An APT charge based descriptor for atomic level description of chemical Raman enhancement by adsorption of 4-Mercaptopyridine on semiconducting nanaoclusters: A theoretical study

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An APT charge based descriptor for atomic level description of chemical Raman enhancement by adsorption of 4-Mercaptopyridine on semiconducting nanaoclusters: A theoretical study



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ARTICLE INFO	A B S T R A C T					
Keywords: Binding energy Static Raman activity Polarizability APT charges	Density functional theory (DFT) based calculations are carried out to study effect of molecular charge on both the binding energy as well as chemical Raman enhancement of deprotonated 4-Mercaptopyridine (ligand) bound to the semiconducting nanocluster, Zn_3Se_3 and metal substituted nanoclusters, Zn_2MSe_3 (M: Ag, Cu). Change of molecular charge from 0 to -1 increases binding energy of the ligand for Zn_3Se_3 cluster and decreases Raman activity of vibrational modes. On the other hand, the ligand bound to the metal substituted nanoclusters, Zn_2MSe_3 shows minimal decrease in binding energy and a noteworthy enhancement in Raman activity of the vibrational modes, on varying the molecular charge from 0 to -1 . Static Raman activities of vibrational modes are analyzed using change of molecular polarizability components with normal coordinates of the modes. An APT (Atomic Polar Tensor) charge based descriptor is used for characterization of the chemical Raman en- hancement. The descriptor measures substrate induced charge concentration per unit displacement of an atom involved in a mode of vibration. We also show that significantly enhanced intensity of vibrational modes is associated with atoms of relatively greater magnitudes of the APT charge based descriptor.					

1. Introduction

Surface enhanced Raman scattering (SERS) has been an intense research topic, since its first observation and explanation by pioneers [1-7]. Enhancement of spectral intensities emerges from scattering of light by a system of metal nanoparticles tagged with a molecule and charge transfer interactions between ligand molecule and the nanoparticles. In analytical chemistry, importance of the subject comes from the fact that SERS technique amplifies the Raman signal by an enhancement factor around 1012 [8-10]. The signal enhancement is interpreted using impacts of electromagnetic mechanism (EM) and chemical effects (CHEM) [11-14]. The EM enhancement is seen as resonance between energy of laser excitation and surface plasmon energy of noble metal substrate (surface plasmonic resonance) [15]. The chemical effects include (a) ground state chemical interactions between molecule and nanoparticle that are not associated with excitation of nanoparticle-molecule system, (b) charge transfer transitions between analyte molecule and the substrate (charge transfer effects) and (c) Molecular resonance: electronic transitions from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of analyte molecule or valence band to conduction band of substrate material [13,15]. The mechanisms are intimately tied to one another and the states associated with the surface Raman enhancement are part of molecule-nanoparticle system [16]. Difference in extents of contribution from the mechanisms to the total surface Raman enhancement, depends on parameters associated with each resonance at each excitation wavelength and selection rule [16].

The CHEM enhancements arising from adsorption of a ligand molecule on a metal substrate and ground state chemical interactions between the two, can be measured from quantum chemical calculations of static Raman intensities [15]. Factors that influence these Raman activities are: size of the cluster, charge, binding site and orientation of cluster with respect to ligand [15]. The present work is focused to gain atomic level information on variation of the CHEM enhancement with change in the molecular charge of ligand bound nanoclusters. For this, we used static tensor polarizability components and their numerical derivatives with respect to a normal mode [16–19] and an APT (Atomic Polar Tensor) [20,21] charge (derived from dipole moment of molecule [22]) based descriptor to characterize the chemical Raman enhancement of the SERS spectra. The descriptor quantifies amount of induced APT charge that an atom carries per unit displacement from equilibrium position, in a mode of vibration.

