Supporting Information

Non-Equilibrium Chemical Effects in Single Molecule SERS Revealed by *ab initio* Molecular Dynamics Simulations

Sean A. Fischer,¹ Edoardo Apra,¹ Niranjan Govind,^{1,*} Wayne P. Hess,² and Patrick Z. El-Khoury,^{2,*}

¹Environmental and Molecular Sciences Laboratory and ²Physical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99354, USA.

*niri.govind@pnnl.gov, patrick.elkhoury@pnnl.gov

Table S1. Isolated molecule (DMS) and isolated metal cluster (tetrahedral Ag_{20}): vertical transition energies from optimized minima (re-optimized at each level of theory).

Method	DMS	Ag ₂₀	(eV)
	(eV)	State 1	State 2
td pbe/def ₂ SVP	3.09	3.29	3.78/4.04
(def_2TZVP)	(3.05)	(3.24)	(3.72/4.00)
td b3lyp/def ₂ SVP	3.51	3.55	-
td pbe0/def ₂ SVP	3.60	3.62	-
td cam-b3lyp/def ₂ SVP	3.96	3.74	-
td lc-pbe0/def ₂ SVP	4.38	3.78	4.05
Experimental	3.70 ^a	3.70 ^b	3.97 ^b

^a 1 μm solution of DMS in ethanol, this work, ^bAg₂₀ isolated in a cryogenic matrix, from Fedrigo, S.; Harbich, W.; Buttet, *J. Phys. Rev. B* **1993**, *47*, 10706.

Figure S1. Absorption spectra of DMS – experiment *vs* theory (all with the def₂SVP basis set). Stick spectra are broadened by 0.2 eV.



Figure S2. Absorption spectra of Ag_{20} – experiment *vs* theory (all with the def₂SVP basis set). Stick spectra are broadened by 0.1 eV



Figure S3. Absorption spectra of DMS and Ag₂₀ – experiment vs theory (basis set dependence)



States of interest for DMS and Ag_{20} – some analysis (pbe/def₂SVP)

<u>Molecular – lowest state, S₁</u> (mostly $\pi \rightarrow \pi^*$ with some $n(sulfur) \rightarrow \pi^*$)

#Pair Coefficient Transition dipole X/Y/Z (au)
 1 62 -> 65 0.125470 0.020807 -0.111288 -0.000019
 2 64 -> 65 0.692110 5.292613 0.095450 0.000279
Sum: 5.313420 -0.015838 0.000260
Norm of transition dipole moment: 5.3134439 a.u.
Oscillator strength: 2.1357946

Figure S4. A) Transition density (c value = 0.0001 from hereon) and B) charge density difference (c value = 0.0005 from hereon) – black is negative and red is positive density for all from hereon



Figure S5. Orbitals involved in the transition (HOMO/LUMO = 64/65)



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Here's one	of the trans	sitions –	- S ₆₀			
#Pair		(Coefficient	Transitio	n dipole X/	Y/Z (au)
1	179 ->	194	-0.104760	0.183751	-0.086049	-0.055337
2	185 ->	191	0.196140	-1.191735	0.182663	0.159947
3	185 ->	198	0.169470	-0.267056	-0.039407	0.052777
4	186 ->	192	0.108520	-0.420161	-0.143135	0.072972
5	186 ->	196	0.137160	-0.397605	-0.286628	-0.143935
6	187 ->	193	-0.132220	-0.639174	-0.080988	-0.061986
7	187 ->	195	0.156450	-0.543640	0.031907	0.358649
8	188 ->	194	-0.117380	-0.342360	-0.360594	-0.048025
9	188 ->	196	-0.119990	-0.348394	0.313249	0.131453
10	189 ->	198	0.288350	-1.664729	-0.624752	-0.024475
11	190 ->	195	0.107890	-0.320202	0.180691	0.024930
12	190 ->	197	0.130410	-0.410325	-0.367991	0.022054
Sum:				-6.361629	-1.281033	0.489025
Norm of th	ransition	dipole	moment: 6	.5077274 a.	u.	
Oscillator	r strength	.: 3.4	1095542			

