Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Vibrational Wave-Packet Dynamics of Silver Pentamer Probed by Femtosecond NeNePo Spectroscopy

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Table S1: Fitting parameters of the frequency contributions for the oscillatory signals shown in Fig. S3 by the function, $f(t) = \sum_i A_i \cos(2\pi t/T_i + \varphi_i) e^{-t/\tau_i}$. Details are given in Fig. S3.

λ_{pump} = 510 nm				λ_{pump} = 402 nm			
ω_e (cm^{-1})	φ (π)	A (a.u.)	τ (ps)	ω_e (cm^{-1})	φ (π)	A (a.u.)	τ (ps)
256	0.7	23	1.1	258	0.7	52	1.3
213	1.0	10	1.2	212	1.0	10	1.2
203	0.4	8	1.3	201	0.8	36	1.3
158	0.1	101	1.9	156	0.4	154	1.6
101	0.1	129	2.5	101	0.2	185	2.1
75	0.4	40	2.1	75	0.5	64	1.6
55	0.4	70	3.3	56	0.1	103	2.5
29	1.3	11	1.1	26	2.0	27	1.6

Table S2: Experimental frequencies and calculated harmonic frequencies (ω_e, in cm^{-1}) of the totally symmetric vibrational modes of neutral planar Ag_5 **1** and bipyramidal Ag_5 **2** using PBE/def2-TZVPP. The displacements of the normal modes for neutral **1** and **2** are present in Fig. S4 and S6. The bipyramidal **2** is calculated to be 49 $kJ \cdot mol^{-1}$ higher than the planar **1** (PBE/def2-TZVPP).

Fs NeNePo[a]	Raman[b]	Harm. (**1**)	Harm. (**2**)
			180
157	162	152	
	136	143	
101	105, 100	98	106
			83
75	68	71	
56			46

[a] Mean Frequencies for two pump wavelengths.

[b] Raman spectroscopy of Ag_5 in solid argon.[1]

