

Electronic Supplementary information

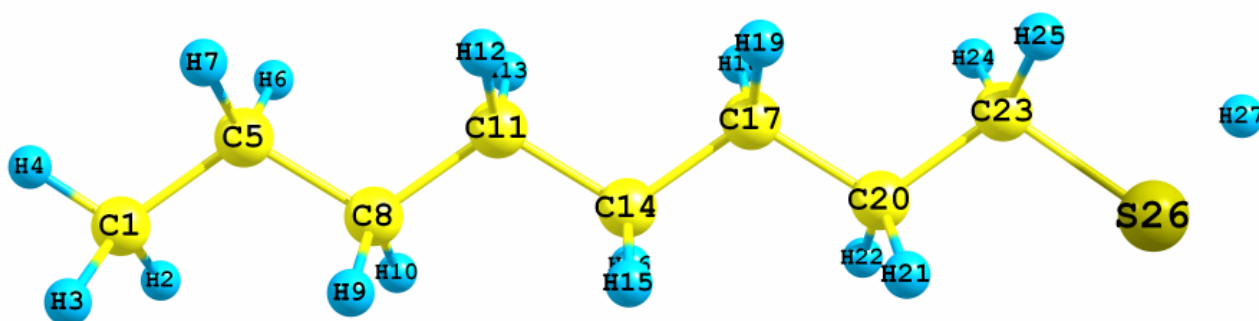
SERS observation of soft C–H vibrational mode of bifunctional alkanethiol molecules adsorbed at Au and Ag electrodes

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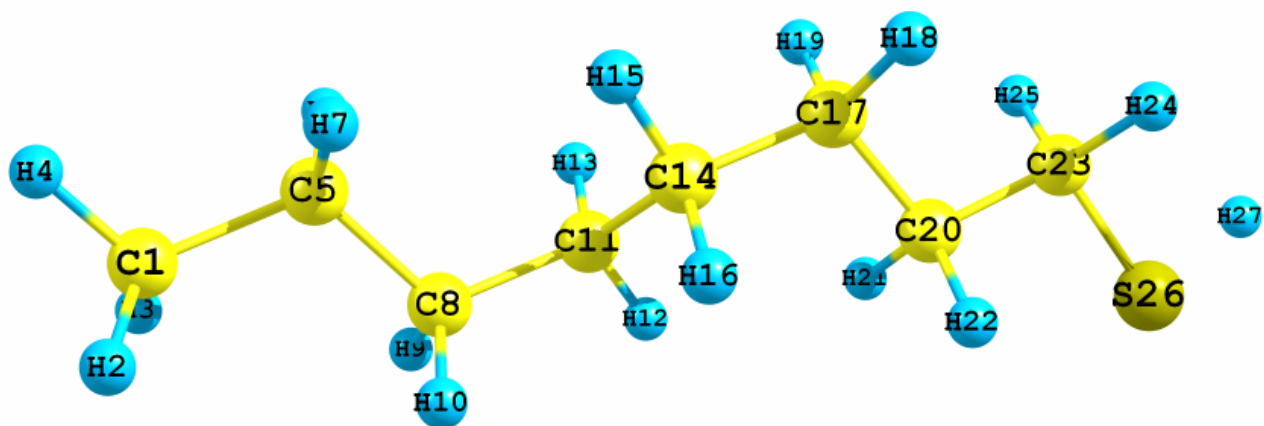
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1. Theoretical modeling of octanethiol (model compound of studied molecules in the present work)