Figure S6. A) Transition density and B) charge density difference







Why (td) pbe:

Concession: Vertical transition energies are always red-shifted from their experimental analogues / something to keep in mind in going through our results and discussion. That said;

- 1- The level of theory used in the main text describes the metal the best (especially the higher lying transition (experimentally at 3.97 eV, a *sp* ← *d* interband transition) when compared to the other levels of theory tested above. If we broaden to match the experiment (0.175 eV), the two predicted peaks at 3.78/4.04 eV (see table S1) coalesce to become a single broad peak (see Figure S7 below), which is red-shifted from its experimental counterpart. Overall, td pbe is doing a better job (qualitatively) with the metal cluster.
- 2- Little to no basis set dependence (SVP and TZVP values are identical for our purpose
- 3- We can take advantage of CD fitting as implemented in NWChem especially handy for AIMD trajectory calculations
- 4- More in support of the choice of level of theory follows (no scaling factors needed in the context of our ensuing vibrational analysis)

Figure S7. Absorption spectra of Ag_{20} – basis set and broadening parameter dependence



Figure S8. Simulated UV-Vis spectra of a DMS molecule chemisorbed on the vertex of the tetrahedral Ag cluster. Vertical transition energies are obtained from optimized minima (reoptimized at each level of theory). Low-lying charge transfer states of interest are highlighted with color-coded asterisks and tabulated below, for convenience.



Table S2. Vertical transition energies extracted from Figure S8.

Method	State 1	State 2	State 3	State 4
	(eV)	(eV)	(eV)	(eV)
td pbe/def ₂ SVP	1.10	1.73	2.08	2.30
(def ₂ TZVP)	1.12	1.75	2.06	2.23

Figure S9. Td pbe/def₂SVP *vs* td pbe/def₂TZVP spectra.



Describing the states of interest (states 1-4 as defined in Figure S8): Note: HOMO/LUMO are orbs # 254/255

<u>State 1 – (second singlet)</u> (a molecule to metal CT state)

#Pair Coefficient Transition dipole X/Y/Z (au) 256 0.705180 1 254 -> -1.420258 0.645523 -0.063551 0.645523 -0.063551 -1.420258 Sum: 1.5613689 a.u. Norm of transition dipole moment: Oscillator strength: 0.0658488

Figure S10. A) Transition density and B) charge density difference – black is negative and red is positive density.



Figure S11. Orbitals associated with this transition



State 2 (13th singlet) (a molecule to metal CT state)

#Pa:	ir			Coefficient	t Transit	ion dipole >	K/Y/Z (au)
-	L 253	->	257	-0.222270	0.530821	-0.370044	-0.004452
4	2 254	->	260	0.639000	2.398592	0.025785	0.132892
	3 254	->	261	0.122520	-0.056803	-0.001119	-0.018672
4	4 254	->	262	-0.112690	-0.607382	-0.453277	0.010758
Sum:					2.265228	-0.798654	0.120526
Norm of	f transi	tion	dipole :	moment: 2	2.4049180 a	.u.	
Oscilla	ator str	engtl	n: 0.2	446813			

Figure S12. A) Transition density and B) charge density difference – black is negative and red is positive density.





Figure S13. Orbitals associated with this transition

State 3 (27th singlet) (mostly localized at the sulfur linker and adjacent vertex of the tetrahedron)

#Pair				Coefficient	Transiti	on dipole X	/Y/Z (au)
1	251	->	260	0.146620	-0.113074	0.581204	-0.104575
2	252	->	259	0.185890	-0.796168	-0.033067	0.145330
3	253	->	261	0.498870	3.493449	-2.625950	0.019646
4	253	->	262	-0.150030	-0.033245	0.006192	0.013504
5	253	->	263	-0.322920	-0.529890	0.372280	0.007661
6	254	->	262	0.123760	0.667048	0.497804	-0.011815
Sum:					2.688120	-1.201537	0.069751
Norm of t	ransit	tion	dipole	moment: 2	.9452581 a.	u.	
Oscillato	or stre	engti	h: 0.4	418767			

Figure S14. A) Transition density and B) charge density difference – black is negative and red is positive density.