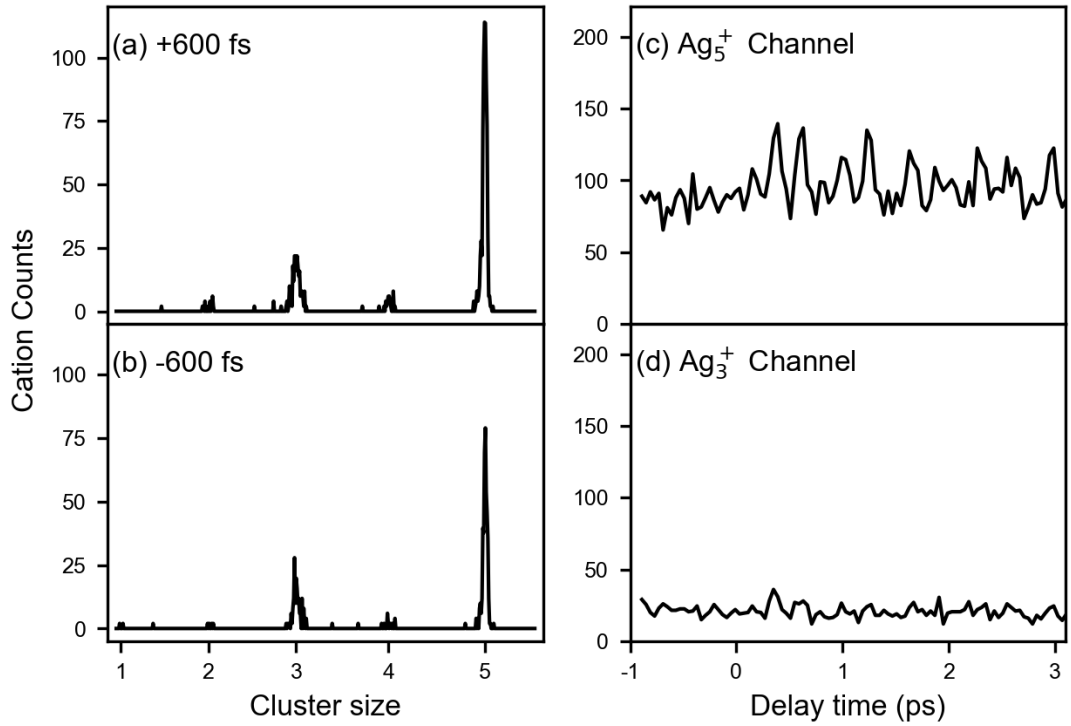

Fig. S1: Quadrupole mass spectra (500 ms accumulation time) of silver cluster cations Ag_n^+ (n = 1 - 5) obtained for λ_{pump} = 510 nm and λ_{probe} = 402 nm: (a) delay time = + 600 fs; (b) delay time = -600 fs. Fs NeNePo transients (one scan) obtained for Ag_5^+ cation (c) and Ag_3^+ cation (d) in -1 ps to +3 ps.

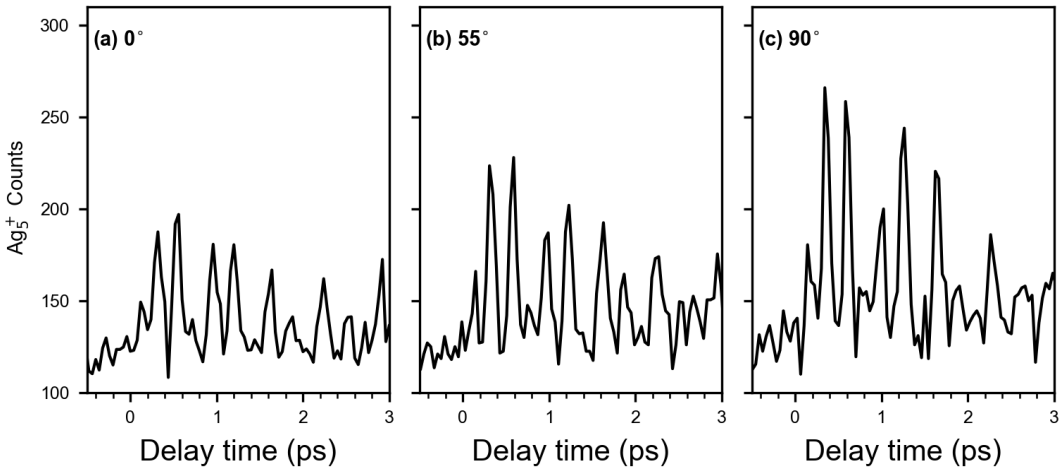

Fig. S2: Two-color fs NeNePo transients (λ_{pump} = 510 nm, λ_{probe} = 402 nm) of Ag_5 monitoring the Ag_5^+ signal at different relative polarization angles (θ) over a range of -0.5 to 3.0 ps for (a) 0° (b) 55° and (c) 90°.