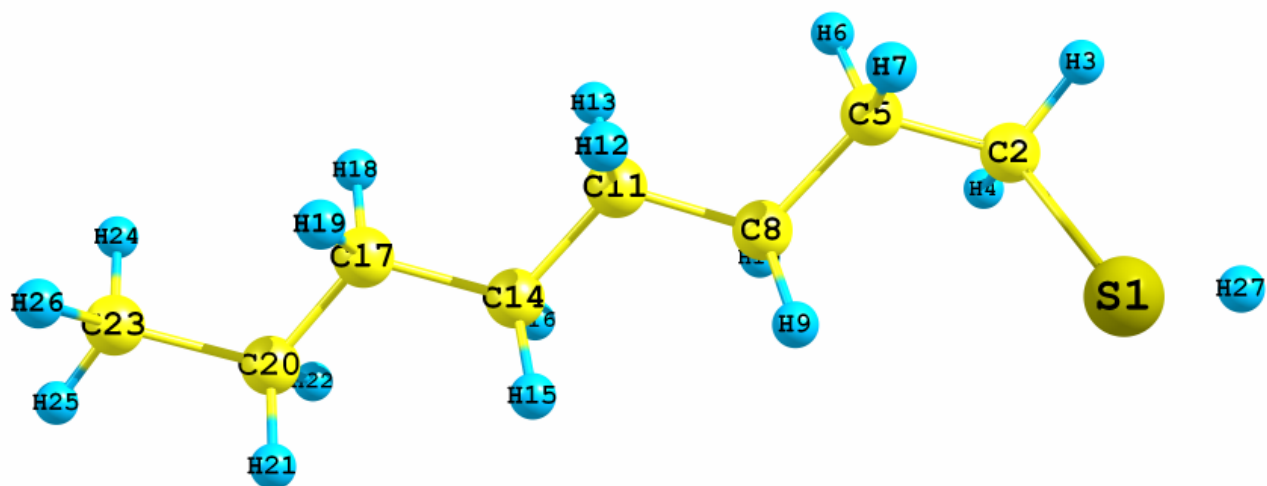
All calculations were performed using Gaussian for Windows package version G03W [S1]. Geometry optimization and frequency calculations were accomplished with DFT method, using B3LYP functional. Calculations were done using 6-311++G(2d, p) basis set. Presented frequencies are not scaled.



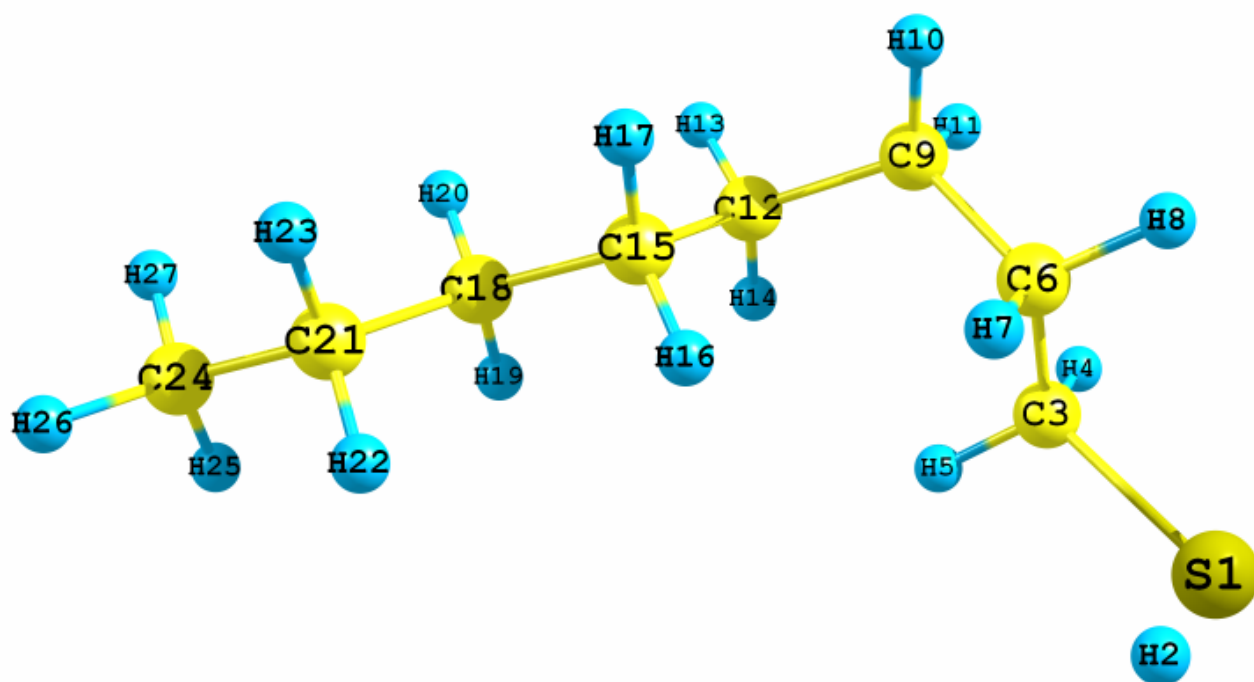
Structure **1** (trans conformer)



