

Supplementary information: Chemical bonding effects in Raman response of benzenethiol adsorbed on small silver clusters.

Semion K. Saikin,^{1,2} Roberto Olivares-Amaya,¹ Dmitrij Rappoport,¹

Michael Stopa³ and Alán Aspuru-Guzik¹

¹ Department of Chemistry and Chemical Biology, Harvard University,
Cambridge, MA 02138, USA.

² Department of Physics, Kazan State University,
Kazan 420008, Russian Federation.

³ Center for Nanoscale Systems, Harvard University,
Cambridge, MA 02138, USA.

E-mail: saykin@fas.harvard.edu, aspuru@chemistry.harvard.edu

(Dated: July 16, 2009)

I. ELECTRONIC EXCITATION SPECTRA

The absorption spectra of the simulated Ag_n clusters and PhS-Ag_n complexes, $n = 6, 8 - 11$ are shown in Figs. 1 and 2. For $n = 6$, the structure of the silver cluster in the PhS-Ag_n complex differs from the one of the bare silver cluster because of the cluster reconstruction. This is discussed in Sec. 3.1 of the manuscript in more details.

II. OFF-RESONANCE RAMAN SPECTRA

The relative intensities of the computed Raman lines of isolated benzenethiol as compared to the relative Raman intensities measured for neat benzenethiol¹⁻³ are given in Tab. I. The intensities are in good agreement except of the $\omega_1^{\text{exp}} = 1004 \text{ cm}^{-1}$ vibrational mode. Changing the exchange functional in DFT simulations results in minor improvements only.

The Raman spectra of PhS-Ag_n complexes, $n = 1, 6, 8, 11$ computed at the excitation energy 0.62 eV (2000 nm excitation wavelength) are shown in Fig. 3. The excitation energy used is below the lowest electronic transition in the structures. The complex PhS-Ag shows a strong enhancement of totally symmetric vibrational modes, while in the other complexes, the non-bonding interaction between the aromatic ring and the cluster results in a suppression of the integrated Raman scattering cross section and a redistribution of intensities between the totally symmetric and non-totally symmetric modes. See Sec. 3.2 of the manuscript.

III. RAMAN EXCITATION PROFILES

The Raman excitation profiles (REPs) and low-frequency electron excitation spectra for PhSH and PhS-Ag_n complexes, $n = 1, 6, 8, 11$ for the computed vibrational modes, $\omega_1 = 1019 \text{ cm}^{-1}$, $\omega_2 = 1059 \text{ cm}^{-1}$, $\omega_3 = 1136 \text{ cm}^{-1}$, and $\omega_4 = 1656 \text{ cm}^{-1}$, are shown in Figs. 4-8. The range of excitation energies is 1.6 – 3.0 eV. In logarithmic scale the REPs for isolated PhSH , Fig. 4, are almost linear in the excitation energy, which is consistent with the semiclassical theory of Raman scattering.⁴ For the complexes PhS-Ag_n , $n = 1, 6, 8, 11$, Figs. 5-8, a resonance-type structure of REPs originates in the electronic excitations to mixed metal-molecular states.

IV. DISCUSSIONS

The frequency shifts of four totally symmetric vibrational modes $\omega_1 = 1019 \text{ cm}^{-1}$, $\omega_2 = 1059 \text{ cm}^{-1}$, $\omega_3 = 1136 \text{ cm}^{-1}$, and $\omega_4 = 1656 \text{ cm}^{-1}$ in PhS-Ag $_n$, $n = 1, 6 - 11$ complexes are collected in Tab. II. On average, the values of the shifts are larger for the complexes where total Raman scattering is quenched, PhS-Ag $_n$, $n = 6, 7, 8, 11$.

-
- ¹ K. B. Biggs, J. P. Camden, J. N. Anker, and R. P. Van Duyne, *J. Phys. Chem. A*, 2009, **113**, 4581.
- ² K. T. Carron and L. G. Hurley, *J. Phys. Chem.*, 1991, **95**, 9979.
- ³ R. L. Aggarwal, L. W. Farrar, E. D. Diebold and D. L. Polla, *J. Raman Spectrosc.*, in press.
- ⁴ D. A. Long, *The Raman Effect*, Wiley, Chichester, 2002.