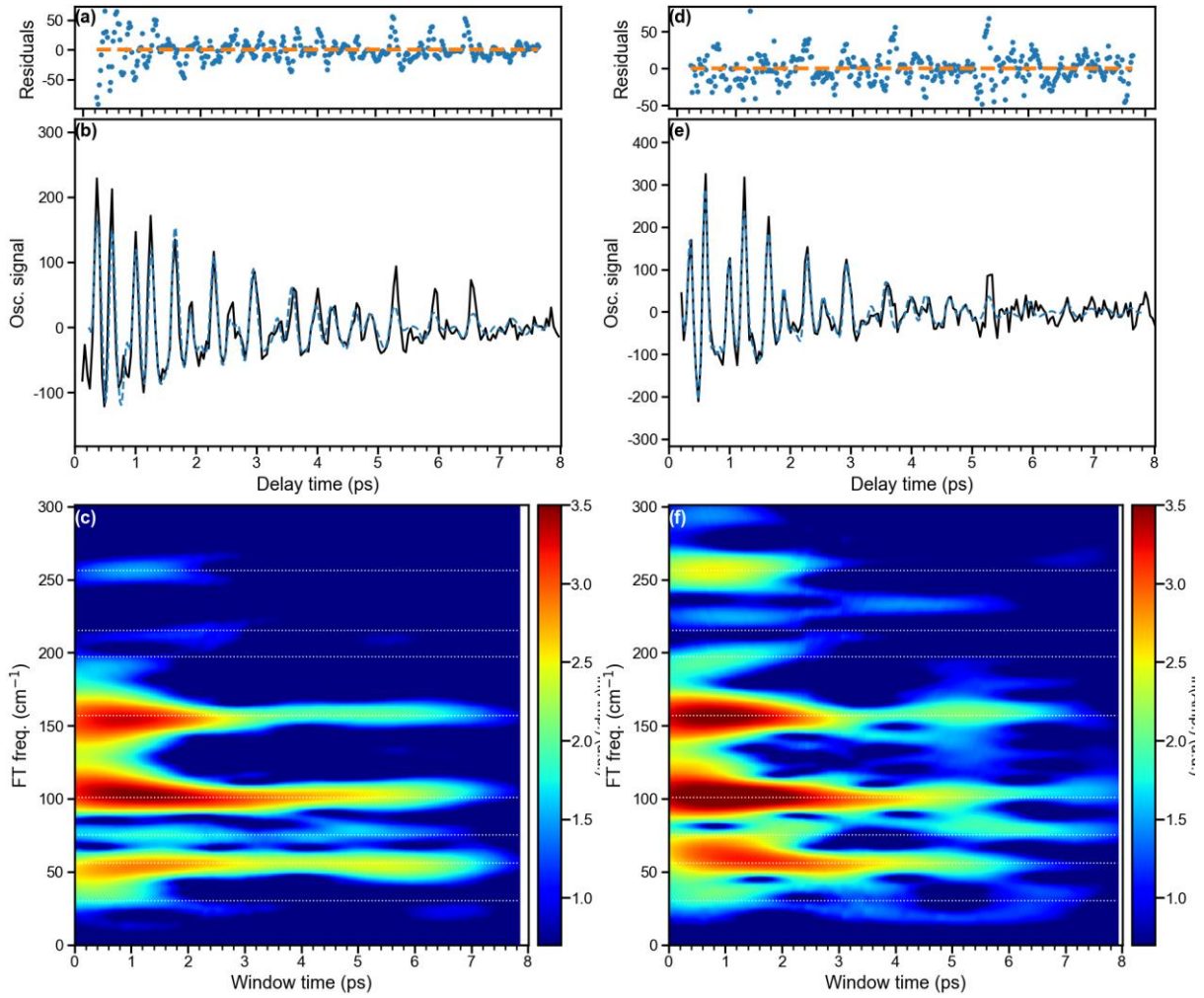

Fig. S3: Oscillatory time-dependent Ag_5^+ signal (black) and fitting curves (blue) (b) and (e), the fitting residuals (a and d) and STFT spectrograms (c) and (f). (a)-(c) are obtained by a pump pulse of 510 nm. (d)-(f) are obtained by a pump pulse of 402 nm. The experimental oscillations are fitted by a sum over all cosine functions containing all significant frequency contribution, as $f(t) = \sum_i A_i \cos(2\pi t/T_i + \varphi_i) e^{-t/\tau_i}$. The initial amplitudes A_i, oscillation periods T_i (or frequencies, $1/(\omega_e c)$) and lifetimes (τ_i) are taken from the STFT spectrogram shown in (c) and (f). The initial phases (φ_i) are set to 0. The fitting results are given in Table S1. The residuals of the fitting curves are given in (a) and (d). The STFT spectrograms are obtained by applying a 4 ps window time, providing a frequency resolution of 9 cm^{-1}.