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In this study, we used semiconducting nanoclusters, Zn₃Se₃ and metal substituted Zn₂MSe₃ (M: Ag, Cu) as substrates, deprotonated 4-Mercaptopyridine as ligand. The surface enhanced Raman spectra of the ligand bound to the substrate, in ground state, is analyzed taking into account ground state chemical interactions between the molecule and the nanoclusters. Earlier studies report SERS spectra of the systems using various theoretical and experimental methods. Time dependent density functional theory (TD-DFT) [23] based studies of Birke et al., on Raman spectra of 4-Mercaptopyridine (4MPy) on various ZnSe nanoclusters [24], show that band intensities of Raman spectra depend on surface binding energy of ligand. They report that calculated charge transfer enhancements of strong bands is as high as 10⁴ compared to the experimental SERS spectra. Observations of Islam et al. on SERS spectra of 4MPy adsorbed on ZnSe surface report that contribution of charge transfer transition is strong for enhancement of vibrational Raman intensities and the enhancement is comparable to that of silver nanoparticles [14]. Experimental studies of Islam et al. report that adsorption of 4-Mercaptopyridine on crystalline ZnSe enhances the surface phonon modes of the crystal strongly [25]. Lombardi et al. report the ways to optimize the enhancement factor by modifying the semiconducting nanostructures [26]. A comparison of static and near-resonance Raman spectra for 4-Mercaptopyridine adsorbed on Ag13 cluster shows that relative intensities in near-resonance spectrum are completely different from that of static spectrum [17]. The TD-DFT studies of Li et al. on SERS spectra of pyridine adsorbed on AumAgn (m + n = 6) bimetallic cluster reveal that while static Raman intensities are enhanced by an order of 10, resonance Raman scattering enhances the intensities of spectral lines on the order of 10^3 – 10^5 [27]. Recently, non-plasmonic surface enhanced Raman spectroscopy is studied by chemical enhancement mechanisms by Kim et al. [7].

Importance of semiconducting substrates comes from the fact that they exclude surface plasmonic resonance due to low electron density in conduction band and enhancement of Raman signal comes only from CHEM effects [14]. Also, the molecular properties of semiconducting substrates are modified by doping or substituting metal atoms [28–31]. We considered two metal substituted Zn_2MSe_3 (M: Ag, Cu) clusters for the study. The present work is limited to a small cluster, Zn_3Se_3 and two metal atoms (Ag and Cu).

We report that, change of molecular charge from 0 to -1 increases the binding energy of the ligand to Zn_3Se_3 cluster and slightly decreases energy of the ligand for the metal substituted clusters, Zn_2MSe_3 (M: Ag, Cu). While in neutral state, Zn_3Se_3 is a better substrate for chemical Raman enhancement of the ligand, the metal substituted clusters, Zn_2MSe_3 (M:Ag, Cu) are effective substrates for Raman enhancement in anionic form. Chemical Raman enhancement of vibrational modes in specific cases corresponds to change in polarizability tensor components between equilibrium geometry and geometry distorted along the symmetry coordinates for modes of vibration. Atoms involved in a mode of vibration with higher Raman enhancement factor, show larger magnitudes of the APT charge based descriptor.

2. Theory for static Raman calculations

The study investigates Raman spectra obtained from FREQ calculations of Gaussian09 [32], that uses static dipole approximation [17]. The calculated Raman activities are dipole derivatives with respect to zero electric field [33]. Insights into intensity variations of Raman spectral lines are gained by examining static polarizability tensor. According to Placzek theory of Raman scattering [34], far from any resonance, the static polarizability components with *m* and *n* polarization directions are given by [17]:

$$\alpha^{\rm mn} = 2 \sum_{i,k} \frac{\mu_{0,s_i}^m \mu_{0,s_i}^n}{E_{0,s_i}} \tag{1}$$

Here, μ_{0,s_i} is transition dipole moment between ground (0) and

excited state (s_i) wavefunctions in the Born-Oppenheimer adiabatic form. The summation is over all electronic excited states, (*i*) of molecule-nanocluster complex and all vibrational states *k* of a given electronic state. The E_{0,S_l} is electronic energy gap between ground and excited state.

The Raman intensity is proportional to the square of derivative of the static polarizability [17]. The Raman activity of a vibrational mode is related to derivative of the static polarizability, α^{mn} with respect to normal mode Q_k at the equilibrium geometry [17]. Differentiating Eq. (1) to the first order with respect to nuclear coordinate Q, gives [17]

$$\left(\frac{\partial \alpha^{\rm mn}}{\partial Q_k}\right)_0 = A + B \tag{2}$$

where

$$A = -2\sum_{i}\sum_{k}\frac{\mu_{0,s_{i}}^{m}\mu_{0,s_{i}}^{n}}{E_{0,s_{i}}^{2}} \left(\frac{\partial E_{0,s_{i}}}{\partial Q_{k}}\right)_{0} \langle f|k\rangle\langle k|i\rangle$$
(3)

$$B = 2 \sum_{i} \sum_{k} \frac{1}{E_{0,s_i}} \left[\mu_{0s_i}^m \left(\frac{\partial \mu_{0,s_i}^n}{\partial Q_k} \right)_0 \langle f|k \rangle \langle k|Q_k|i \rangle + \left(\frac{\partial \mu_{0,s_i}^m}{\partial Q_k} \right)_0 \mu_{0,s_i}^n \langle f|Q_k|k \rangle \langle k|i \rangle \right]$$
(4)

