Supporting Information for: Molecular Vibration Induced Plasmon Decay

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Analysis of the transitions in the LR-TDDFT calculations for Ag_4 with 5 quanta of vibrational energy
Time step: 100fs

The transverse mode is composed of two nearly degenerate peaks (the *x*- and *y*-components of the Π_u transition of perfectly straight nanowires). At 100 fs, the nanowire has not significantly distorted from its initial linear configuration. The two peaks comprising the transverse mode appear around 5.01 eV with an oscillator strength of f ~ 0.7. These excited states are:

Excited State 32: 5.0099 eV 247.48 nm f=0.7399 <S**2>=0.000
19 -> 39 0.11266
34 -> 40 -0.10597
37 -> 41 0.47821 (Σ_1 -> Π_1 (*y* component))
38 -> 44 0.43914 (Σ_2 -> Π_2 (*y* component))
Excited State 33: 5.0183 eV 247.06 nm f=0.6667 <S**2>=0.000
35 -> 40 -0.10308
37 -> 42 0.45719 (Σ_1 -> Π_1 (*x* component))
38 -> 43 0.33699 (Σ_2 -> Π_2 (*x* component))
38 -> 45 -0.31289

The 37->41 and 37->42 transitions are Σ_1 -> Π_1 transitions. The 38->43 and 38->44 transitions are Σ_2 -> Π_2 transitions. Both of these transitions between delocalized orbitals are known to result in large transition dipole moments.[1] These transitions are shown in blue throughout the SI.

Questions we will answer: The two primary transitions are mixed with other excitations/deexcitations. How might these contributions change over time? How does the splitting between the x and y components of the transverse mode change over time?

Excited state 29 also has some oscillator strength (most likely because of its 37->42 and 38->43 contributions). However, it is currently much weaker than states 32 and 33.

Excited State 29: 4.9047 eV 252.79 nm f=0.0806 <S**2>=0.000
18 -> 39 -0.10159
35 -> 40 -0.16619
37 -> 40 -0.15889
37 -> 42 0.12613
38 -> 43 0.29070
38 -> 45 0.53853

It is important to note that the peaks with the largest weights are *not necessarily* the ones that contribute the most to the oscillator strength. They often do for 'normal' molecules, but we see exceptions to this commonly in the case of systems with delocalized orbitals exhibiting collective excitation peaks. (The 38->45 transition becomes important to the analysis at later times.)

States 32 and 33 arise because of constructive interference between the two Σ_n -> Π_n transitions. Due to configuration interaction, two (or more, if additional states are mixed) states arising from destructive interference of these transitions must be present.[1] The destructive interference states that are related to the strong transverse modes are 24, 25 and 26:

Excited State 24: 4.3490 eV 285.09 nm f=0.0057 <S**2>=0.000
19 -> 39 0.61591
37 -> 41 -0.30076
38 -> 44 0.17227
Excited State 25: 4.4416 eV 279.14 nm f=0.0233 <S**2>=0.000
18 -> 39 0.12320
20 -> 39 -0.24790
37 -> 42 -0.41396
38 -> 43 0.48491
38 -> 45 -0.11114
Excited State 26: 4.4550 eV 278.31 nm f=0.0084 <S**2>=0.000
19 -> 39 -0.32377
37 -> 41 -0.37927
38 -> 44 0.49747

These peaks are in reasonable agreement with the energy of the "new peak" around 4.3 eV that is forming at later time steps. We get two peaks that involve 37->41 and 38->44 because of the +/- combinations with the 19->39 transition. (The 19->39 transition is probably not very important since the splitting and oscillator strengths of these peaks are not very large regardless of whether we consider the + or – combination.)

Time step: 200fs

At 200fs, the nanowire is more distorted from linear compared to the system at 100 fs. The two excited states responsible for the transverse plasmon still occur around similar energy (5.01-5.05 eV), although the *x* component (corresponding to the direction in which activation of

the vibrational mode has offset the geometry) of the peak has changed slightly in energy and its oscillator strength is somewhat reduced:

Excited State 32: 5.0089 eV 247.53 nm f=0.7351 <S**2>=0.000
19 -> 39 0.11172
37 -> 41 0.48076
38 -> 44 0.43650
Excited State 34: 5.0474 eV 245.64 nm f=0.4920 <S**2>=0.000
18 -> 39 -0.12490
37 -> 42 -0.40892
38 -> 43 -0.17733
38 -> 45 0.46680

These are still the two modes in the correct range with the strongest oscillator strength. However, the 38->45 mode (shown in green) mixes into state 34 rather strongly, which seems to cause more splitting of the two peak energies, an oscillator strength for 34 that differs significantly from f ~ 0.7, and unequal weights of the 37->42 and 38->43 transitions.