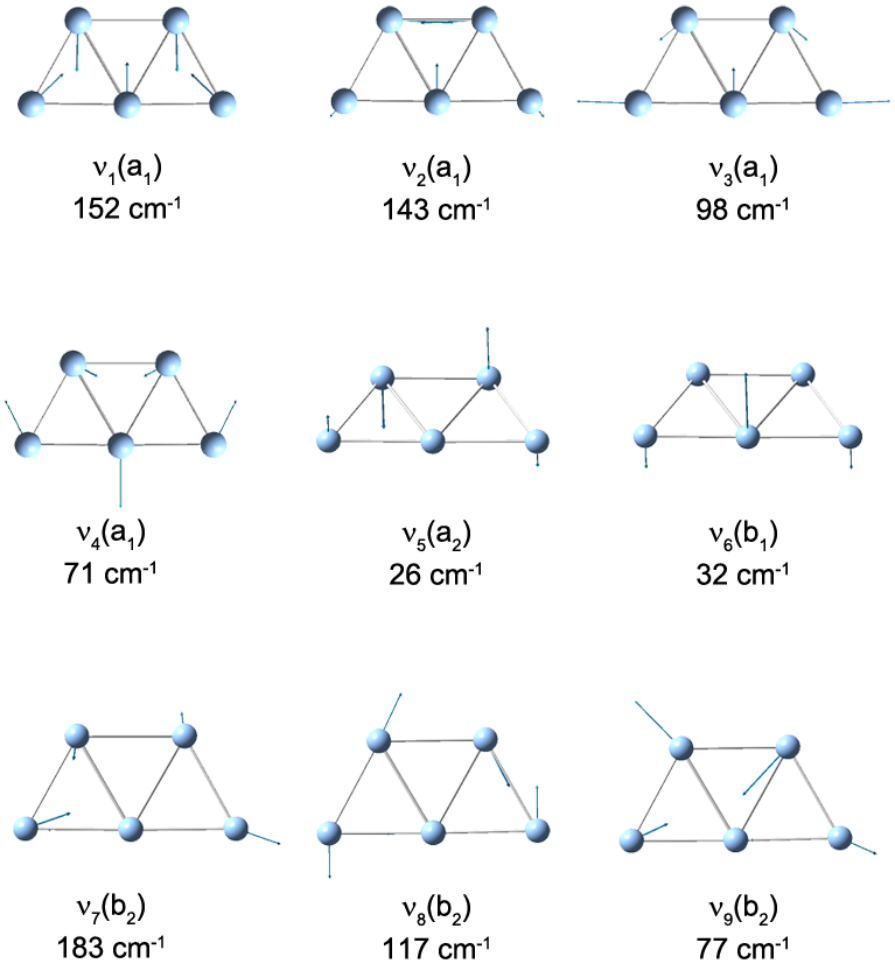

Fig. S4: The nuclear displacements of the harmonic vibrational normal modes of planar Ag_5 **1**.

