Supplementary Information for "Effect of Quantum Tunneling on the Efficiency of Excitation Energy Transfer in Plasmonic Nanoparticle Chain Waveguides"

Niranjan V. Ilawe,^a M. Belén Oviedo,^{b,c} and Bryan M. Wong^a*

^aDepartment of Chemical & Environmental Engineering and Materials Science & Engineering Program,

University of California-Riverside, Riverside, CA 92521, United States

^bUniversidad Nacional de Córdoba, Facultad de Ciencias Químicas, Departamento de Química Teórica

y Computacional, Córdoba, Argentina

°INFIQC, CONICET, X5000HUA, Córdoba, Argentina

*Corresponding author. E-mail: <u>bryan.wong@ucr.edu</u>. Homepage: <u>http://www.bmwong-group.com</u>

Contents

p. S2, Computational details on the calculation of group velocities

p. S3, Figure S1: Induced dipole moments in the first 4 NPs (separated by a 5 Å interparticle distance) of the nanoparticle chain

p. S4, Figure S2: Linear fitting of the first 4 nanoparticle locations vs. time for the electronic excitation to reach the nanoparticle

Computational Details on the Calculation of Group Velocities.

To calculate the group velocities in nanoparticle chain ensembles, previous studies¹ have investigated pulse propagation through these ensembles as a function of time. These analyses were carried out by plotting the pulse position, defined as the location of maximum field amplitude, as a function of time. A linear fit of this plot yields the group velocities (cf. Ref. 1 in the Supplementary Information or Ref. 40 in the main manuscript). However in our system, since the excitation is a continuous laser excitation, we cannot characterize the location of the excitation as a pulse moving along the nanoparticle chain. Therefore, we assume that once the induced dipole moment in a nanoparticle increases beyond a minimum threshold value, the excitation has reached/arrived at that particular nanoparticle. In this study, we assume this minimum threshold value to be 0.001 eÅ. Furthermore, as described in the main manuscript, due to the finite length of the chains, some end effects due to back transfer of excitation energy are seen, especially in the shorter chains. Therefore, we only consider the first 4 nanoparticles in the fitting and calculation of the group velocities.

For example, consider the nanoparticle chain with a 5 Å interparticle distance. We calculate the time at which the norm of the induced dipole moments in each of the nanoparticles of the chain goes beyond 0.001 eÅ, as shown in Fig 1. The red lines in each of the subplots marks the time at which the norm of the dipole moment reaches the threshold value. Note that for NP1, since this NP is directly excited by the laser perturbation, the induced dipole moment in the NP almost instantaneously goes beyond the threshold value.



Figure S1: Induced dipole moments in the first 4 NPs (separated by a 5 Å interparticle distance) of the nanoparticle chain. The figures in the red boxes denote the times at which the norm of the induced dipole moments in the NPs reach a threshold value of 0.001 eÅ.

These extracted time values are then plotted as a function of the nanoparticle location as shown in Figure 2. A linear fit of these points yields the group velocity (i.e., the slope of the line) of the system.



Figure S2: Linear fitting of the first 4 nanoparticle locations vs. time for the electronic excitation to reach the nanoparticle. The points are labelled corresponding to the NPs that they belong to. The slope of the fitted line (*m* in the legend) gives the group velocity of the chain in Å/fs.

From the fitted data, we obtain the group velocity as 2.341 Å/fs or 2.341×10^5 m/s. A similar procedure is carried out for all the nanoparticle chains to obtain their group velocities. The tabulated data for all of our calculations are given in the main manuscript.

References.

1. S. A. Maier, P. G. Kik and H. A. Atwater, Phys. Rev. B, 2003, 67, 205402.