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

Supplementary Information

Nuclear Quantum Dynamics on the Ground Electronic State of Neutral Silver Dimer $^{107}Ag^{109}Ag$ Probed by Femtosecond NeNePo Spectroscopy

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1. Fs-NeNePo Spectra

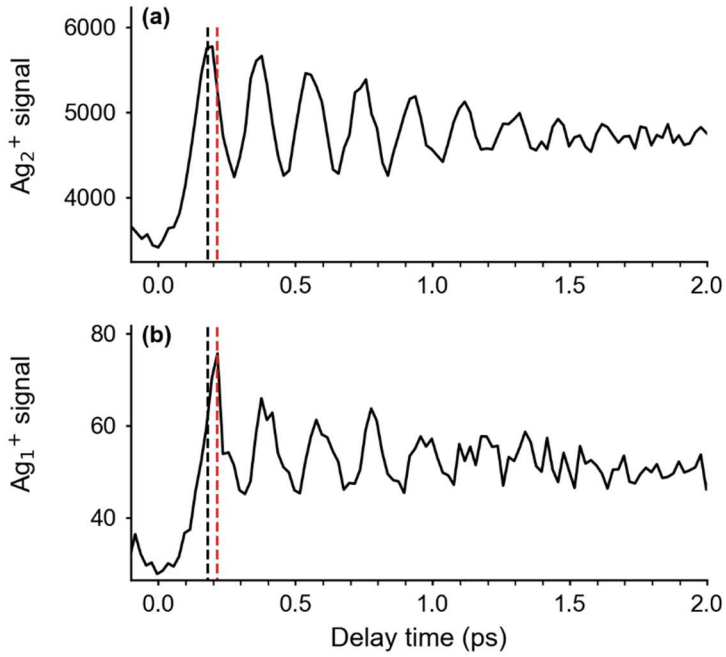

Fig. S1: NeNePo spectra (λ_{pump} = 510 nm, λ_{probe} = 402 nm) obtained by monitoring (a) the $^{107,109}Ag_2^+$ fragment and (b) the $^{107}Ag^+$ fragment over a delay time of -0.1 to 2.0 ps. Black (red) dashed line marks the delay time of the first maximum in the Ag_2^+ (Ag^+) ion signal.

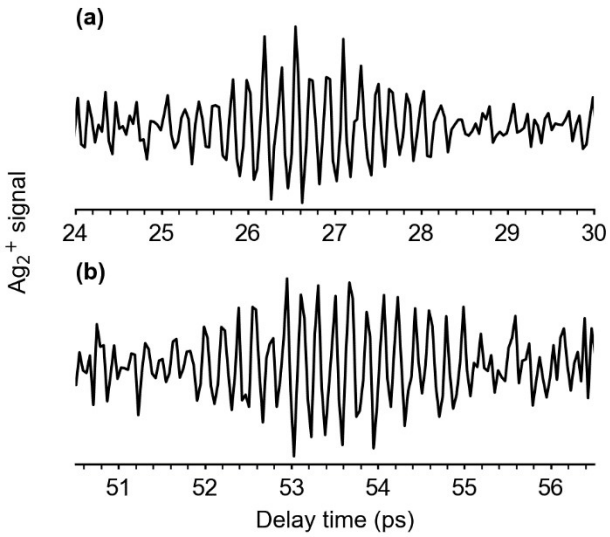

Fig. S2: Recurrences of Ag_2^+ cation signal measured by NeNePo excitation (λ_{pump} = 1010 nm, λ_{probe} = 402 nm). (a) Delay time from 24 to 30 ps for the first recurrence of the wave packet. (b) Delay time from 51 ps to 58 ps for the second recurrence.

