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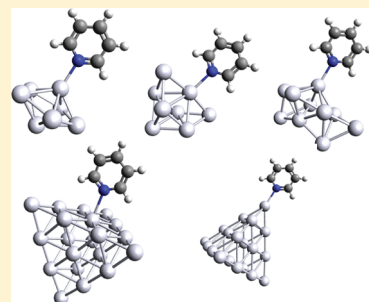
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S Supporting Information

ABSTRACT: We present the first density functional simulations of coherent anti-Stokes Raman scattering (CARS) and an analysis of the chemical effects upon binding to a metal surface. Spectra are obtained from first-principles electronic structure calculations and are compared with available experiments and previously available theoretical results following from Hartree–Fock polarizability derivatives. A first approximation to the nonresonant portion of the CARS signal is also explored. We examine the silver pyridine cluster models of the surface chemical signal enhancement, previously introduced for surface-enhanced Raman scattering. Chemical resonant intensity enhancements of roughly 10^2 are found for several model clusters. The prospects of realizing further enhancement of CARS signal with metal surfaces is discussed in light of the predicted chemical enhancements.

SECTION: Surfaces, Interfaces, Catalysis



Coherent anti-Stokes Raman Scattering (CARS)¹ is an increasingly popular four-wave mixing optical technique for spectroscopy and chemically specific microscopy. The advantages offered over simple spontaneous Raman spectroscopy are the coherent signal blue-shifted away from fluorescence and rapid acquisition from the collective response of many chromophores. Recent advances in the microscopic applications of this technique have improved signal collection through the use of tightly focused beams,² which relax the phase-matching condition, and techniques for limiting the nonresonant (NR) signal.^{3,4} Spectroscopic studies have separated the resonant from NR signals in the time domain³ and designed more efficient^{5,6} collection sequences. The enhancement of CARS by intense plasmon fields could potentially enhance the signal further and is the motivation for this work. To address this problem theoretically, we have developed code to simulate CARS spectra of molecules bound to cluster models of metal surfaces, which is described below.

The enhancement of spectroscopies by the intense fields of nearby collective excitations in metals or semiconductors has experienced a renaissance in recent years, especially surface-enhanced Raman scattering (SERS).⁷ Given the nonlinear dependence of the CARS signal on input power ($I_{\text{CARS}} \propto E_1^2 E_2$), one might expect surface-enhanced CARS (SE-CARS). The first report of CARS occurring near a surface plasmon was published decades ago⁸ and was followed by reports of CARS observed from single molecules⁹ and on the tips of scanning-tunneling microscopes.¹⁰ Despite these advances, the paucity of SE-CARS spectra and scattering cross sections available in the literature indicates that this remains a difficult experiment to perform and completely characterize. We will try to offer some indication of

chemical enhancement effects of SE-CARS, and in the last section, we point out challenges facing application of the spectroscopy that should be given further attention.

Past theory has focused^{11,12} on understanding the classical electrodynamic features of CARS spectroscopy until Hartree–Fock (HF) polarizability derivatives were combined with (static) density functional theory (DFT) vibrational frequencies to produce the first ab initio CARS spectra.^{13,14} HF theory's neglect of electron–electron interaction is especially unphysical for systems with significant correlation, like metals. For this reason, we replace HF for the calculation of CARS on metal cluster models. In this work, we present the first CARS spectra calculated entirely with DFT. Prior to applying the method to metal clusters, we test the model on a few known experimental spectra from previous work to make some estimation of its usefulness.

Theory. The CARS spectra in this paper are calculated in the double-harmonic approximation developed by the Aarhus group,¹³ which follows from the much older double harmonic approximation to Raman spectra,¹⁵ which we briefly review. The typical CARS experiment applies two lasers of frequencies ω_1 and ω_2 , which scatter twice and once, respectively, off of the target material. Signal radiation collected at $2\omega_1 - \omega_2$ peaks when the Stokes shift, $\omega_1 - \omega_2$, coincides with a vibrational transition of the scatterer. On the scale of a single molecule, CARS is governed by the second hyperpolarizability ($\chi^{(3)}(-2\omega_1 - \omega_2; \omega_1, -\omega_2, \omega_1)$). We include terms where the central resolution in the sum-over-states expression for $\chi^{(3)}$ only includes excited vibrational states