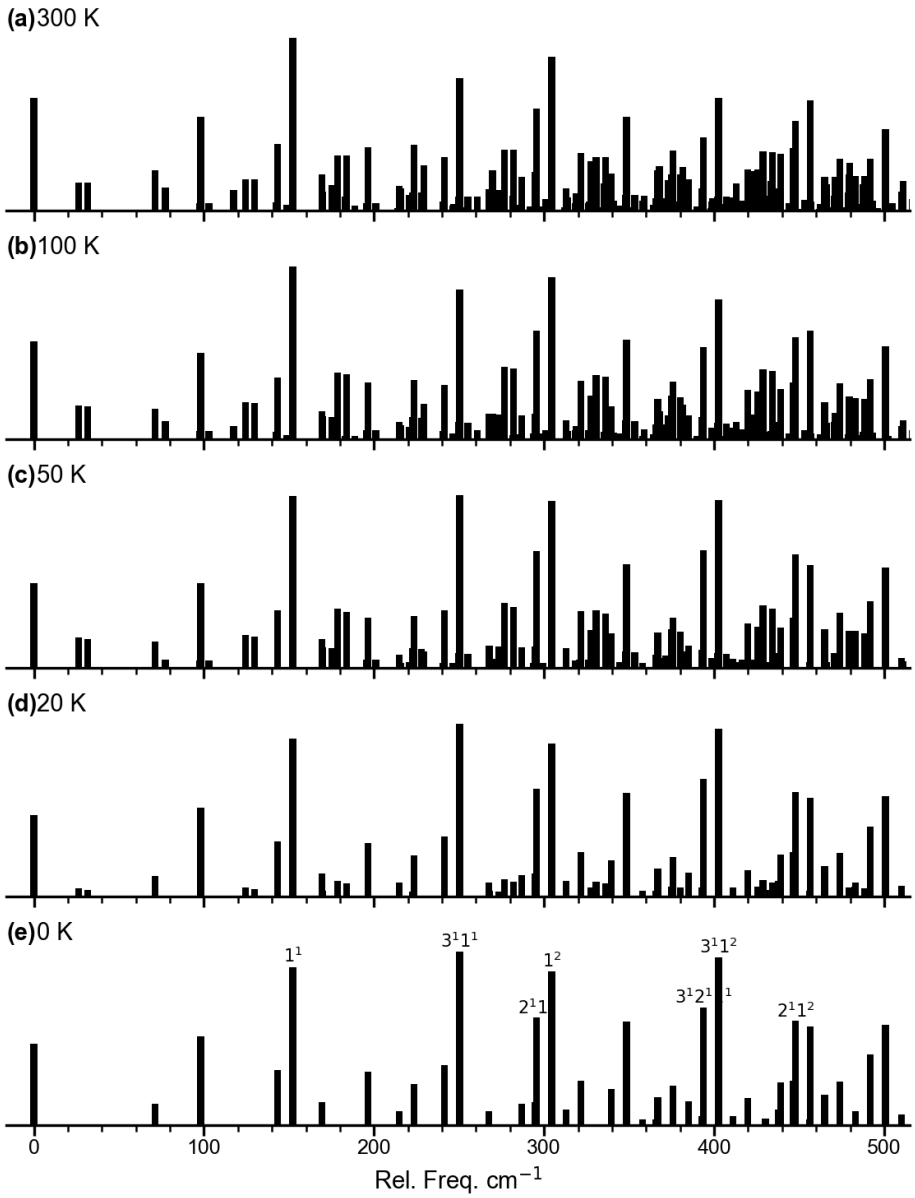

Fig. S5: Distributions of vibrational levels of planar neutral Ag_5 calculated from Franck-Condon simulations of photodetachment at different temperatures.