TABLE I: The relative intensities of the computed Raman lines for isolated benzenethiol as compared to the experimental data for neat benzenethiol, Refs. 1–3. The relative intensities are defined with respect to the 1027 cm^{-1} vibrational mode. The excitation wavelength is 785 nm. The frequencies are in cm^{-1} .

Mode	ω_1	ω_3	ω_4	ω_5	ω_6	ω_7
Freq. PhSH	1004	1094	1583	414	701	918
PhSH ^{comp}	1.0	1.0	0.9	0.5	0.3	0.4
PhSH ^{exp} Ref. 1	3.0	0.5	0.3	0.7	0.7	0.3
PhSH ^{exp} Ref. 2	4.5	0.4	0.4	0.6	0.7	0.2
PhSH ^{exp} Ref. 3	2.9	0.6	1.0	1.0	0.5	0.4

TABLE II: The relative shifts of four totally symmetric vibrational modes in PhS–Ag_n, $n = 1, 6 - 11$, complexes as compared to the unperturbed frequencies in isolated benzenethiol, $\Delta\omega_n = \omega_n(\text{PhS–Ag}_k) - \omega_n(\text{PhSH})$. The computed frequencies for isolated benzenethiol are $\omega_1 = 1019 \text{ cm}^{-1}$, $\omega_2 = 1059 \text{ cm}^{-1}$, $\omega_3 = 1136 \text{ cm}^{-1}$, and $\omega_4 = 1656 \text{ cm}^{-1}$. The values of the shifts are given in cm^{-1} .

Complex	$\Delta\omega_1$	$\Delta\omega_2$	$\Delta\omega_3$	$\Delta\omega_4$
PhS–Ag ₁	-0	-4	-21	-10
PhS–Ag ₆	-7	-8	-26	-28
PhS–Ag ₇ (I)	-7	-9	-31	-33
PhS–Ag ₇ (II)	-4	-5	-24	-17
PhS–Ag ₈	-5	-5	-29	-16
PhS–Ag ₉	-1	-2	-18	-8
PhS–Ag ₁₀	-1	-3	-18	-9
PhS–Ag ₁₁	-6	-6	-28	-19

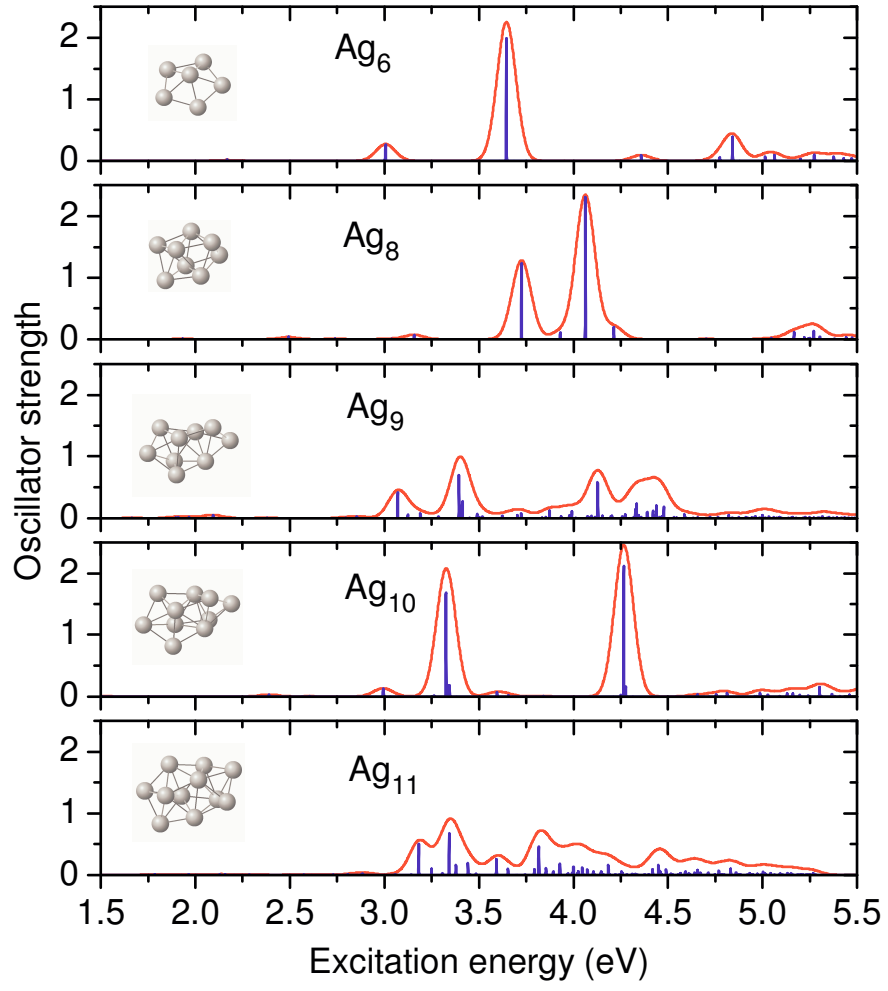


FIG. 1: Absorption spectra of the computed Ag_n clusters, $n = 6, 8 - 11$.