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on the electronic ground state because these are resonant with the wavelength differences of the experiment. $\chi^{(3)}$ is then a product of polarizabilities, albeit with perturbed nuclear geometries. Expanding the polarizability as a power series to first order along each mode, as in the harmonic approximation for Raman cross sections, the expression for the resonant CARS susceptibility becomes

$$\chi_{\text{R}}^{(3)}(ijkl) \approx \frac{2}{\hbar} \sum_n \frac{d\alpha_{ij}(\omega_1)}{dQ_n} \frac{d\alpha_{kl}(\omega_1)}{dQ_n} (\omega_n - (\omega_1 - \omega_2) - i\varepsilon)^{-1} + \frac{2}{\hbar} \sum_n \frac{d\alpha_{ii}(\omega_1)}{dQ_n} \frac{d\alpha_{jj}(\omega_1)}{dQ_n} (\omega_n + (\omega_1 - \omega_2) + i\varepsilon)^{-1} \quad (1)$$

The formula above incorporates some simplifications emerging from spherical averaging¹⁶ explained in the Supporting Information. Here, ε is a phenomenological line width (inverse lifetime), $\{ijkl\}$ are Cartesian indices, and Q_n are nuclear displacements along mode n .

Non-Resonant Approximation. There is also a contribution to the CARS signal that is NR with any of the applied frequencies or their differences, $\chi_{\text{NR}}^{(3)}$, which we discuss below. Including this term and averaging over the molecular orientations, the expression for the CARS signal in an isotropic medium becomes

$$I_{\text{CARS}} \propto |(\chi_{\text{R}}^{(3)} + \chi_{\text{NR}}^{(3)})|^2$$

where $\chi^{(3)} = \frac{1}{15} \sum_{ij} (\chi_{ijji}^{(3)} + \chi_{ijij}^{(3)} + \chi_{iijj}^{(3)}) \quad (2)$

The single-scatterer expression given above ignores the coherent amplification from many molecules in an illuminated volume (d^3 , where d is the diameter of the coherent volume), $I_{\text{CARS}} \propto d^2$, which is experimentally vital to realize intense signal, especially in microscopy.¹⁷ Also note that the dimensions of molecular polarizability are different from the macroscopic property, although one may convert between them approximately. This ignores local-field effects and has been not pursued here. Although $\chi_{\text{NR}}^{(3)}$ is nearly constant in regions of interest, it contributes to the observed four-wave mixing signal and distorts it in the vicinity of resonances of $\chi^{(3)}$ because of the cross term in eq 2. We will consider only the electronic contributions to this signal, which, for a sequence of applied fields in which we are interested in, breaks into two diagrams.¹⁸ The first resembles the resonant CARS diagram but sums over electronically excited states. The second resembles a two-photon absorption–emission process and usually becomes dominant at high pump energy, where $2\omega_1$ is near electronic resonance. The relative magnitude of the NR signal varies significantly³ with small changes in the pulse sequence and other factors such as light polarization¹⁹ because the NR electronic dynamics is very fast on the vibrational time scale. To obtain quantitative simulation, one needs precise characterization of the experiments, and this is one reason for the infrequent appearance of absolute CARS cross sections in the literature. We are interested in how well the NR contribution could be modeled by the first diagram, that is, $\chi_e^{(3)} \approx \chi^{(1)}(\omega_1)\chi^{(1)}(\omega_1)/\omega_1$. This approximation is admittedly very rough but desirably efficient. We will use this approximation to the NR signal chiefly to obtain spectra in qualitative agreement with those available from the literature and verify that DFT and TDDFT can be usefully paired to simulate CARS spectra. Approximations of this sort were made long ago by

Wang²⁰ and are appropriate when the applied radiation is far below resonance ($2\omega_1\hbar \ll (E_1 - E_0)$, where E_i are energies of adiabatic electronic states). This condition roughly holds for the organic species studied here where ~ 700 nm light is applied. The finite time scale of the electronic scattering process can also be represented by the imaginary part of these quantities.²¹ The NR signal from a metal nanoparticle is expected to dominate the background of SE-CARS and depend on excitations spatially extended beyond the range of a TDDFT simulation. Nanoscale simulations of four-wave mixing are not well developed, and interfacing those with TDDFT would be an undertaking beyond the scope of this work. For the purposes of surface chemical enhancement, we will not include the NR signal.