States 27, 29, and 30 (energy range: 4.65-4.90 eV) have moderately strong oscillator strengths (f ~ 0.12-0.14). This is likely because of transitions out of orbitals 37 and 38 into orbitals 42-45.

Excited State 27: 4.6465 eV 266.83 nm f=0.1429 <S**2>=0.000
18 -> 39 0.67394
38 -> 43 -0.10175
38 -> 45 0.15865
Excited State 29: 4.8732 eV 254.42 nm f=0.1252 <S**2>=0.000
35 -> 40 0.44781
37 -> 40 0.12331
37 -> 42 -0.17974
38 -> 43 -0.31171
38 -> 45 -0.34831
Excited State 30: 4.9035 eV 252.85 nm f=0.1270 <S**2>=0.000
35 -> 40 0.53885
37 -> 40 -0.11480
37 -> 42 0.19641
38 -> 43 0.29834
38 -> 45 0.20813

Furthermore, states around 4.35-4.45 eV are also present and arise from destructive interference of these transitions:

Excited State 24: 4.3538 eV 284.77 nm f=0.0050 <S**2>=0.000
19 -> 39 0.60967
37 -> 41 -0.30630
38 -> 44 0.18429
Excited State 25: 4.4369 eV 279.44 nm f=0.0140 <S**2>=0.000

18 -> 39 0.12171
37 -> 42 -0.46297
38 -> 43 0.46533
38 -> 45 -0.20573
Excited State 26: 4.4549 eV 278.31 nm f=0.0094 <S**2>=0.000
19 -> 39 -0.33580
37 -> 41 -0.37117
38 -> 44 0.49558

Note: Again, 24 and 26 have very similar contributions, but mix in with the 19->39 transition in +/- ways. The oscillator strength contribution from the 19->39 transition is probably relatively small since both of these states have small, relatively similar oscillator strengths.

Time step: 300fs

At 300fs, the nanowire is more distorted from linear compared to the system at 100 or 200 fs. The two excited states responsible for the transverse plasmon still occur around similar energy (5.01-5.10 eV), although the *x* component of the peak has increased further in energy and its oscillator strength is further reduced:

Excited State 33: 5.0083 eV 247.56 nm f=0.7034 <S**2>=0.000
19 -> 39 0.11153
30 -> 40 0.12186
37 -> 41 0.48511
38 -> 44 0.42160
Excited State 36: 5.1023 eV 243.00 nm f=0.2650 <S**2>=0.000
18 -> 39 -0.13285
31 -> 40 -0.23456
37 -> 42 -0.34087
38 -> 45 0.50390

The oscillator strength of the other strong mode in this region has decreased (now only 0.2650). The energy of this part of the transverse mode has increased. This correlates with a slight increase in the energy of the transverse mode that is observed in the Ehrenfest dynamics with real-time TDDFT. In addition, the transitions responsible for this mode have changed. Orbital 43 is no longer significantly involved, and 45 has a strong role. The 38->43 transition now appears to be involved in lower energy excited states, which makes sense because the Σ_2->$\Pi_2(x)$ (38->43) orbital energy difference is decreasing (Figure 7).

Lower energy excited states 28 and 31 include contributions from 38->43 (note: these still have a constructive interaction between 37->42 and 38->43). These states are:

Excited State 28: 4.7805 eV 259.35 nm f=0.1769 <S**2>=0.000
18 -> 39 0.50707

35 -> 40 0.32929
37 -> 42 -0.21830
38 -> 43 -0.24288
Excited State 31: 4.8825 eV 253.94 nm f=0.2891 <S**2>=0.000
18 -> 39 0.26620
35 -> 40 0.19893
37 -> 40 -0.16402
37 -> 42 0.29462
38 -> 43 0.34700
38 -> 45 0.32792

In addition, the "destructive interference" excited states are still present and include 38->43:

Excited State 26: 4.4621 eV 277.86 nm f=0.0369 <S**2>=0.000
37 -> 40 -0.11949
37 -> 42 -0.44384
38 -> 43 0.46807
38 -> 45 -0.22729

There are also the two destructive ones that involve 37->41 and 38->44; these are related to the *y* transverse mode that has not changed in energy/oscillator strength:

Excited State 24: 4.3771 eV 283.26 nm f=0.0022 <S**2>=0.000
19 -> 39 0.55821
37 -> 41 -0.34866
38 -> 44 0.25743
Excited State 25: 4.4613 eV 277.91 nm f=0.0149 <S**2>=0.000
19 -> 39 -0.41577
37 -> 41 -0.31671
38 -> 44 0.47209

Time step: 400fs

At 400fs, the nanowire is significantly more distorted from linear compared to the system at earlier times. The *y* component of the transverse plasmon still arises around 4.99 eV:

Excited State 34: 4.9947 eV 248.23 nm f=0.4790 <S**2>=0.000
20 -> 39 0.10593
26 -> 40 0.11258
30 -> 40 0.35455
37 -> 41 0.44174
38 -> 44 0.34371

At 400 fs the oscillator strength of this peak is actually starting to decrease. It is also interesting to note that more transitions now have strong weights. These observations are related, since the

interaction with the 26->40 and 30->40 transitions splits this peak into two peaks, so the oscillator strength is divided. The other related peak is:

```
Excited State  37: 5.0937 eV  243.41 nm  f=0.1691  <S**2>=0.000
     26 -> 40       -0.22892
     30 -> 40        0.59297
     37 -> 41       -0.22451
     38 -> 44       -0.17289
```

(Again, is important to note that the peaks with the largest weights are *not necessarily* the ones that contribute the most to the oscillator strength.)

The other transverse peak in this energy range is:

```
Excited State  36: 5.0434 eV  245.84 nm  f=0.1076  <S**2>=0.000
     18 -> 39       -0.36067
     31 -> 40        0.48547
     38 -> 45       -0.31693
```

Again, the 38->45 transition has become important. Moreover, the 38->43 transition does not exceed Gaussian's default cutoff to show the weight of this transition. Instead, the 38->43 transition contributes primarily to a variety of excited states at lower energy (which again makes sense since the Σ_2->$\Pi_2(x)$ energy difference is lowered in energy):

```
Excited State  30: 4.8289 eV  256.75 nm  f=0.3330  <S**2>=0.000
     18 -> 39        0.25769
     37 -> 40        0.12332
     37 -> 42        0.47757
     38 -> 43       -0.29703
     38 -> 45       -0.24747
Excited State  27: 4.6593 eV  266.10 nm  f=0.0178  <S**2>=0.000
     36 -> 40        0.66165
     37 -> 42       -0.14612
     38 -> 43       -0.11056
     38 -> 45        0.13281
Excited State  24: 4.4781 eV  276.87 nm  f=0.1774  <S**2>=0.000
     22 -> 39       -0.13008
     36 -> 40        0.21873
     37 -> 40       -0.17953
     37 -> 42        0.30654
     38 -> 43        0.51282
     38 -> 45       -0.16173
Excited State  21: 4.2695 eV  290.39 nm  f=0.0130  <S**2>=0.000
     22 -> 39        0.68350
     38 -> 43        0.17025
```

We also see the destructive peak that correlates with the 'normal' transverse peak that is essentially unaffected by the vibration:

Excited State 23: 4.4097 eV 281.16 nm f=0.0027 <S**2>=0.000
20 -> 39 0.30381
37 -> 41 -0.43419
38 -> 44 0.46659

Time step: 500fs

At 500fs, the nanowire is very distorted from linear. The *y* component of the transverse plasmon still arises around 4.98-5.13 eV. It again arises from excitations involving 37->41 and 38->44, which are again slightly split due to interactions with other transitions:

Excited State 38: 4.9815 eV 248.89 nm f=0.1654 <S**2>=0.000
20 -> 39 0.11391
26 -> 40 0.57706
37 -> 41 0.31641
38 -> 44 0.19359
Excited State 41: 5.1346 eV 241.47 nm f=0.5304 <S**2>=0.000
26 -> 40 -0.40067
30 -> 40 -0.14831
37 -> 41 0.42285
38 -> 44 0.29172

Very few other strong peaks can be observed in the ~5 eV region. Because the 37->41 and 38->44 transitions are related to the *y* component of the excitation that is orthogonal to the vibration in the *x* direction (and, more importantly in this case, to the applied electric field in the *x* direction), we should not observe many peaks in this region of the Ehrenfest spectrum, which agrees with the observations. There is a small 38->45 contribution to several excited states as follows, but the oscillator strengths are low:

Excited State 37: 4.9500 eV 250.47 nm f=0.0315 <S**2>=0.000
27 -> 40 0.64788
37 -> 42 0.18633
38 -> 45 -0.17542
Excited State 43: 5.2312 eV 237.01 nm f=0.0997 <S**2>=0.000
17 -> 39 0.59485
38 -> 45 0.32645
Excited State 48: 5.3769 eV 230.59 nm f=0.0510 <S**2>=0.000
17 -> 39 -0.20541
24 -> 40 -0.18393
34 -> 41 0.11639
37 -> 42 0.24844
38 -> 45 0.37221
38 -> 47 0.41836

We note the destructive peak related to 37->41 and 38->44 (again, still essentially unchanged):

Excited State 22: 4.4189 eV 280.58 nm f=0.0259 <S**2>=0.000
37 -> 41 -0.40579
38 -> 44 0.56923

So, a question arises: where has all the oscillator strength gone?
This can be answered by considering the energy region from 4.40-4.93 eV, in which a number of new states with reasonable oscillator strength appear:

Excited State 21: 4.4011 eV 281.71 nm f=0.2080 <S**2>=0.000
36 -> 40 0.47056
37 -> 40 0.16786
37 -> 42 -0.12132
38 -> 43 -0.45153
Excited State 24: 4.5213 eV 274.22 nm f=0.1568 <S**2>=0.000
22 -> 39 0.50751
36 -> 40 -0.36036
37 -> 40 0.12598
38 -> 43 -0.27318
Excited State 26: 4.6089 eV 269.01 nm f=0.1468 <S**2>=0.000
22 -> 39 0.48655
36 -> 40 0.37184
37 -> 40 -0.15293
38 -> 43 0.25205
Excited State 34: 4.9273 eV 251.63 nm f=0.1176 <S**2>=0.000
17 -> 39 0.13742
27 -> 40 -0.27336
37 -> 42 0.51730
38 -> 43 -0.12842
38 -> 45 -0.32017

These states have contributions from 38->43 and occasionally 37->42, which is likely why they have relatively large oscillator strengths. However, there is significant mixing from other transitions (notably 36->40 and 37->40, as well as excitations from occupied orbitals much lower in energy), so the picture is not extremely clean.

Conclusions (LR-TDDFT calculations, 100-500 fs)

Overall, the change in the geometry as time progresses during the simulation is responsible for decreasing the energy of the 38->43 transition. In consequence, how this transition mixes with other transitions is affected. The oscillator strengths of the excited states change, and a significant portion of the oscillator strength is shifted into lower energy excited states.

Orbitals involved in the transverse plasmon excitation from the Ehrenfest dynamics

The transverse plasmon excitation is characterized by two electronic transitions: Σ_1 -> Π_1 and Σ_2 -> Π_2. The orbitals involved in both transitions are shown for some representative snapshots extracted from the Ehrenfest dynamics having as initial molecular structure and momenta the ones generated by imparting zero-point vibrational energy into the out-of-chain bending mode. In particular they are shown for the configurations extracted at 100, 200, 300, 400 and 500 fs in Fig. S1, Fig. S2, Fig.S3, Fig.S4 and Fig.S5, respectively.

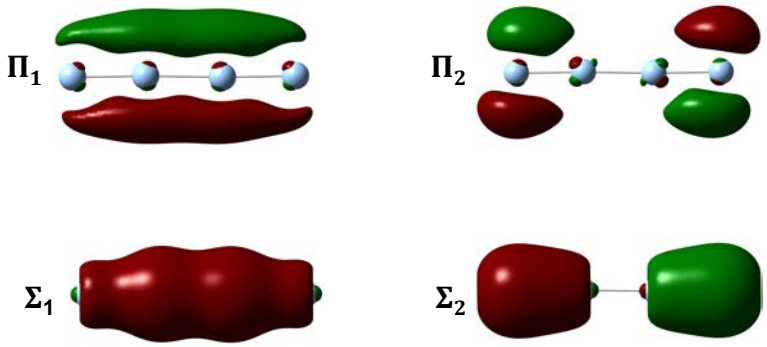

Figure S1. Orbitals involved in the transverse plasmon excitation for the configuration extracted from the Ehrenfest dynamics at 100 fs.