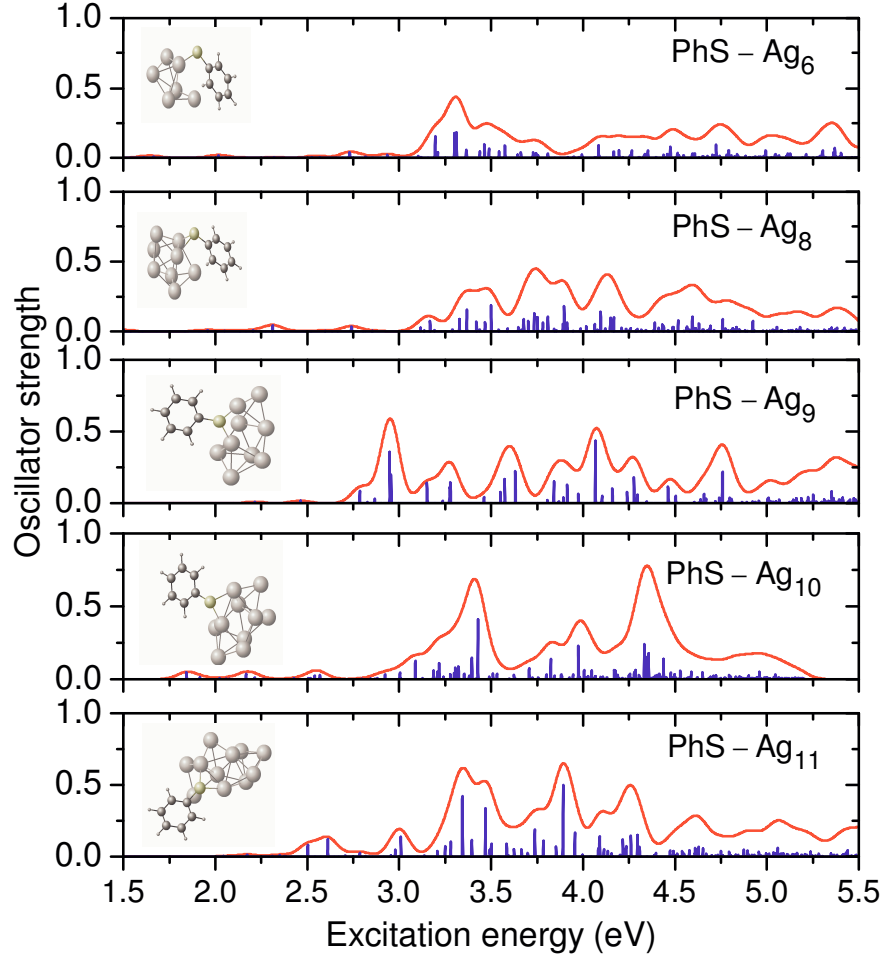


FIG. 2: Absorption spectra of the computed PhS-Ag_n complexes, $n = 6, 8 - 11$.