2. FFT Spectra

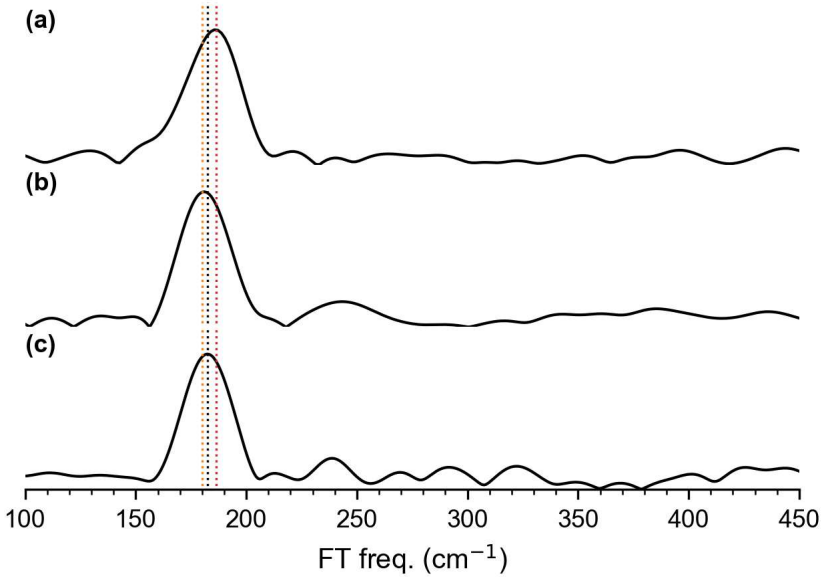

Fig. S3: The fast Fourier transform (FFT) analysis of the NeNePo spectra from 0 ps to 2.5 ps delay time. (a) λ_{pump} = 510 nm, (b) λ_{pump} = 1010 nm, (c) λ_{pump} = 1140 nm. The maximum frequency position depends on the pump wavelength: 186.5 cm^{-1} at 510 nm (red dashed line), 180.0 cm^{-1} at 1010 nm (yellow dashed line), and 182.5 cm^{-1} at 1140 nm (green dashed line).

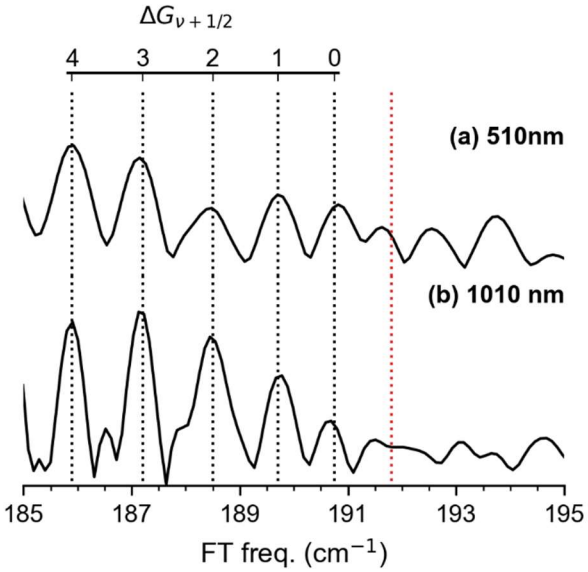

Fig. S4: The fast Fourier transform (FFT) analysis of the NeNePo spectra in the frequency range from 185 cm^{-1} to 195 cm^{-1} for the time range of 0 ps - 60 ps for (a) λ_{pump} = 510 nm and (b) λ_{pump} = 1010 nm. The tentative assignment of the $\Delta G_{v+1/2}$ values is shown in black.