Here *i* and *f* are the initial and final vibrational states in the ground electronic state and *k* is an intermediate vibrational excited state for the *k*th normal mode. If energy of exciting light is inadequate for electronic excitation, the term A gives Rayleigh scattering and B gives Raman scattering for both totally symmetric and non-totally symmetric modes in the molecule [17]. The term B consisting of $\mu(\frac{\partial \mu}{\partial Q_k})_0 \langle f|Q_k|i\rangle$ along with electric field components, determine the Raman selection rule. Expansion of electronic wavefunction in the derivative of dipole transition moments according to Herzberg-Teller (HT) formulation [17,18,26,34] gives HT selection rules. These theoretical concepts are used to interpret the chemical Raman enhancement of species investigated in the present study.

3. Computational methods

All systems in the study were investigated in neutral and anionic states to gain insights into effect of charge on targeted molecular and spectral properties. The two different states of each species were represented by (q, s), where 'q' is charge and 's' is spin multiplicity. The clusters, of Zn_3Se_3 (0, 1), Zn_2AgSe_3 (0, 2) and Zn_2CuSe_3 (0, 2) with hexagonal structure were optimized using B3LYP [35] functional of density functional theory (DFT) [36] (See Tables S1(a) to (c) for coordinates). All the atoms except Ag, were modelled using the basis set, 6-31 + G(d) [37] and the basis set, LANL2DZ [38] was used for the atom, Ag. The ligand, deprotonated 4-Mercaptopyridine (-SPyr) is optimized at B3LYP/6-31 + G(d) level of theory in both neutral as well as anionic states.

Preferential site of the clusters for adsorption of the ligand (neutral state) was identified by single point energy calculations carried out at B3LYP/6-31+G(d) level of theory, on various configurations/conformations generated in the following way. Two configurations of the complex geometry, Zn₃Se₃:SPyr (0, 2), which differ in site of adsorption of the ligand on the cluster, i.e., either Zn or Se of the cluster were selected for the calculation (See Table S2(a)). Similarly, for metal substituted clusters, Zn₂MSe₃ (where M: Cu, Ag), three ligand binding sites, i.e., Zn, Se and the metal atom (Ag or Cu) were considered. The orientation of the ligand was fixed by bond angle, $\theta (\angle S$ of ligand-a1-Se, where a1 = Zn/Ag/Cu) and dihedral angle, $\delta (\angle \text{ ligand S-a1-Se-Zn}$ where a1 = Zn/Ag/Cu). For each angle of θ , (combinations: 70°, 100°, 130°; 90°, 120°, 150°; 60°, 90°, 120°), different values for the angle δ (\pm 90°, \pm 120°, \pm 150° and \pm 180°) were chosen (See Tables S2(b)

and (c)). Minimum energy structures were identified from relative electronic energy calculations. The stable geometries were subjected to optimization and Hessian calculations at B3LYP/6-31 + G(d) (LANL2DZ was used for Ag atom) level of theory. Two different charge states of Zn₃Se₃:SPyr; Zn₂AgSe₃:SPyr; and Zn₂CuSe₃:SPyr considered for the calculations were (0, 2), (-1, 1); (0, 1) (-1, 2); and (0, 1) (-1, 2) respectively (See Tables S3(a)–(f) for coordinates). All real frequencies obtained from Hessian calculations confirm that the energies of geometries were minima on their respective potential energy surface.

The binding energy (E_{bind}) of the cluster to ligand is calculated using the equation:

$$E_{\text{bind}} = E_z(\text{complex}) - (E_z(\text{cluster}) + E_z(\text{ligand}))$$
(5)

where E_z (complex), E_z (cluster), E_z (ligand) are zero point corrected electronic energies of the species. The binding energy calculations of complex geometries with zero charge were with respect to zero charge state of both the cluster as well as ligand and the calculations for -1 charge state of complex geometries were carried out with reference to cluster of charge zero and ligand of charge, -1.