Performance of TDDFT. In the case of spontaneous Raman, DFT is known to provide accurate spectra,^{22,23} but to establish the usefulness of TDDFT polarizability derivatives for CARS, we compare them here with those from TDHF and experiment.^{24,25} The spectra of anthracene and perylene are shown in Figures 1 and 2, respectively. For anthracene (Figure 1), the NR approximation achieves a reasonable distortion that matches the experimental line shape in a satisfactory way. The relative phasing of each peak can vary because of the anisotropy of $\chi_{\text{NR}}^{(3)}$. The peak intensities are well reproduced, with the exception of the mode at 1590 cm^{-1} , which is exaggerated, as was seen in previous work.¹³ Motion along this mode lengthens the bonds between the tertiary carbons, stretching the short axis of the molecule. The spectrum of perylene (Figure 2) is again roughly accurate, although the relative intensities of the two important peaks are switched. Comparing against the spectra from ref 13 and knowing that the perylene has a low-lying first excited state at roughly $24\,000\text{ cm}^{-1}$,²⁶ these are likely artifacts of our approximation to the NR signal. The exaggeration of the first peak height is more severe in the TDDFT than that in the HF results, and the distortion due to the NR signal is significantly different in the HF and B3LYP spectra. Going back to the polarizabilities themselves, TDDFT predicts the α_{xx} component, the long-axis along which perylene is oriented, to be a factor of 2 larger than that in HF.

Many common functionals are known to exaggerate polarizabilities²⁷ of delocalized systems due to the incorrect asymptotic behavior of the local density approximation exchange potential. Roughly speaking, the CARS intensity in the resonant approximation should go as the square of this quantity. Although the B3LYP functional seems sufficient for these hydrocarbons, which extend in space as far as the metal clusters, we will examine in the next section whether an asymptotically correct exchange functional²⁸ would be desirable for studies of larger molecules. The lack of correlation effects in HF may favor TDDFT for a metal cluster study.

Surface Effects. Metal surfaces largely enhance (spontaneous) Raman spectra via the increased fields that exist in the vicinity of a surface plasmon excitation,^{29–31} although there is also a chemical effect^{32–35} that arises from the metal perturbing the electronic structure of an attached molecule. Classical electrodynamics can account for the former,³⁶ and TDDFT calculations can be used to describe the latter.^{34,35,37} Recent algorithmic developments have brought both theories into a single self-consistent calculation³⁸ and also provided a rigorous quantum treatment³⁹ of the matter–field interaction in a SERS event. Large ($\sim 10^{12}$) enhancement factors⁴⁰ for SE-CARS were predicted decades ago on the basis of classical electromagnetic Mie theory, although experiments have not realized anything comparable. Enhancements of

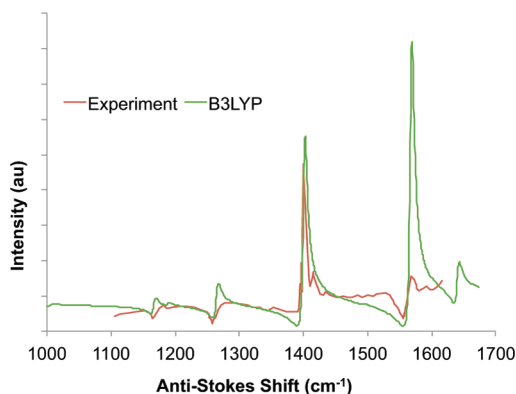


Figure 1. A comparison of experimental anthracene CARS spectra with those obtained from TDDFT simulations. Agreement is satisfactory, with the exception of the mode near 1560 cm^{-1} .