Figure S15. Orbitals associated with this transition



State 4 (43rd singlet) (mostly localized at the linking sulfur and vertex of the tetrahedron)

#Pair			Coefficient	Transiti	on dipole X	/Y/Z (au)
1	246 ->	255	-0.178080	0.295558	0.450452	-0.016595
2	246 ->	256	0.315550	-0.011183	-0.028622	-0.901345
3	250 ->	258	0.189480	0.355190	0.467018	-0.628940
4	251 ->	259	0.128000	0.064616	0.068451	0.330906
5	251 ->	260	0.133630	-0.103056	0.529711	-0.095310
6	251 ->	262	0.109740	-0.225553	-0.026275	0.089038
7	252 ->	258	-0.112070	0.003195	0.000903	0.323643
8	252 ->	259	0.327130	-1.401101	-0.058192	0.255752
9	252 ->	260	0.149600	0.050260	0.103307	0.398687
10	252 ->	261	-0.106670	-0.057048	-0.112422	0.000658
11	254 ->	262	-0.194820	-1.050050	-0.783632	0.018598
12	254 ->	265	-0.127030	-0.203988	-0.309757	-0.001967
Sum:				-2.283160	0.300944	-0.226874
Norm of ti	ransition (dipole	moment: 2	.3140563 a.	u.	
Oscillato	r strength	: 0.1	3017669			

Figure S16. A) Transition density and B) charge density difference – black is negative and red is positive density.



Figure S17. Orbitals associated with this transition



Statements that can be made (so far):

- 1- Lowest two states in the Ag₂₀-DMS complex are charge transfer states
- 2- If taken at face value, the above results (even the lc-pbe0 values) suggest that green excitation (514 nm or 2.41 eV) in SERS is resonant with a CT state. Major implications for SERS selection rules (resonant as opposed to non-resonant SERS). We refrain from further commenting on this issue until further experimental proof is gathered.

One measure of charge-transfer character: Δr – extent of delocalization for a given transition (see J. Chem. Theory Comput. 2011, 7, 2498–2506)

Baseline 1: Δr for the molecular transition (zero because of symmetry):

Sum	of square	of	transition	coefficient:	0.494759	
	#Pair	Ork	oitals	Coefficient	Contribution (E	Bohr and Angstrom)
	1	62	65	0.1254700	0.000000	0.000000
	2	64	65	0.6921100	0.000000	0.000000

Baseline 2: Δr for the dominant 'metallic' transition:

Sum	of	square	of	transition	coefficient:	0.290682	
	#₽a	air	Orl	bitals	Coefficient	Contribution (Bohr	and Angstrom)
		1 1	79	194	-0.1047600	0.0419286	0.0221877
		2 1	85	191	0.1961400	0.1640368	0.0868045
		3 1	85	198	0.1694700	0.0465831	0.0246507
		4 1	86	192	0.1085200	0.0886785	0.0469267
		5 1	86	196	0.1371600	0.1050945	0.0556136
		6 1	87	193	-0.1322200	0.0619101	0.0327614
		7 1	87	195	0.1564500	0.1535599	0.0812604
		8 1	88	194	-0.1173800	0.0535996	0.0283637
		9 1	88	196	-0.1199900	0.1023088	0.0541395
	1	.0 1	89	198	0.2883500	0.1349653	0.0714205
	1	.1 1	90	195	0.1078900	0.0921791	0.0487791
	1	.2 1	90	197	0.1304100	0.1104580	0.0584519

 Δr for State 1 of interest in the complex:

Sum	of	square	of	transition	coefficient:	0.497279			
	#₽a	air	Ork	oitals	Coefficient	Contribution	(Bohr	and	Angstrom)
		1 2	54	256	0.7051800	17.2528878		9.2	L298357

Δr for State 2 of interest in the complex:

Sum of	square of	transi	tion coefficient:	0.485435	
#Pai	r Orb	itals	Coefficient	Contribution (Bo	ohr and Angstrom)
1	253	257	-0.2222700	0.4070873	0.2154213
2	254	260	0.6390000	11.1923838	5.9227549
3	254	261	0.1225200	0.5037617	0.2665792
4	254	262	-0.1126900	0.1142209	0.0604431

 Δr for State 3 of interest in the complex:

ngstrom)
73207
86957
28623
17499
38049
91652
n 782 39

 Δr for State 4 of interest in the complex:

Sum	of	square	e of	transition	coefficient:	0.420895	
	#Pair		Orbitals		Coefficient	Contribution (Bohr	and Angstrom)
		1 2	246	255	-0.1780800	0.7669348	0.4058445
		2 2	246	256	0.3155500	2.3944072	1.2670658
		3 2	250	258	0.1894800	0.1322929	0.0700064
		4 2	251	259	0.1280000	0.0849577	0.0449577
		5 2	251	260	0.1336300	0.1289069	0.0682146
		6 2	251	262	0.1097400	0.4335198	0.2294088
		7 2	252	258	-0.1120700	0.0804218	0.0425574
		8 2	252	259	0.3271300	0.4269893	0.2259530
		9 2	252	260	0.1496000	0.1917190	0.1014533
	1	.0 2	252	261	-0.1066700	0.0136895	0.0072442
	1	1 2	254	262	-0.1948200	0.3937313	0.2083536
	1	.2 2	254	265	-0.1270300	0.4431804	0.2345210

Orbital decomposition analysis (allows fragmenting the molecule-metal complex into molecule + metal)

Orbital decomposition analysis using 'sphericalized' atomic densities in free states (Hirshfeld)

Ref: Tian Lu, Feiwu Chen, Calculation of Molecular Orbital Composition, Acta Chim. Sinica, 69, 2393-2406

Table S3. Contribution of X (X denotes either Ag_{20} or DMS or the linker atom, which seems to be important from a close look at the above-analysis) to orbitals 246-265 in the Ag20-DMS complex (all the above excitations in the complex are contained within this sub-set of orbitals)

Orbital	% Contribution				
Number	Ag ₂₀	DMS	S-Linker		
246	62	38	31		
247	4	96	15		
248	92	8	7		
249	100	0	0		
250	100	0	0		
251	99	1	0		

252	100	0	0
253	80	20	17
254	8	92	41
255	100	0	0
256	100	0	0
257	100	0	1
258	100	0	0
259	98	2	1
260	90	10	1
261	95	5	4
262	30	70	4
263	100	0	0
264	100	0	0
265	78	22	2

If one looks at the % contribution values, one can readily visualize the orbitals (and transitions) to some extent, without inspecting the orbitals.

Figure S18. DOS and PDOS plot for the DMS-Ag20 complex. Relative energies of the HOMO and LUMO orbitals are noted.



Ensemble averaged Raman and SERS

Figure S19. Experimental micro-SERS and micro-Raman spectra. The samples were prepared by spin casting a 1 mM solution of DMS/CHCl₃ either on a glass cover slip (Raman) or a 20 nm thick corrugated silver film.







Figure S21. Raman; theory vs experiment; larger basis set recovers some of the discrepancies observed in Figure S20 because of the small basis set. Note that no scaling factors are used.



Figure S22. SERS – theory vs experiment; small basis set. Note that no scaling factors are used.



Figure S23. SERS – theory vs experiment; larger basis set. Note that no scaling factors are used.



Figure S24. Infrared spectra; basis set dependence. Note that no scaling factors are used.



The reader is also referred to our previous experimental works on DMS and assignments therein (Faraday Discuss. 2015, 184, 339-357, *Nano Lett.* 2014, *14*, 4114 (Supporting information section)).