The binding energy trends were explained by quantifying the intermolecular interactions between the ligand and the cluster. The natural bonding orbital (NBO) [39] method analyzes wavefunction of one centered lone pair electrons and two centered bond pair electrons in terms of localized Lewis orbitals and that of remaining electrons as delocalized non-Lewis orbitals [40]. The stabilization energy, $E^{(2)}$ of the interactions, due to transfer of electron density from the filled nonbonding electronic orbitals to unfilled anti-bonding orbitals is estimated by:

$$E^{(2)} = -2 \frac{\langle \sigma_i | F | \sigma^*_j \rangle}{E^*_j - E_i}$$
(6)

Where σ_i is occupancy of filled donor bonding orbital, σ_j^* is the occupancy of the unfilled acceptor anti-bonding orbital and F is effective orbital Hamiltonian, E^*_j is energy of unfilled acceptor anti-binding orbital, E_i is the energy of filled donor bonding orbital.

Vibrational Raman spectra of the ligand and complex geometries were analyzed by relating the observed Raman activity, enhancement factor and depolarization ratio of the modes, and total molecular polarizability of the systems.

Raman signal enhancement by CHEM effect was measured using enhancement factor (EF) of vibrational modes, calculated using the following equation,

$$EF = \frac{I_{Cluster-L}}{I_L}$$
(7)

Where $I_{Cluster-L}$ and I_L are the Raman intensities of a given mode in a ligand bound cluster and that of same mode in the isolated ligand. Here, for neutral complex geometries, the ligand was - SPyr of charge zero, and for anionic complex geometry the ligand was - SPyr⁻ (charge = -1).

The trends with Raman intensities were analyzed using the data on change in static polarizability components with normal coordinates of a mode (Eq. (2)) [41]. The change was estimated from difference between polarizability tensor components of equilibrium geometry and the corresponding tensor components of geometry, distorted along symmetry coordinates for a mode of vibration as described in previous study [42]. In the current work, atomic positions were displaced by 0.2 Å and bond angles were changed by 10°, along normal coordinates of the vibrational modes. At far from resonance conditions, the magnitudes of $\frac{\partial \alpha^{min}}{\partial Q}$ are numerically related to term B of Eq. (2), which determines the Raman or HT selection rules [17]. Also, complex systems that show higher Raman enhancement factors were verified using the magnitudes of change in static molecular polarizability tensor components ($\delta \alpha$) obtained from the following equation.

Here m and n refers to polarization directions.

The depolarization ratio (ρ) of a modes, as obtained from FREQ calculations of Gaussian09 [32], is the ratio between perpendicular and parallel components of Raman scatted intensities and it was further used to characterize vibrational modes. A vibrational mode is totally symmetric, if $\rho < 0.75$ and non-totally symmetric modes, if $\rho = 0.75$ [43]. Generally, totally symmetric modes of vibrations (maintain full symmetry of the molecule) appear with high intensity in Raman spectra as wavefunctions corresponding to ground and excited vibrational states overlap significantly. Non-totally symmetric modes (removes certain symmetry elements) show vanishing spectral intensity as ground and excited vibrational wavefunctions differ with respect to symmetry species, resulting in reduced overlap [43,44]. But, finite spectral intensities for non-totally symmetric modes of vibrations comes from intermolecular or intramolecular coupling [43,44].

Molecular polarizabilities responsible for Raman activity of vibrational modes can be partitioned into atomic contributions [45]. Spatial partitioning of molecular polarizabilities is carried out using multipolemoments and their changes under the influence of external fields [45]. We obtained the atomic contributions to the polarizability, from the change in atomic charge (dipole moment derived) distribution over the ligand atoms, that comes as a result of ligand binding to the nanocluster. The APT charge, q_i of an atom, i in a molecule is atomic dipole moment derived as given below [20]

$$q_{i} = \frac{1}{3} \left(\frac{\partial \mu_{x}}{\partial x_{i}} + \frac{\partial \mu_{y}}{\partial y_{i}} + \frac{\partial \mu_{z}}{\partial z_{i}} \right)$$
(9)

Here, μ_x , μ_y and μ_z are *x*, *y* and *z* components of dipole moment of the molecule and x_i , y_i and z_i are coordinates *i*th atom.