3. Dunham Expression

The Dunham expression is extended to the cubic anharmonic contents $\omega_e y_e$ in order to fit $\Delta G_{v+1/2}$ of highly-lying vibrational levels, which presents in Eq. 1. The molecular constants for the Ag_2 ground electronic state $X^1\Sigma_g^+$ are evaluated by applying a non-linear least-squares fit to the Eq. 2.

$$G(v) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2 + \omega_e y_e\left(v + \frac{1}{2}\right)^3 \quad (1)$$

$$\Delta G_{v+\frac{1}{2}} = G_{v+1} - G_v = \omega_e - 2\omega_e x_e(v+1) + 3\omega_e y_e\left(v^2 + 2v + \frac{26}{24}\right) \quad (2)$$

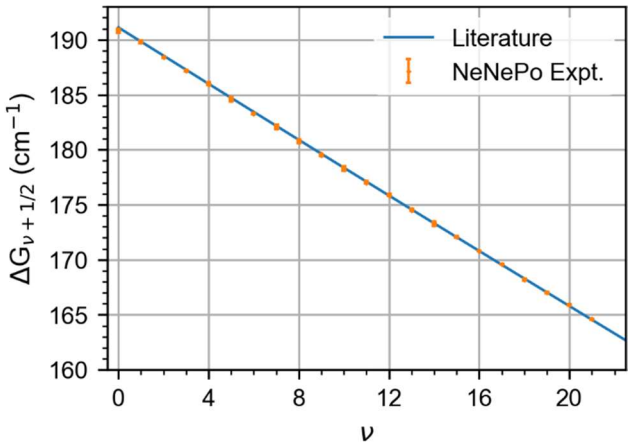

Fig. S5: Experimental FFT frequencies of vibrational levels (in orange) and a $\Delta G_{v+1/2}$ vs ν plot (blue) for the $^{107}Ag^{109}Ag$ isotopologue. The literature molecular constants are obtained from vibrationally resolved absorption spectroscopy of Ag_2 from Ref. 1. We also fit molecular constants with an assignment of $\Delta G_{1/2}$ = 193.4 cm^{-1}. The resulting constants and the Birge-Sponer plot are given in Fig. S6. The constants show worse agreement. These indicate that the FT frequency band at 193.4 cm^{-1} is an artifact resulting from the fast Fourier transformation.

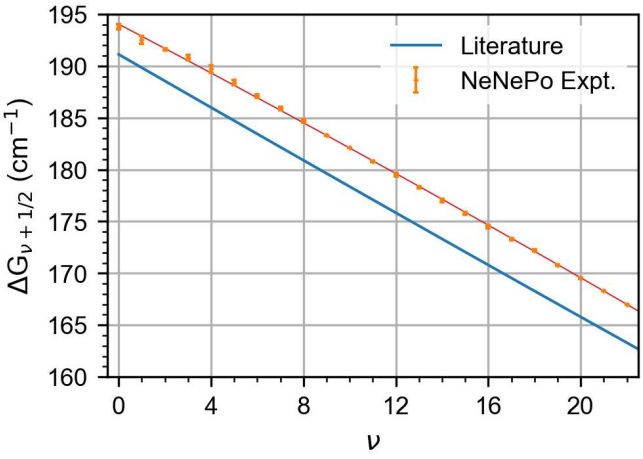

Fig. S6: Experimental FFT frequencies of vibrational levels (in orange) and a $\Delta G_{v+1/2}$ vs ν plot (blue) for $^{107}Ag^{109}Ag$ isotopologue. The experimental $\Delta G_{v+1/2}$ values are taken from the assignment that the $\Delta G_{1/2}$ (ν = 0) is at 193.8 cm^{-1}. The resulting vibrational constants are ω_e = 195.2(2) cm^{-1}, $\omega_e x_e$ = 0.581(13) cm^{-1} and $\omega_e y_e$ = -0.9(3)·10^{-3} cm^{-1}. The literature molecular constants are obtained from Ref. 1.