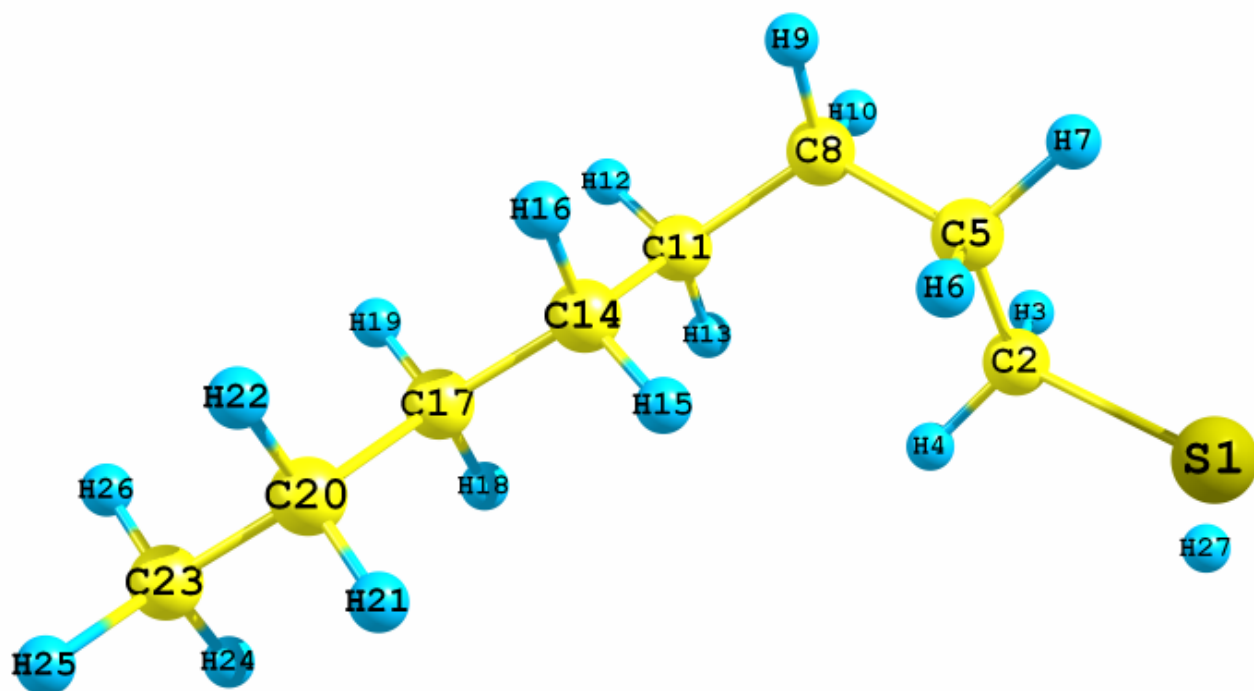
Structure **2** (gauche conformer)



Structure **3** (gauche conformer)



Structure 4 (gauche conformer)



Structure 5 (gauche conformer)

Fig. S1. Optimized structures of Trans (1) and Gauche (2-5) conformers used for calculations of Raman spectra.