Substrate induced atomic dipole moment derived charge carried by an atom of the ligand per unit displacement of a normal mode (Δq_{ir}) described below was used to interpret the observed trends with polarizability components and surface Raman enhancement profiles. For an atom *i*, vibrating in a direction *r* (*x*, *y*, *z*), the descriptor, Δq_{ir} , is the ratio between charge induced on ligand atom, *i*, by the substrate and spatial extent of vibrating atom, dr (= $|r_{i0} - r_i|$), in a direction, about its equilibrium position. It is given by

$$\Delta q_{\rm ir} = \left| \frac{q_{\rm ic} - q_{\rm il}}{r_{\rm i0} - r_{\rm i}} \right|$$
(10)

Where q_{ic} and q_{il} are the charges of an atom *i* in ligand bound to nanocluster and isolated ligand respectively. We refer the APT charge based descriptor as substrate induced charge concentration of atoms over normal modes. It identifies the atomic sites where charge polarization is high.

All the calculations were carried out using Gaussian09 [32] quantum chemical calculations program.

4. Results and discussion

First, the binding energies of clusters bound to the ligands are analyzed. Next, analysis on ground state molecular interactions between ligand and cluster is provided to support the trends with binding energy of the systems. Subsequently, Raman spectra of vibrational modes were analyzed using Raman activities, enhancement factors, changes in molecular polarizability components with normal modes, total change in the polarizability components on complexing the ligand with the nanocluster and depolarization ratio of modes. Finally substrate induced charge concentration with respect to normal coordinates of the vibrational modes is interpreted to validate the observed profiles of surface enhanced Raman spectra.

4.1. Binding energies of complex geometries

$$\delta \alpha = \alpha_{\text{complex}}^{\text{mn}} - (\alpha_{\text{cluster}}^{\text{mn}} + \alpha_{\text{ligand}}^{\text{mn}})$$

While the cluster, Zn₃Se₃ shows C_{3h} symmetry, the Zn₂MSe₃ (M: Ag,

(8)



Fig. 1. Optimized geometries of clusters: Zn₃Se₃, Zn₂AgSe₃ and Zn₂CuSe₃; ligand bound cluster with zero charge: Zn₃Se₃:SPyr, Zn2AgSe3:SPyr, Zn2CuSe3:SPyr and ligand bound clusters with charge -1: Zn₃Se₃:SPyr⁻, Zn₂AgSe₃:SPyr⁻, Zn₂CuSe₃:SPyr⁻. Charge and spin multiplicity values of each geometry are shown in parenthesis. The binding energy (*E*_{bind}) are given in kcal/mol. Every atom, X, in a geometry is assigned a number, n, and denoted as Xn, in the discussion. The distance between the S-atom of the ligand and cluster atoms bonded directly to the S-atom of the ligand is given in Å. Note: Coordinates of cluster geometries, Zn₃Se₃, Zn₂AgSe₃ and Zn₂CuSe₃ are shown in Table S1. Structure and relative electronic energetic data for various conformations of Zn₃Se₃:SPyr (0,2),Zn₂AgSe₃:SPyr (0,1) and Zn₂CuSe₃:SPyr (0,1) are shown in Table S2. Coordinates for optimized geometries of Zn₃Se₃:SPyr (0,2), Zn₂AgSe₃:SPyr (0,1), Zn₂CuSe₃:SPyr (0,1), Zn₃Se₃:SPyr⁻(-1,1), Zn₂AgSe₃:SPyr⁻ (-1,2)and Zn₂CuSe₃:SPyr⁻ (-1,2) are shown in Table **S**3

Cu) clusters exhibit $C_{2\nu}$ symmetry (See Fig. S1 for structural details). The modelled structures are on par with the results of the previous reports by Xu et al. [31]. Single point energy calculations on various conformations of complex geometries show that the Zn atom of the Zn₃Se₃ and metal atom of the Zn₂AgSe₃ and Zn₂CuSe₃ are the preferential sites for bonding of the ligand in zero charge state (See Tables S2(a) and (b)).