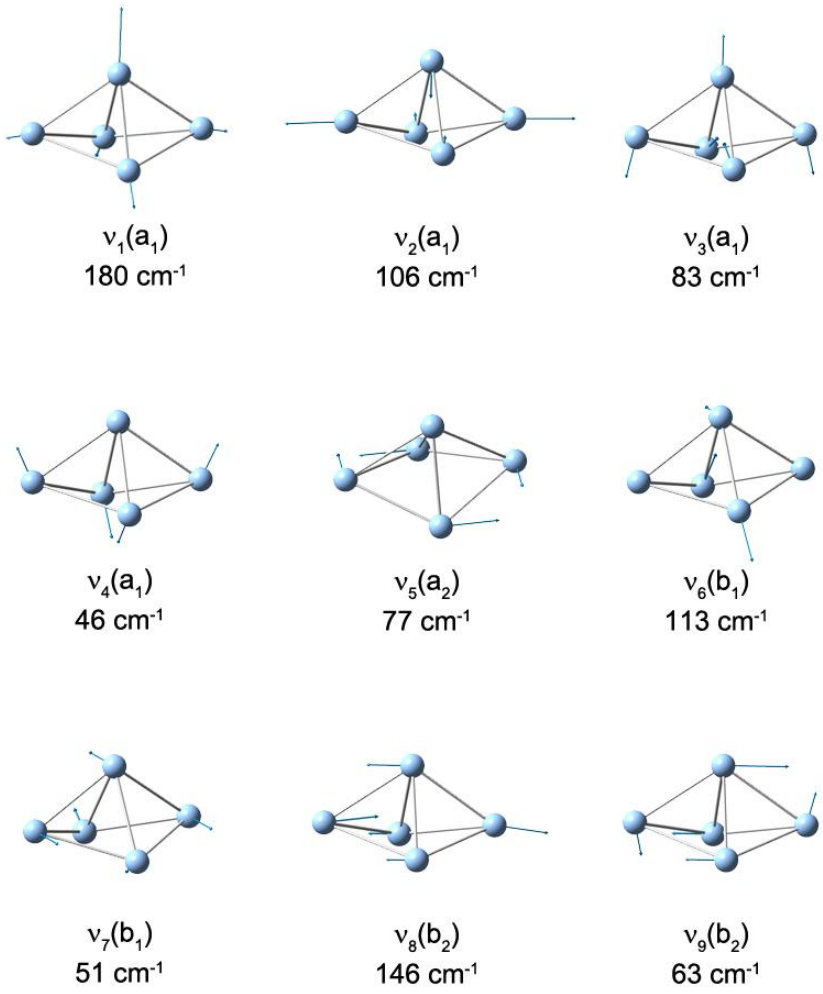

Fig. S6: The nuclear displacements of the harmonic vibrational normal modes of bipyramidal Ag_5 **2**.

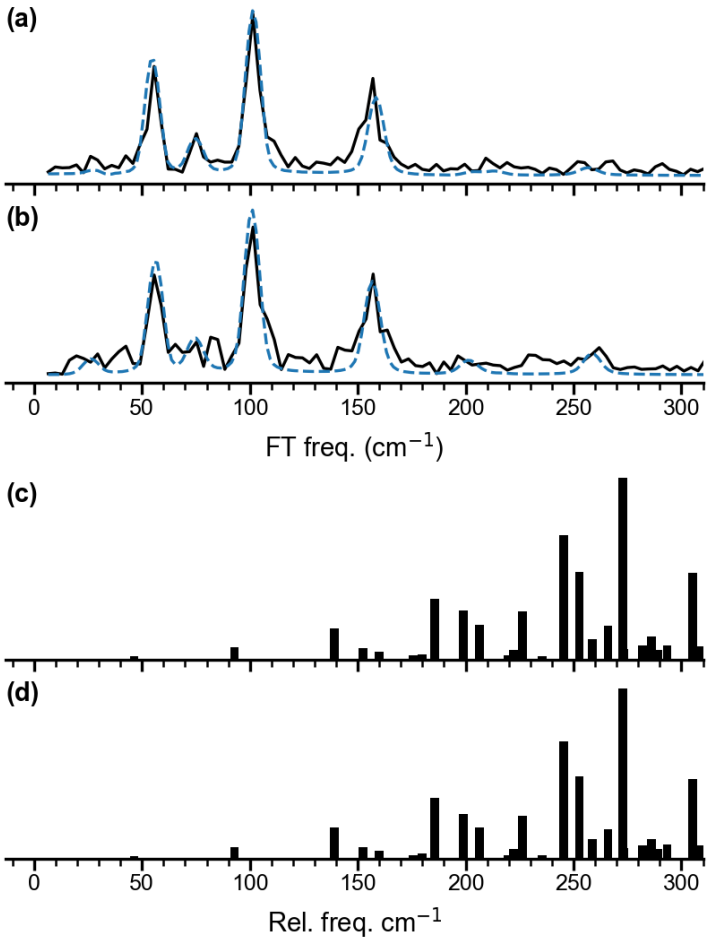

Fig. S7: FT amplitude spectra of the oscillatory Ag_5^+ yield and the best fitting curves shown in Fig. 2c and d. (a) for λ_{pump} = 510 nm and (b) for λ_{pump} = 402 nm. (c) and (d) Predicted population for the vibrational levels of bipyramidal Ag_5 **2** determined from the Franck-Condon factors for Ag_5 ($^2B_1$, C_{2v}) ← Ag_5^- ($^3A_1'$, D_{3h}) photodetachment transition at 20 K (c) and 0 K (d).