AIMD Results

Figure S25. Panel A: Total energy as a function of propagation time from a constant temperature AIMD simulation of the isolated molecule. Ten randomly selected structures from the trajectory shown in A were used as starting structures for UV-Vis simulations; the results are shown in panel B where the static spectrum (0.2 eV broadening) is compared to the AIMD (also 0.2 eV broadening) and experimental spectra. Panel C shows the Fourier transform of the homo-lumo gap along this trajectory. One can notice that the gap is most affected/modulated by the aromatic C=C vibrations (expected, since the corresponding transition is of the $\pi \rightarrow \pi^*$ type). Panel D shows the vibrational density of states obtained from the Fourier transform of the velocity autocorrelation function. Interestingly, the AIMD spectrum is distinct from its static analogue. Beyond Frank-Condon (vertical) effects seems to affect the UV-Vis spectrum, as DMS is symmetric (C_{2h}); spectra computed along the AIMD trajectory sample starting structures in which symmetry is reduced.



Figure S26. Vibrational density of states from a constant energy simulation (a separate simulation initiated from a randomly selected structure along the above described constant temperature trajectory) of the isolated molecule (10 ps total). Also shown on the same plot is the experimental Raman spectrum.



Figure S27. Panel A: Total energy as a function of propagation time from a constant temperature AIMD simulation of Ag_{20} . Ten randomly selected structures from the trajectory shown in A were used as starting structures for UV-Vis simulations; the results are shown in panel B where the static spectrum (0.175 eV broadening) is compared to the AIMD (also 0.175 eV broadening) and experimental UV-Vs spectra. Panel C shows total energy as a function of propagation time from a constant Energy AIMD simulation of Ag_{20} . Panel D shows the vibrational density of states of Ag_{20} calculations from the trajectory shown in C.



Figure S28. Vibrational density of states from five different constant energy simulations initiated from different structures sampled from the constant energy AIMD trajectory of Ag20-DMS discussed in the main text.



Figure S29. Total (panel A) density of states and the molecular contribution to the total density of states (panel B) at the minimum energy conformation (termed static) and at different simulation times along a constant temperature AIMD simulation of the Ag₂₀-DMS complex (pbe/def₂-SVP, see Figure 2 in the main text). Structural evolution along the constant temperature AIMD simulation is accompanied by changes in the energies of the occupied and valence molecular orbitals. The decreased energy difference between the HOMO-1 and HOMO orbitals (-2 to -2.5 eV in panel A) which coalesce into a single peak centered around -2.3 eV for 3 different randomly selected UV-Vis snapshots, is noted.



Figure S30. Panels A and C show the temporal evolution of the energy differences between two different sets of molecular orbitals in the Ag_{20} -DMS complex, extracted from the Ag_{20} -DMS AIMD trajectory shown in Figure 2 in the main text. Note that the orbitals considered in this analysis are relevant to the molecule-to-metal charge transfer states 1 and 2, respectively, as defined in Figure 2 in the main text. The corresponding Fourier transforms of the data shown in panels A and C are shown in panels B and D, respectively. They both reveal that the C-S stretching vibration in the Ag_{20} -DMS complex essentially modulates the fluctuating energy differences.



Figure S31. Total vibrational density of states (VDOS) from Fourier transforms of velocity autocorrelation functions, decomposed into contribution by element for the isolated DMS molecule (panel A) and the Ag₂₀-DMS complex (panel B). The results shown in panel A were obtained from a 10 ps constant energy simulation of the isolated DMS molecule. The results shown in panel B were obtained by averaging the velocity autocorrelation functions from 5 different simulations (shown in the supporting information section) of the Ag₂₀-DMS complex (simulation time of ~3.5 ps/trajectory). The experimental frequency shifts are shown as vertical dashed lines for reference. They were obtained following 514 nm (2.41 eV) excitation of a thin DMS film deposited either on glass (Raman, panel A) or on a sputtered silver substrate (SERS, panel B). A good agreement between the experimental and theoretical frequency shifts is more obvious in panel A, as line broadening - as a result of conformational sampling of a DMS molecule interacting with the metal cluster - in panel b renders the correlation less obvious to discern from the corresponding plot.

