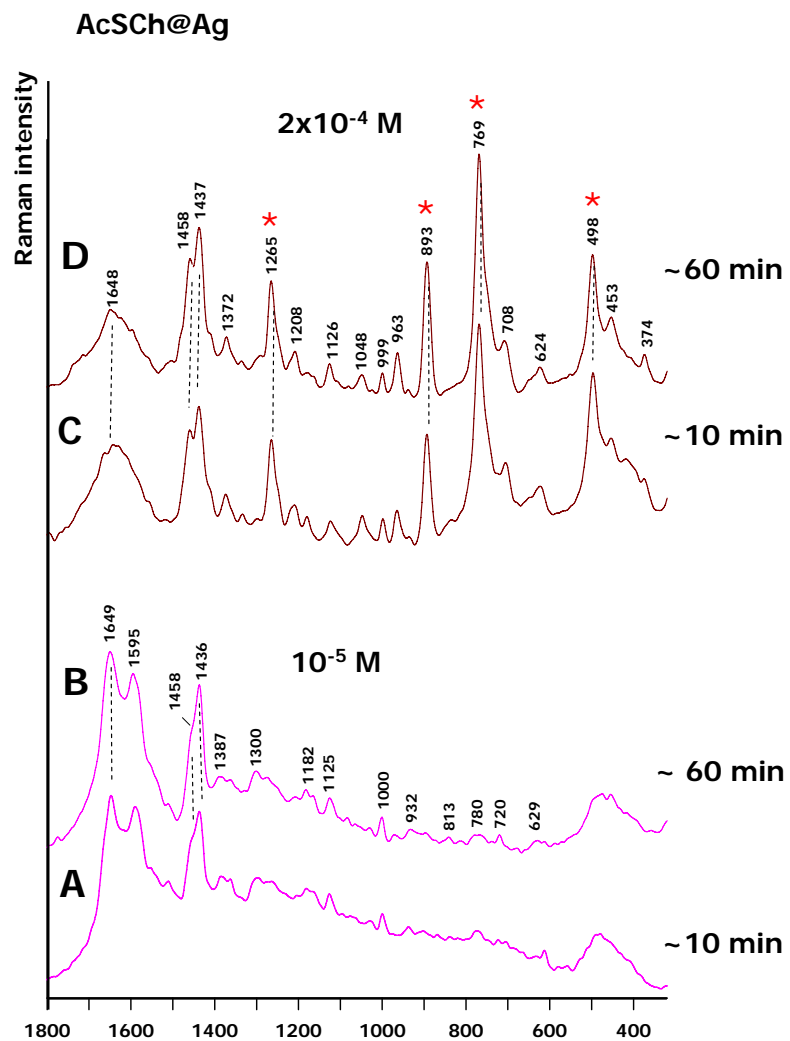


Figure S1. SERS data of AcSCh on AgNPs obtained 10 and 60 minutes after sample preparation. (A,B) spectra recorded at 10^{-5} M. (C,D) spectra recorded at 2×10^{-4} M. SERS data of SCh as a function of concentration. Characteristic SCh vibrational markers (modes 1-4, Table 1) are indicated by magenta asterisks.