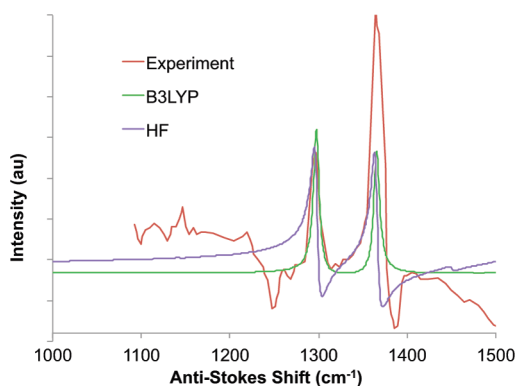


Figure 2. TDDFT and experimental perylene CARS spectra. The approximation to the NR signal employed is compromised by a low-lying first excited state, but there is still semiquantitative agreement.

$\sim 10^3$ have been reported⁴¹ but are not common. SE-CARS remains an ongoing pursuit.

On the basis of the SERS precedent, a cluster model CARS spectra should represent the chemical effects of the bulk. The small molecule is coupled to metallic states, but to a first approximation, the electronic states with significant density on the small molecule remain local enough to fit within the cluster. Thus, the polarizability gradients responsible for the resonant signal should approximately depend on the electronic structure only near the small molecule, and our DFT/TDDFT approach can be used to examine chemical enhancement of CARS. A CARS experiment for pyridine on silver colloid has been recently published⁴² and reports a $10\times$ CARS signal enhancement and a SERS enhancement of 10^4 . Cluster models have been systematically investigated⁴³ for simulating the chemical portion of the enhancement. We use the well-known silver pyramid cluster model,⁴⁴ which was also used for a recent surface-enhanced hyper-Raman scattering (SEHRS) simulation of this system.³³ Some additional clusters were also optimized for this work (see Supporting Information), with the expectation that chemical enhancement of CARS would more significantly vary than that for SERS. Indeed, they do vary, although the trends can be understood. The structures employed are summarized in Figure 3 and given in Supporting Information.

The CARS spectrum of an isolated pyridine molecule (Figure 4) already appears significantly distorted by NR contributions, especially the bright peaks near 1030 cm^{-1} , in accordance with some available spectra.⁴⁵ The resonant enhancement of bright peaks ($I_{\text{pyr-Ag}}/I_{\text{pyr}}$) relative to the isolated pyridine spectrum are tabulated in Table 1 for the clusters examined. Whether DFT or HF polarizabilities are used, the enhancement trends are found to be quite similar. The ring-breathing mode of pyridine at 611 cm^{-1} stretches the ring pulling the nitrogen atom away from the *para*-carbon on the other side of the ring and is strongly enhanced by the presence of the metal surface. The most strongly enhanced peaks near 1020 and 1058 cm^{-1} also correspond to ring distortions that involve the Ag–N bond. The experimental⁴² SE-CARS spectrum between 700 and 1400 cm^{-1} shows two broad, structured peaks centered near 1000 and 1150 cm^{-1} . As in our computational results, the peak near 1000 cm^{-1} is brightest. Detailed discussion is given in the Supporting Information.

Like other SE Raman spectroscopies, the chemical enhancement can be understood from a simplified picture of the changes that the electronic system undergoes when the substrate is brought into contact with the metal.^{46–48} Following previous work, the resonant signal in eq 1 should be proportional to the square of the Raman polarizability derivative, $|(d\alpha_{ij}/dQ_k)^2|^2$. The polarizability itself in the low-energy region in which we are interested is often dominated by a low-lying bright state of energy ω_e . Taking the static limit and ignoring changes in the transition moments along modes $\mu_\alpha = \langle e|\mu_\alpha|0\rangle$ gives a two-state expression for the derivative, $(d\alpha_{\alpha\beta}/dQ_k) \approx -(\mu_\alpha\mu_\beta/\omega_e^2)(d\omega_e/dQ_k)$. This analysis suggests that the ratio of the signal from a single adsorbed species to a free species goes as $I_{\text{Ag-Pyr}}/I_{\text{Pyr}} \propto (\omega_{\text{Pyr}}/\omega_{\text{Ag-Pyr}})^8$, where the ω is an estimate of the lowest bright transition energy in the respective species. The proportionality constant absorbs the ratio of adsorbed and free transition moments and $(d\omega_e/dQ_k)$. Estimating ω_{Pyr} as the occupied–unoccupied gap and $\omega_{\text{Pyr-Ag}}$ as the difference between the Ag HOMO and energy of the pyridine LUMO in the cluster, the Ag_7 , $\text{Ag}_{20}(\text{s})$, and $\text{Ag}_{20}(\text{v})$ enhancement factors are estimated to be 6, 416, and 701. The integrated static enhancements obtained from the ab initio calculations are 4, 559, and 1070, roughly the correct order of magnitude and the correct trend.