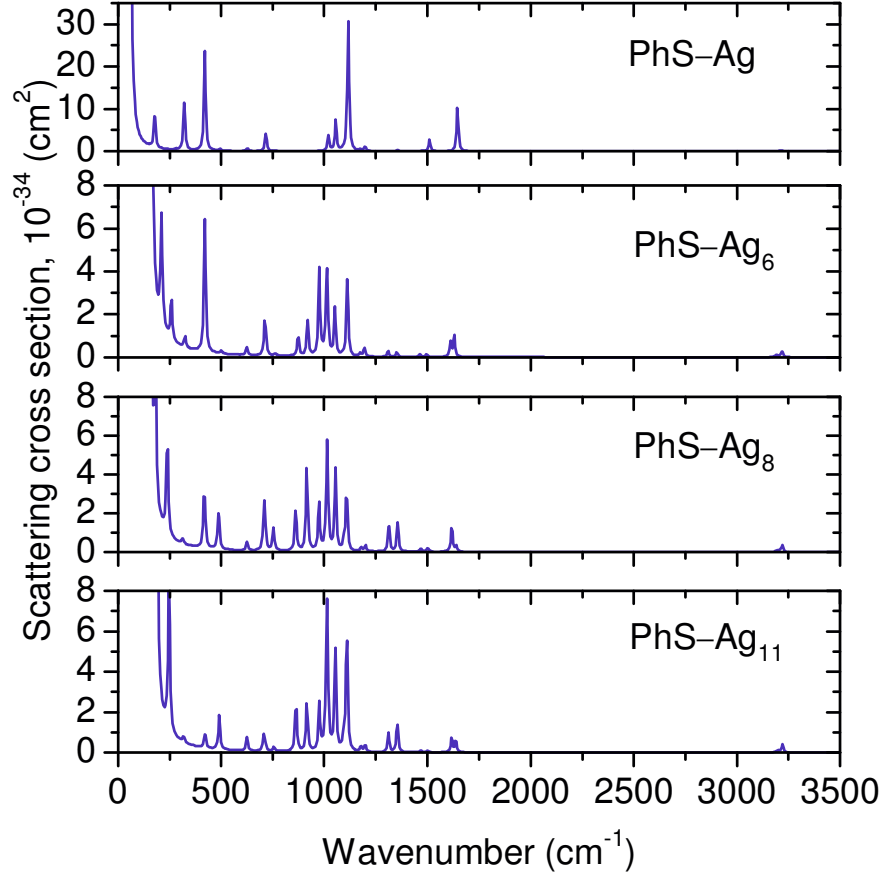


FIG. 3: Off-resonance Raman spectra of the computed PhS-Ag_n complexes, $n = 1, 6, 8, 11$. The excitation energy is 0.62 eV, which corresponds to 2000 nm wavelength.

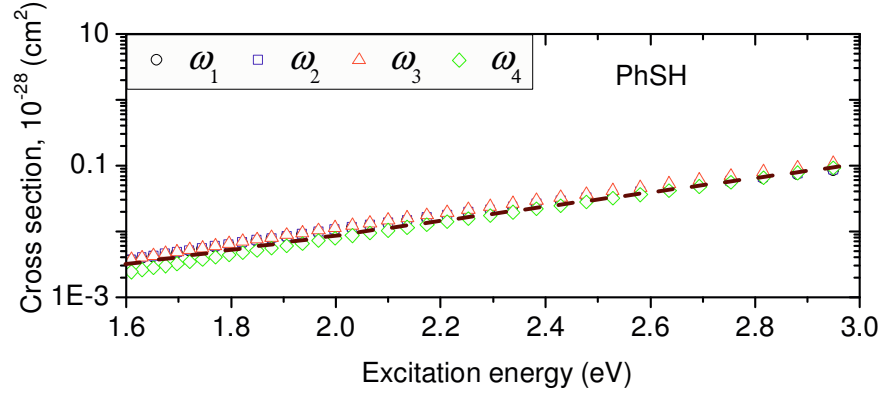


FIG. 4: Raman excitation profile for the vibrational modes $\omega_1 = 1019 \text{ cm}^{-1}$, $\omega_2 = 1059 \text{ cm}^{-1}$, $\omega_3 = 1136 \text{ cm}^{-1}$, and $\omega_4 = 1656 \text{ cm}^{-1}$ in isolated benzenethiol.