4. Simulated Oscillations

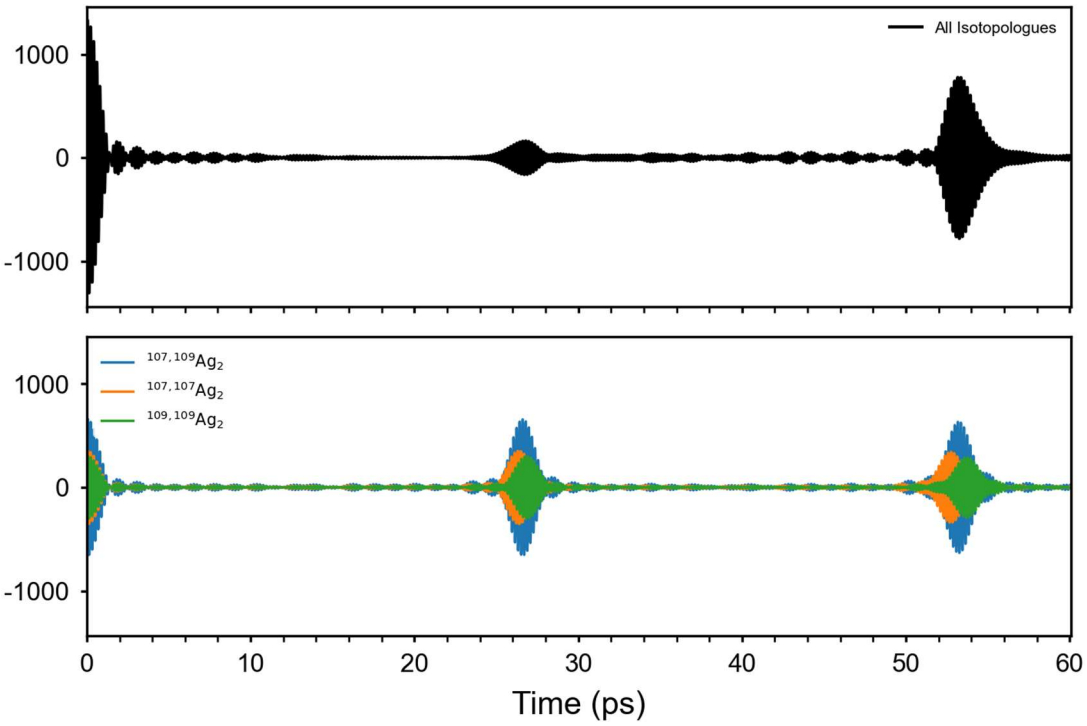

Fig. S7: Simulated oscillations reflecting the vibrational wave packet dynamics for silver dimers in the delay time range 0 ps – 60 ps. The plotting represents the sum over all frequency contribution, each represented by a sinusoidal function $f(t) = A\sin(2\pi t/T+\phi)$ corresponding to the classical wave. The intensities and frequencies of the $^{107,109}Ag_2$ isotopologue are taken from the experimental FT amplitudes and FT frequencies of the fs-NeNePo spectrum with λ_{pump} = 510 nm. The initial phase is set to zero for simplification. The frequency values of the two minor isotopologues ($^{107,107}Ag_2$ and $^{109,109}Ag_2$) are calculated from the vibrational constants, which are shifted from $^{107,109}Ag_2$ by the ratio of the reduced mass (see Section 4 of the main article). Their relative intensities are calculated by the natural abundance. Magnified sections of the simulations are given in Fig. S8.