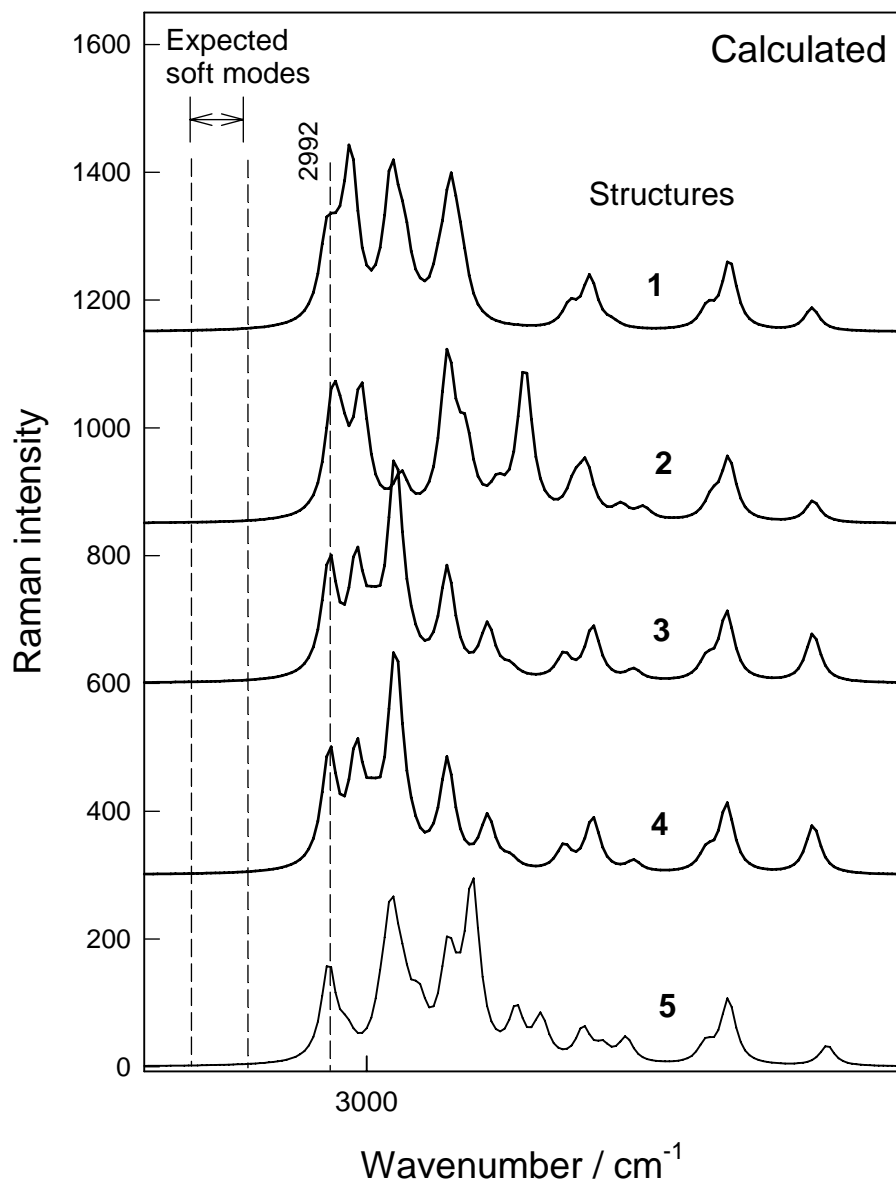


Fig. S2. Calculated Raman spectra in the C–H bond stretching frequency region for trans (1) and gauche (2-5) conformers. Frequencies are not scaled. Frequency region where soft C–H modes are expected to be observed is also shown.

Presented data show that gauche defects are not able to produce soft C–H modes experimentally observed in our work.