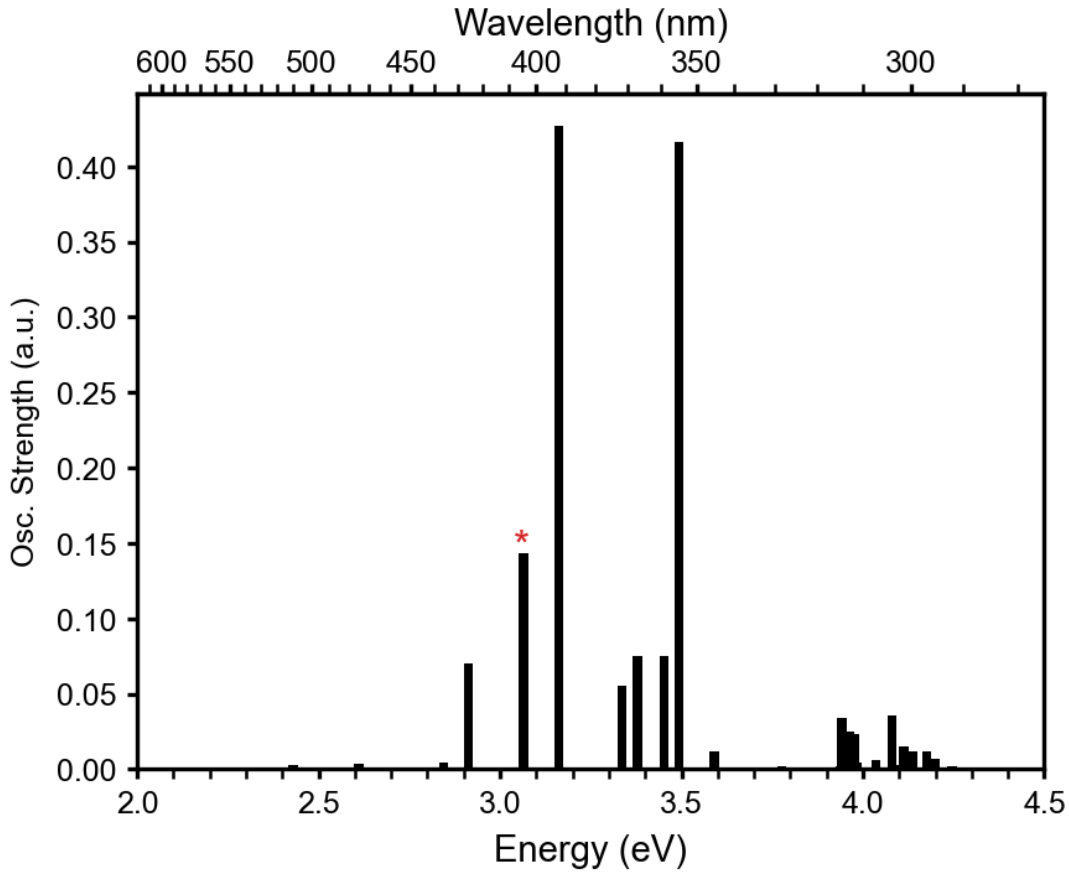

Fig. S8: Calculated excitation energy and oscillator strength of transition for the electronic excited states of Ag_5 (**1**). The TDDFT calculations are performed using PBE/def2-TZVPP. The results are similar to previous *ab initio* calculations.[2] The hypothesized resonant excited state ($^2B_2$) is marked in red, which is located at 3.11 eV obtained by ultraviolet-visible absorption spectroscopy of Ag_5 in neon matrix.[3]