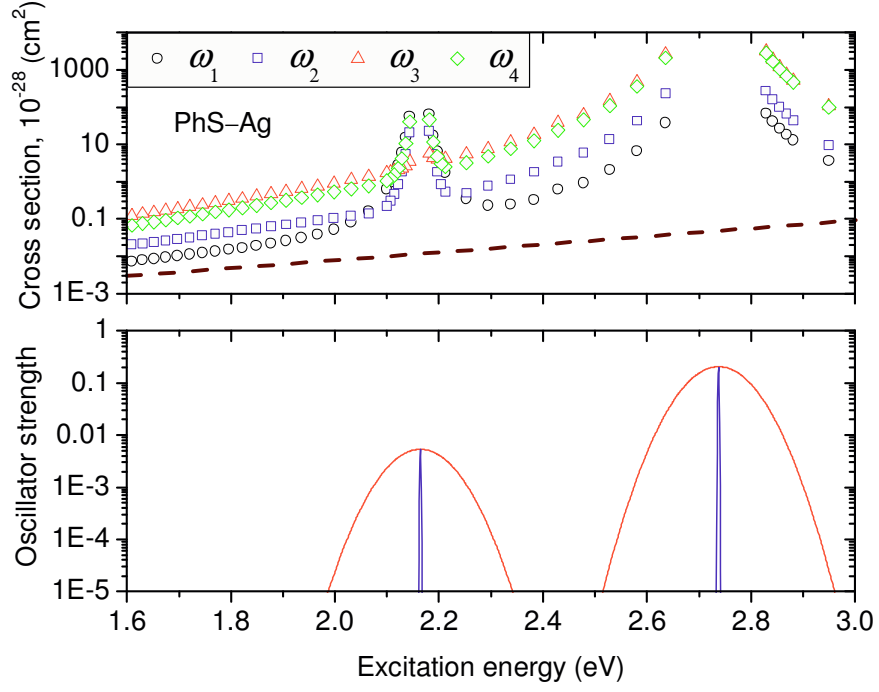


FIG. 5: Raman excitation profile for the vibrational modes $\omega_1 = 1019 \text{ cm}^{-1}$, $\omega_2 = 1059 \text{ cm}^{-1}$, $\omega_3 = 1136 \text{ cm}^{-1}$, and $\omega_4 = 1656 \text{ cm}^{-1}$ in the PhS-Ag complex.

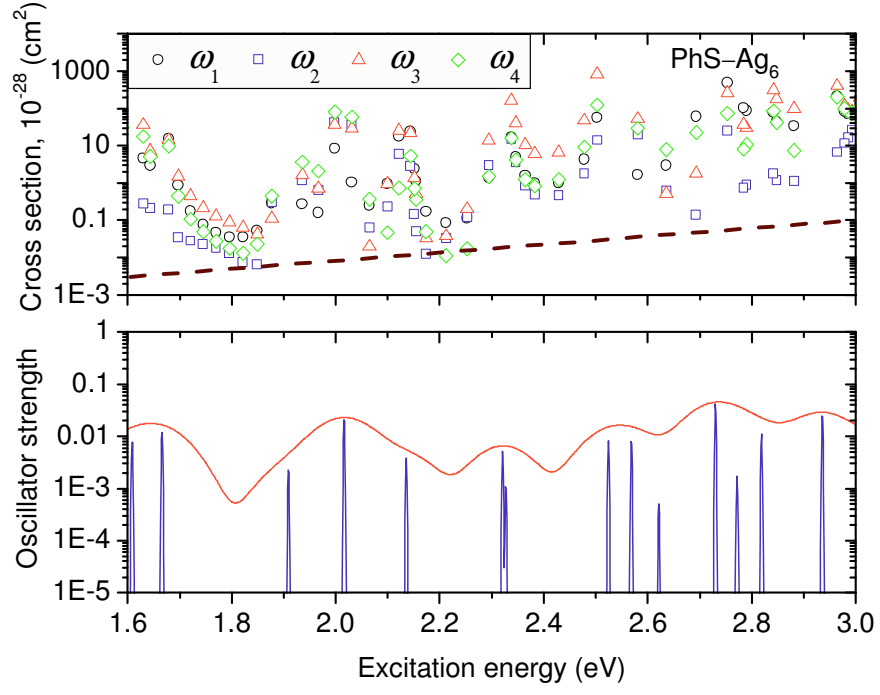


FIG. 6: Raman excitation profile for the vibrational modes $\omega_1 = 1019 \text{ cm}^{-1}$, $\omega_2 = 1059 \text{ cm}^{-1}$, $\omega_3 = 1136 \text{ cm}^{-1}$, and $\omega_4 = 1656 \text{ cm}^{-1}$ in the PhS-Ag₆ complex.