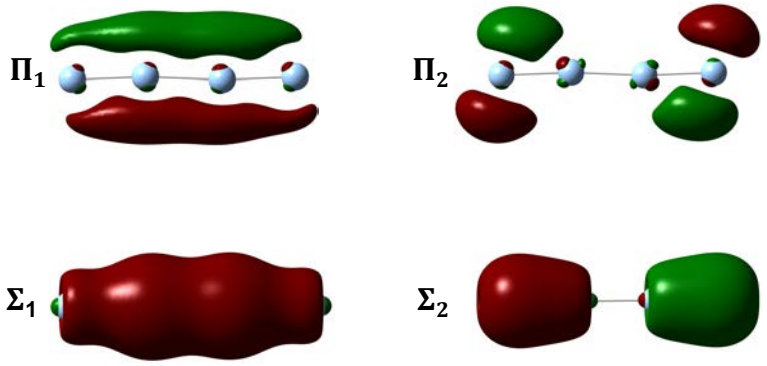

Figure S2. Orbitals involved in the transverse plasmon excitation for the configuration extracted from the Ehrenfest dynamics at 200 fs.

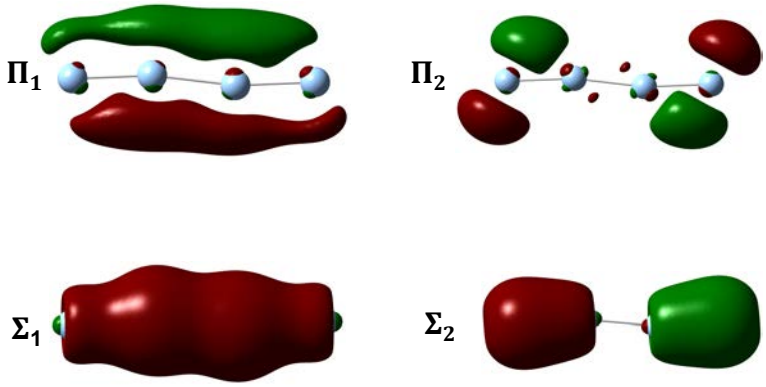

Figure S3. Orbitals involved in the transverse plasmon excitation for the configuration extracted from the Ehrenfest dynamics at 300 fs.

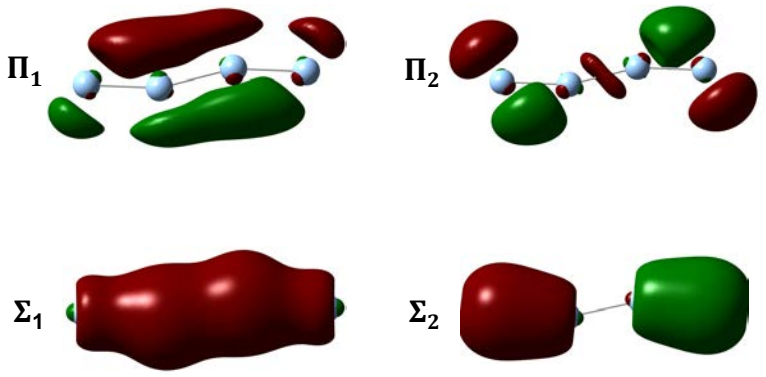

Figure S4. Orbitals involved in the transverse plasmon excitation for the configuration extracted from the Ehrenfest dynamics at 400 fs.

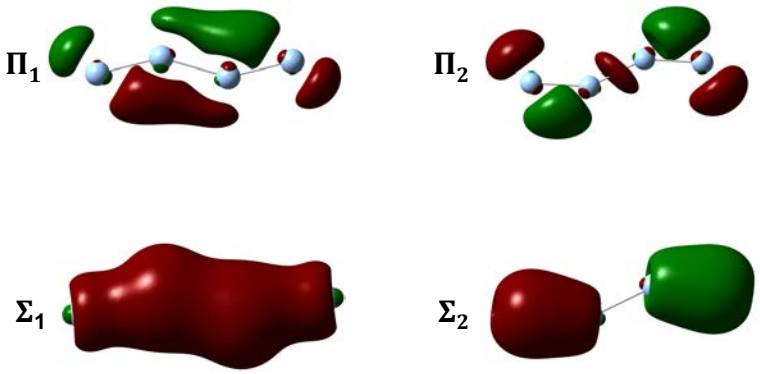

Figure S5. Orbitals involved in the transverse plasmon excitation for the configuration extracted from the Ehrenfest dynamics at 500 fs.

References

1. Guidez, E. B.; Aikens, C. M., Theoretical Analysis of the Optical Excitation Spectra of Silver and Gold Nanowires. *Nanoscale* **2012,** *4*, 4190-4198.