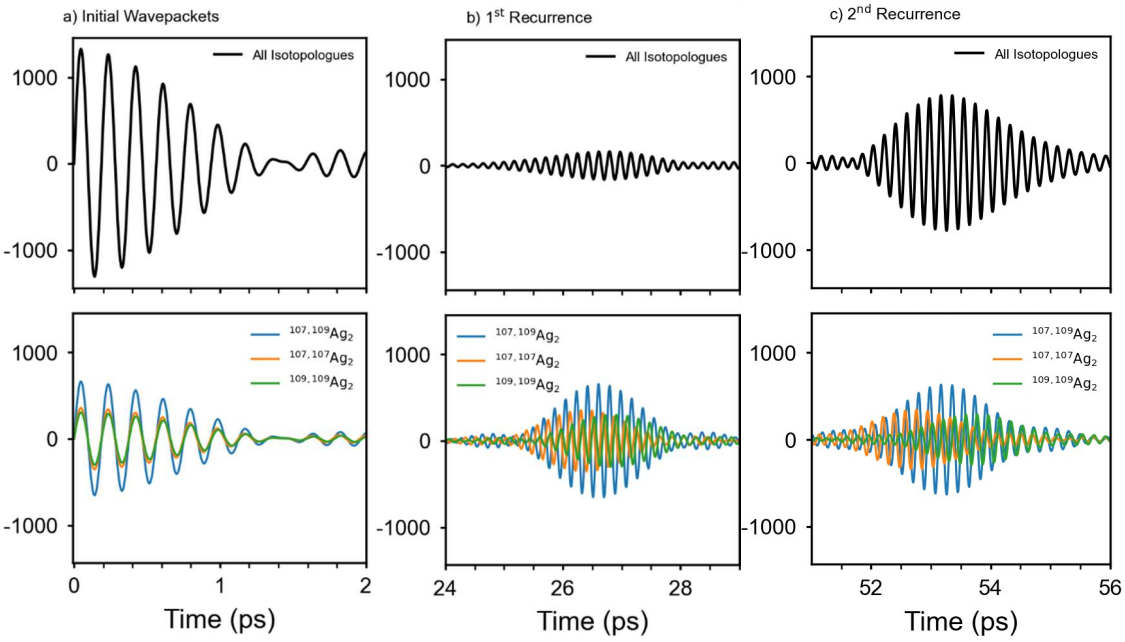

Fig. S8: Magnified sections of the simulations in Fig. S7 for different delay times: (a) 0 ps to 2 ps time (initial oscillation), (b) 24 ps to 29 ps time (first recurrence) and (c) 51 ps to 56 ps second recurrence).

5. FFT Band List

Table S1: FFT band frequencies for $\Delta G_{v+1/2}$ for the $X^1\Sigma_g^+$ ground state of Ag_2. Observed and calculated positions, residuals (Obs. – Calc.) and assignments (Ass.) are listed. All values are in cm^{-1}.

$\lambda_{pump} = 510\,nm$				$\lambda_{pump} = 1010\,nm$			
Obs.	Calc.	Res.	Ass.	Obs.	Calc.	Res.	Ass.
190.9	191.0	-0.1	1-0	190.8	190.9	-0.1	1-0
189.8	189.7	0.1	2-1	189.8	189.7	0.1	2-1
188.4	188.5	-0.1	3-2	188.4	188.5	-0.1	3-2
187.2	187.2	0.0	4-3	187.2	187.2	0.0	4-3
186.0	185.9	0.1	5-4	185.9	185.9	0.0	5-4
184.7	184.8	0.1	6-5	184.5	184.5	0.1	6-5
183.3	183.4	-0.1	7-6	183.3	183.4	-0.1	7-6
182.2	182.1	0.1	8-7	182.0	182.0	0.0	8-7
180.9	180.8	0.1	9-8	180.7	180.8	-0.1	9-8
179.6	179.6	0.0	10-9	179.5	179.6	-0.1	10-9
178.4	178.3	0.1	11-10	178.2	178.3	-0.1	11-10
177.1	177.1	0.0	12-11	177.0	177.0	0.0	12-11
175.9	175.8	0.1	13-12	175.8	175.8	0.0	13-12
174.6	174.5	0.1	14-13	174.5	174.5	0.0	14-13
173.4	173.3	0.1	15-14	173.2	173.3	-0.1	15-14
172.1	172.0	0.0	16-15				
170.8	170.7	0.0	17-16				
169.6	169.5	0.1	18-17				
168.2	168.3	-0.1	19-18				
167.0	167.1	-0.1	20-19				
165.9	165.8	0.1	21-20				
164.6	164.6	0.0	22-21				

References

1. B. Kleman and S. Lindkvist, *Ark. Fys.*, 1955, **9**(4), 385.