2. Experimental observation of soft C-H mode of octanethiol adsorbed at Ag and Au electrodes

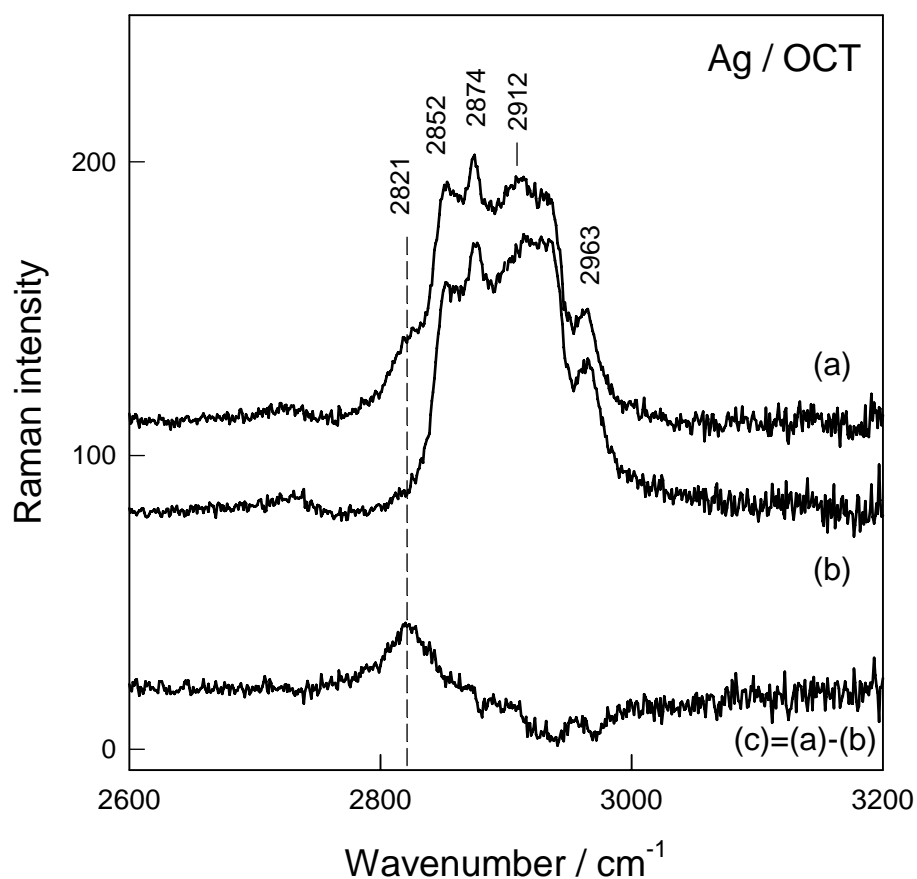


Fig. S3. SERS spectra of octanethiol (OCT) adsorbed at Ag electrode at -0.80 V (a) and 0.00 V (b) potentials. Difference spectrum (c) is also shown. In subtraction procedure spectra were normalized according to the intensity of 2874 cm⁻¹ peak. Electrode was immersed in ethanolic 10⁻³ M OCT solution for 5 s. Spectra were recorded in aqueous 0.01 M phosphate buffer solution (pH=7.0) containing 0.1 M. Na₂SO₄. Excitation wavelength is 785 nm (30 mW), integration time is 300 s.

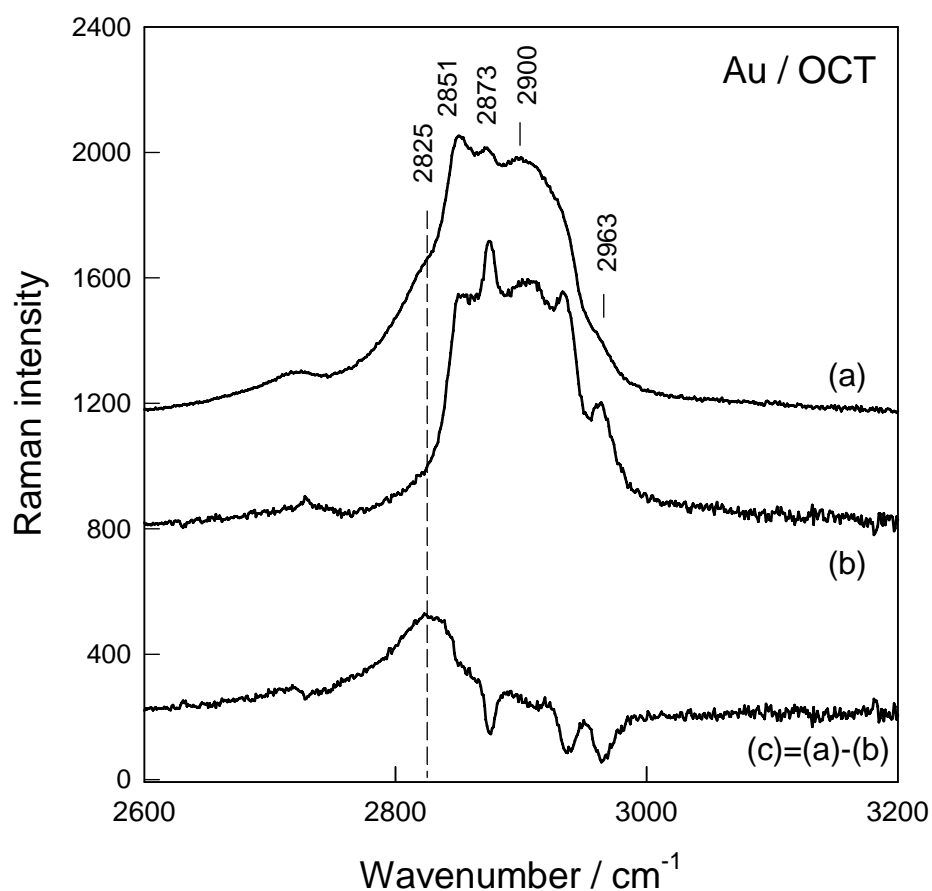


Fig. S4. SERS spectra of octanethiol (OCT) adsorbed at Au electrode at -0.20 V potential. Electrode was immersed in ethanolic 10^{-3} M OCT solution for 1s (a) and 16 h (b). Difference spectrum (c) is also shown. In subtraction procedure spectra were normalized according to the intensity of peak near 2900 cm^{-1} . Spectra were recorded in aqueous 0.01 M phosphate buffer solution (pH=7.0) containing 0.1 M. Na_2SO_4 . Excitation wavelength is 785 nm (30 mW), integration time is 300 s.

Presented spectra show that upon adsorption of OCT at Ag and Au electrodes at short immersion times and appropriate potential low frequency mode in the vicinity of $2821\text{--}2825\text{ cm}^{-1}$ appears, indicating that softening of C–H mode is general phenomenon, which does not depend on the nature of the particular end group.

References

[S1] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukada, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Know, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenburg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004.