We predict a chemical contribution to the enhancement of the CARS signal that is substantial on the scale of observed overall enhancements. Given the certain dominance of the EM mechanism in SERS,⁷ this suggests that our single-molecule results are only one ingredient of a more nuanced experimental picture. In the next section, we propose how this may be investigated by experiment and theory.

Challenges Facing SE-CARS. SEHRS^{33,49,50} is relatively better characterized than SE-CARS^{8,10,41,51,52} and higher hyper-Raman enhancement factors have been realized, although both are nonlinear spectroscopies of significant complexity. We would like to note three reasons this may be so. Previous authors have pointed out the complication of the phase-matching condition by a nearby metal surface,⁴² which can be addressed by adopting a tight-focusing experimental setup. A classical electromagnetic analysis of SE-CARS including these difficulties predicted enhancement factors of 10^{12} .⁴⁰ The surfaces of noble metals are also known to conduct four-wave mixing,^{53,54} which would mask the resonant signal of molecules. Given that this nonlinear effect is the result of short-lived scattering from electronic states of gold, it is possible to separate this background from the resonant signal by pulse timing,^{3,55,56} polarization, or shaping¹² techniques.

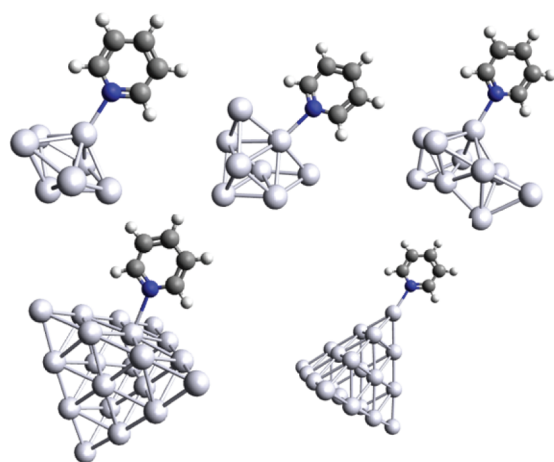


Figure 3. Silver pyridine cluster models employed to simulate SE-CARS. Left to right: {7, 8, 10, 20s, 20v}. For those that possess an even number of electrons, restricted calculations have been employed.

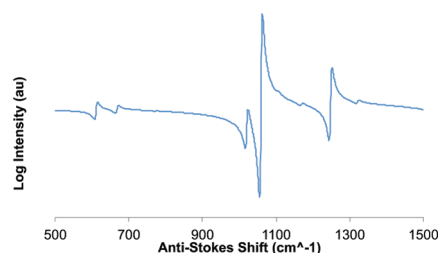


Figure 4. Simulated (PBE0/TZVP) pyridine CARS spectra.

Table 1. Relative Enhancements of Significant CARS Peaks on Cluster Models (frequencies in cm^{-1})^a

vib freq.	Ag ₇	Ag ₈	Ag ₁₀	Ag _{20(s)}	Ag _{20(v)}	Ag _{20(s)} (HF)	Ag _{20(v)} (HF)
611	39.9	1.9	445.8	46.5	0.3	205.9	0.1
667	0.0	0.1	13.6	0.4	0.4	1.0	0.3
1020	78.7	4.0	243.8	681.0	348.7	570.7	165.7
1058	25.2	0.1	0.9	12.3	128.0	1.5	22.4
1247	2.5	25.2	4.5	1.3	17.4	2.1	35.4
1648	0.0	7.2	35.6	1.0	1.0	1.1	0.0
1652	254.2	0.0	42.8	9.5	195.8	3.1	16.5

^a HF results are relative to a pyridine spectrum from HF polarizability derivatives; others are from PBE0 (results from the resonant approximation).