Coordinates of fully optimized complex geometries and their absolute energies are shown in Tables S3 and S4 respectively. The ligand adsorbed clusters of both neutral and anionic forms are shown in Fig. 1. While ligand forms single bond (-S-Zn-) with the Zn₃Se₃, metal substituted clusters show bridge type bond with ligand such that S-end of the ligand is bonded to both the metal atom and Se of the cluster (See Fig. 1). Binding energy (E_{bind}) varies significantly with charge of the complex geometry, Zn₃Se₃:SPyr. E_{bind} of the complex geometry with charges, 0 and -1 is -24.9 and -53.4 kcal/mol respectively. On the other hand, the complex geometries with metal substituted cluster show minimal decrease in binding energy with change in charge from 0 to -1. The E_{bind} for Zn₂AgSe₃:SPyr (Zn₂CuSe₃:SPyr) and Zn₂AgSe₃:SPyr⁻ (Zn₂CuSe₃:SPyr⁻) is -37.5 (-48.7) and -37.3 kcal/mol (-45.6 kcal/mol) respectively.

The data on distance between the sulphur atom of the ligand and cluster atoms bonded directly to it, agree with changes in binding energy trends of the complex geometries. The decrease in Zn4-S distance

from 2.37 to 2.31 Å with change of charge from zero to anionic state of Zn_3Se_3 :SPyr and increase of Se5-S distance in both the metal substituted complex geometries with change of charge from neutral to anionic state (See Fig. 1) are on par with the binding energy trends. Even though, increase of the bond distance Se5-S is noteworthy, the decrease of the binding energies of Zn_2MSe_3 :SPyr (M: Ag, Cu) with change of charge is minimal. This may be due to continuation of metal-sulphur bond. Further discussion on NBO analysis of stabilizing interactions substantiates the energetic trends.

4.2. NBO analysis of charge transfer interactions

Table S5 shows ground state charge transfer interactions between cluster and ligand, with significant stabilization energy. All the interactions transfer charge from sulphur atom of the ligand to the cluster. Magnitudes of interaction energies, $n_S \rightarrow n^*_{Zn4}$ and $n_S \rightarrow \sigma^*_{Zn4-Se4}$ in Zn₃Se₃:SPyr are 63.9 and 2.2 kcal/mol respectively and 143.8 and 5.9 kcal/mol respectively in its anionic counterpart. It supports the higher binding energy of anionic complex compared to the neutral geometry. In case of Ag substituted complex geometries, the neutral state is associated with interactions, $n_S \rightarrow n^*_{Ag6}$ (E² = 19.3 kcal/mol) and $n_S \rightarrow \sigma^*_{Se1-Ag6}$ (E² = 23.1 kcal/mol). The E² of interaction, $n_S \rightarrow n^*_{Ag6}$, in the corresponding charged species is 33.9 kcal/mol. Similarly, the uncharged, Zn₂CuSe₃:SPyr, shows the interactions, $n_S \rightarrow n^*_{Cu6}$ and

 $n_S \rightarrow \sigma^*_{Se1-Cu6}$ of energy, 25.6 and 38.5 kcal/mol respectively and its charged state shows only the former interaction with energy 53.5 kcal/mol. The data justify the binding energy trends of neutral and anionic metal substituted complex geometries.

4.3. Chemical Raman enhancement of vibrational modes

Earlier studies on normal Raman and surface enhanced Raman spectra of 4MPy bound to CdS clusters report that intense bands of the ligand are found at 1023, 1117 and 1594 cm⁻¹ [24]. The wavenumbers also appeared with high intensity when the ligand is bound to ZnS, CdTe and ZnO clusters [24]. The first two wavenumbers, 1023 and 1117 cm⁻¹ are ring breathing modes of pyridine and the third, 1594 cm⁻¹ is wavenumber of symmetric C-H wagging mode of vibration.

We considered above mentioned three modes of vibrations for the analysis. Magnitudes for wavenumbers and Raman activities of the three modes in all the species are shown in Table S6. The ring breathing mode of vibration, involving the ligand ring atoms, N1, C2 and C5 is denoted as ν_1 , the other ring breathing mode coming from vibrations of C1, C3 and C4 is represented as ν_2 and C-H wagging mode that involves the atoms C2, C3, C4, C5, H2, H3, H4 and H5 is indicated as ν_3 (See Fig. 1). The Raman activity, depolarization ratios and Raman enhancement factor for the modes are shown in Fig. 2. The complete Raman and SERS spectra of ligand and the complex geometries are shown in Figs. S2 and S3. Total change in components of polarizability and magnitudes of change in polarizability components with change in normal coordinates of the three modes of vibrations are shown in Table 1. Absolute values of the polarizabilities are shown in Tables S7 and S8. A schematic representation for the geometries in equilibrium and the states distorted along the normal coordinates of the modes ν_1 , ν_2 and ν_3 are shown in Fig. 3.