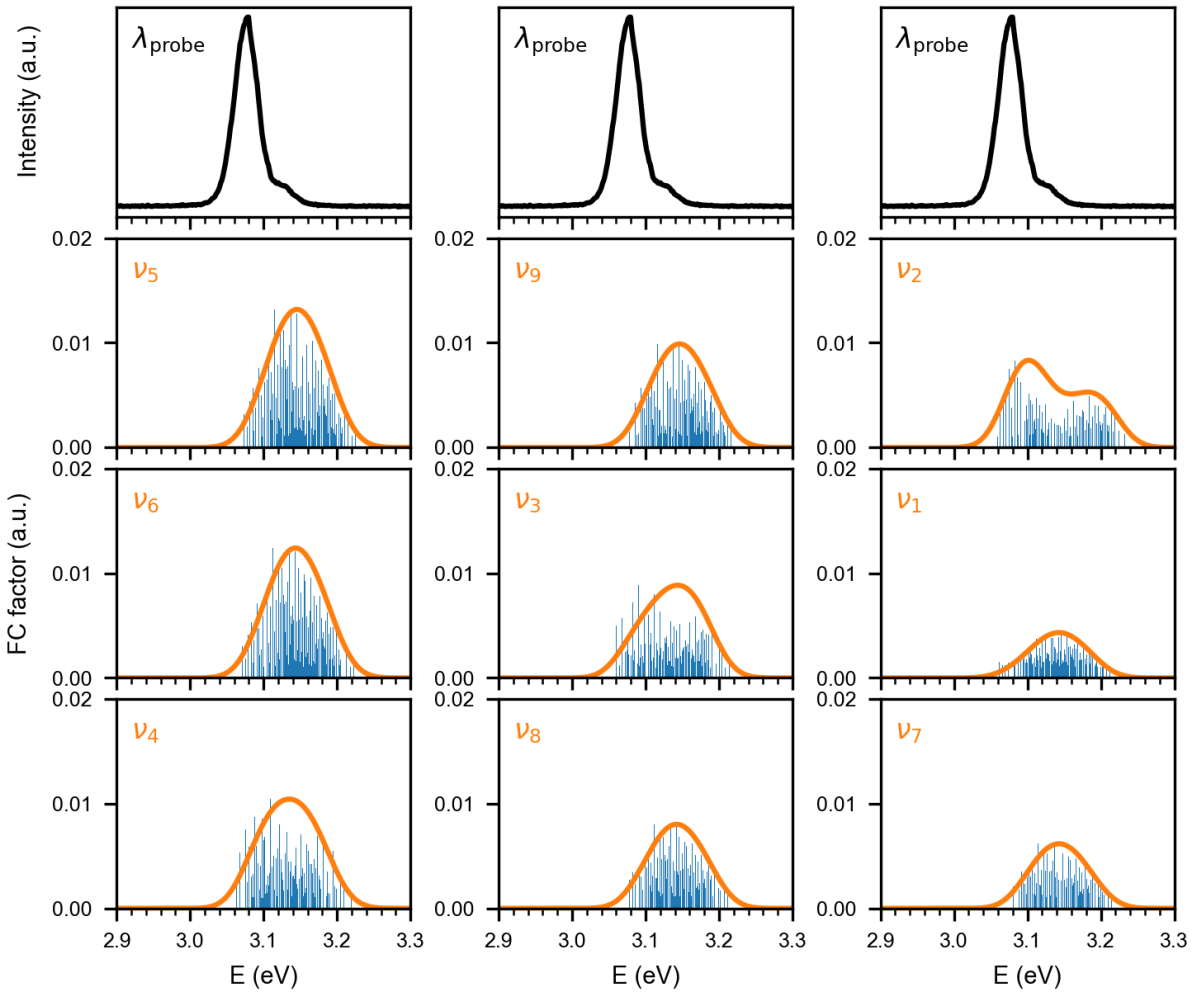

Fig. S9: Calculated Franck-Condon factors of Ag_5 ($^2B_2$) ← Ag_5 ($^2A_1$) for each individual vibrational mode. The entire envelopes of the transitions are convoluted by the probe laser width of 400 cm^{-1} (50 meV). The frequency spectrum of the probe pulse is also given.

References

(1) Haslett, T. L., Bosnick, K. A., Moskovits, M. Ag_5 is a planar trapezoidal molecule. *J. Chem. Phys.* **1998**, *108*, 3453.

(2) Bonačić-Koutecky, V., Veyret, V., Mitrić, R. Ab initio study of the absorption spectra of Ag n (n= 5-8) clusters. *J. Chem. Phys.* **2001**, *115*, 10450.

(3) Lecoultre, S., Rydlo, A., Buttet, J., Félix, C., Gilb, S., Harbich, W. Ultraviolet-visible absorption of small silver clusters in neon: Agn (n= 1-9). *J. Chem. Phys.* **2011**, *134*, 194108.