The rapid dephasing of vibrational quanta on metal surfaces has not received much attention from the SE-CARS community but warrants further study. Unlike spontaneous Raman and hyper-Raman, the resonant CARS wavepacket must pass through a vibrational coherence and interact with light again to contribute signal. This nuclear wavepacket may dephase so rapidly on a metal surface that the electromagnetically enhanced signal is reduced. Detailed pictures of the time dependence of the density matrix in a CARS experiment have been developed in the literature.⁵⁷ The dependence of the CARS signal on vibrational dephasing has been exploited in the past to make measurements of the pure dephasing rates.^{58,59} For a molecule like anthracene in a crystal, relaxation lifetimes are on the order of 10 ps. Plasmons readily

accept energy from molecular vibrations and reduce T_1 relative to the vacuum to roughly 1 ps. This can be calculated from cluster models using the golden rule.⁶⁰ The T_2^* dephasing will have the usual collisional contributions and also a component unique to SE-CARS from the vibrational transition dipole coupling to rapid fluctuations of the plasmon and partially localized vibrational modes. A molecular dynamics simulation coupled to a properly fluctuating classical electric field may be able to theoretically predict both pure-dephasing rates.⁶¹ Pump–probe experiments to measure the SE-CARS dephasing time scale may also shed light on the situation.^{12,62}

For the purposes of simulating SE-CARS, we have presented the first calculations of CARS spectra entirely with DFT. The hybrid functionals employed here provide accuracy comparable to HF, and the conclusions drawn about chemical enhancement of CARS are qualitatively the same whether HF or DFT polarizability derivatives are employed. Approximating the dynamic electronic second hyperpolarizability as a separable product of the dynamic polarizability appears to offer satisfactory modeling of the NR background signal for pump frequencies well below material electronic excitations. The bulk spectra provided with TDDFT are in semiquantitative agreement with available experimental data.

Small cluster models are found to offer simulated SE-CARS spectra of pyridine on silver that are consistent whether HF or TDDFT polarizabilities are used. The most intense peaks of the available experiment are also the brightest peaks in our simulations. On the basis of the results of cluster model calculations, we estimate the chemical enhancement of a silver pyridine SE-CARS experiment to be significant when compared to available experimental information without any treatment of electromagnetic enhancement. Optimistically, this indicates a mechanism for metals to enhance CARS but also suggests that a complete picture of SE-CARS will be more complex than SERS and likely require a treatment of dephasing. Future work should focus on the calculation of the NR signal produced by the metal, perhaps via a classical electromagnetic simulation, although the inclusion of this signal in an “enhancement factor” may be ambiguous. We have pointed out three possible explanations for the difficulty of measuring SE-CARS: phase-matching, background signal, and dephasing. Future work will calculate the rate of vibrational dephasing to ascertain whether the dephasing effects that are unique to a metal–molecule system are significant compared to chemical and electromagnetic enhancements. The other two complications, the NR signal and phase matching, might be avoided with experimental effort. Pure dephasing induced by the metal surface is however a nearly intrinsic part of the SE-CARS experiment.

Computational Details The results of this paper were calculated within the Turbomole electronic structure package.^{63–65} The def2-TZVP basis⁶⁶ was employed in all cases, with matching pseudopotentials for metallic elements. The geometries of organic species were optimized with the same basis and the B3LYP⁶⁷ functional, the metal clusters were optimized, and polarizability derivatives were evaluated with the PBE0^{68,69} functional. Further details can be obtained in the Supporting Information. An empirical inverse lifetime of $\varepsilon = 2 \text{ cm}^{-1}$ has been assumed for the calculations, unless otherwise noted. Throughout the paper, the label HF attached to a spectrum indicates that it was generated with HF polarizability derivatives calculated along the normal modes emerging from a B3LYP calculation, that is, the procedure that was previously available.¹³ However,

note that in that work, $\chi_{\text{NR}}^{(3)} = \chi_e^{(3)}$, whereas in this work, it is approximated as the product of dynamic polarizabilities described above. No subsequent scaling of the vibrational frequencies of DFT has been performed.

■ ASSOCIATED CONTENT

S Supporting Information. Supplemental equations, results, molecular geometries, and detailed computational information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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