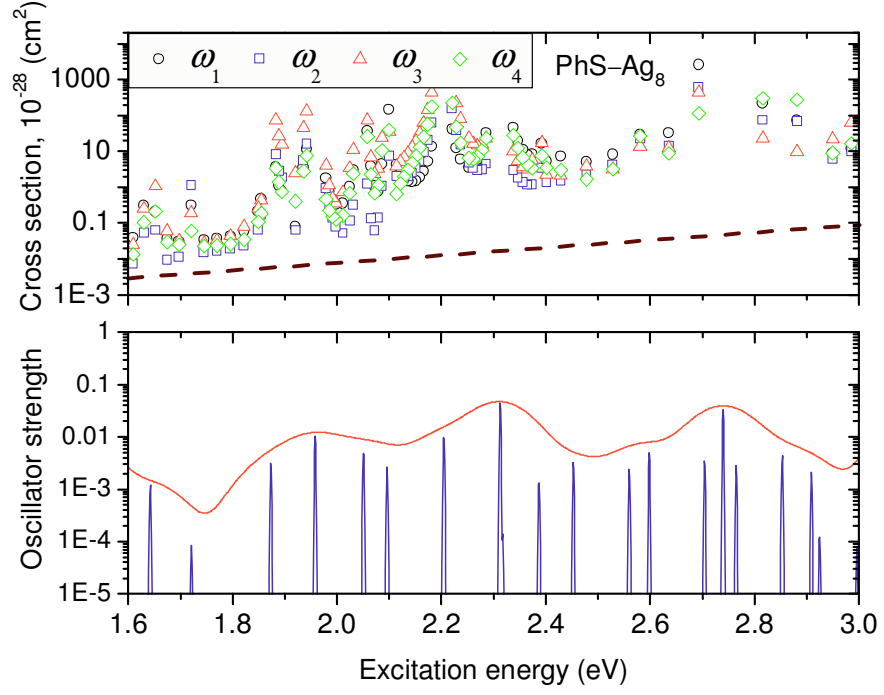


FIG. 7: Raman excitation profile for the vibrational modes $\omega_1 = 1019 \text{ cm}^{-1}$, $\omega_2 = 1059 \text{ cm}^{-1}$, $\omega_3 = 1136 \text{ cm}^{-1}$, and $\omega_4 = 1656 \text{ cm}^{-1}$ in the PhS-Ag₈ complex.

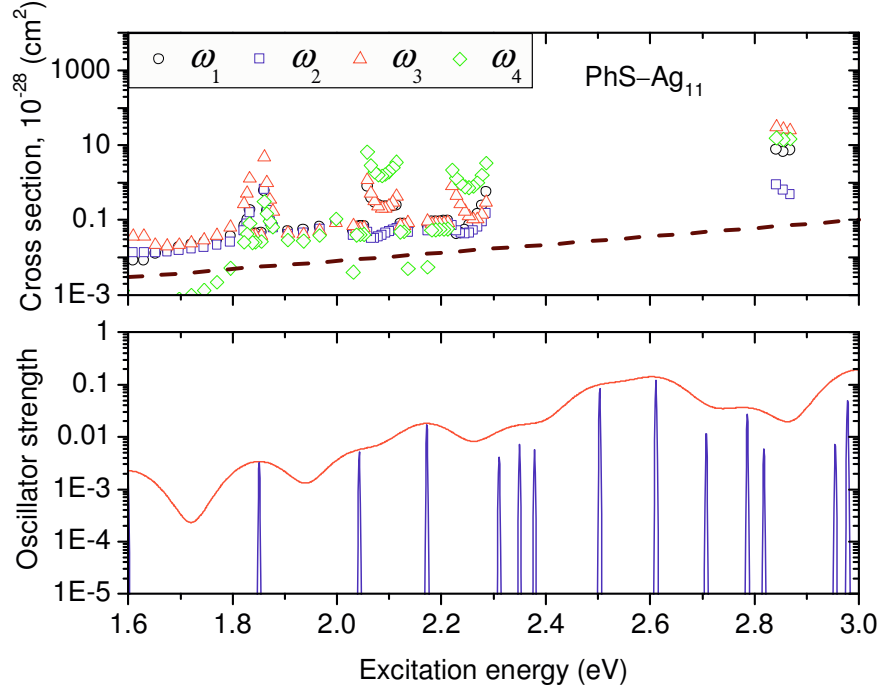


FIG. 8: Raman excitation profile for the vibrational modes $\omega_1 = 1019 \text{ cm}^{-1}$, $\omega_2 = 1059 \text{ cm}^{-1}$, $\omega_3 = 1136 \text{ cm}^{-1}$, and $\omega_4 = 1656 \text{ cm}^{-1}$ in the PhS-Ag₁₁ complex.