Wavenumbers and Raman activities of the modes, ν_1 , ν_2 and ν_3 of the neutral (anionic) ligand are 1002 (994.0), 1115.3 (1120.9), 1615.8 (1614.6) cm⁻¹ and 43.4 (59.3), 44.2 (9.0) and 40.2 (70.2) Å⁴/amu respectively. The related data of complex geometries are shown in Table S6. Chemical Raman enhancement of these modes is discussed below.

Zn₃**Se**₃**:SPyr**: The enhancement factor for the modes ν_1 , ν_2 and ν_3 in neutral state is 13.4, 50.6 and 108.0 respectively and in anionic state, the magnitudes are 1.5 for ν_1 , 5.9 for ν_2 and 1.1 for ν_3 . Support for the significant enhancement of Raman spectral lines in neutral state, comes from larger change in total polarizability components, $\delta \alpha^{xx}$ and $\delta \alpha^{yy}$. While for neutral state, the change of *xx* and *yy* components of total polarizability is 484.4 and 36.1 Bohr³ respectively, for anionic state, $\delta \alpha^{xx} = 67.6 \text{ Bohr}^3$ and $\delta \alpha^{yy} = -11.6 \text{ Bohr}^3$ (See Table 1). Raman activity of the modes is related to the first derivative of the change in polarizability components with respect to the normal coordinates of the modes. Larger enhancement of the mode ν_1 in neutral geometry compared to that in anionic state. Similarly, significant enhancement of other two modes, ν_2 and ν_3 , in neutral state originates from greater magnitudes of $\frac{\partial \alpha^{xy}}{\partial Q}$ (77.1 Bohr³/a.u. for ν_2 and 77.7 Bohr³/a.u. for ν_3) compared to that in anionic form of the geometry.

The mode ν_1 of neutral geometry is enhanced with EF = 13.4, even though the depolarization ratio is 0.75. Ground state molecular interactions might be responsible for increased intensity of Raman spectral line.

Zn₂**AgSe**₃**:SPyr**: Substitution of metal atom Ag, in the cluster, altered the trends of Raman enhancement for modes as observed with Zn₃Se₃:SPyr. The anionic state of the metal substituted complex geometry showed significant Raman enhancement for the modes compared to that of the neutral geometry. While EFs for ν_1 , ν_2 and ν_3 of neutral geometry are 0.8, 0.9 and 0.6 respectively, the magnitudes in anionic state are 2.3 for ν_1 , 47.1 for ν_2 and 4.8 for ν_3 . Greater change in total

polarizability components of anionic state compared to neutral state supports enhanced Raman activity of the modes in anionic state (Table 1). Also, for all the three modes, the $\frac{\partial \alpha^{xx}}{\partial Q}$ and $\frac{\partial \alpha^{zx}}{\partial Q}$ components of anionic state are greater than that in neutral state. This substantiates the observed Raman activity trends for the three modes in both the geometries. The depolarization data of the modes shown in Fig. 2 indicate that the modes are totally symmetric in all the cases.

Zn₂**CuSe**₃**:SPyr**: The anionic state show larger Raman activity for the modes compared to the neutral geometry. The EFs for modes ν_1 , ν_2 and ν_3 for anionic state are 2.2, 33.8 and 4.3 respectively and for neutral state are 0.7, 0.9 and 0.8 respectively. The following data on molecular polarizability support the observed Raman spectral intensities: The *yy* and *zz* components of change in total polarizability is larger in anion state compared to that of neutral state. The first derivative components, $\frac{\partial \alpha^{XX}}{\partial Q}$ and $\frac{\partial \alpha^{YY}}{\partial Q}$ of anionic state are relatively greater than that of neutral state.

Observation of the complete spectra of all the species (Figs. S2 and S3) reveals that they show Raman activity trends similar to those observed with the three modes. Overall, in neutral state, the cluster Zn_3Se_3 and in charged state, the metal substituted clusters are better substrates for Raman enhancement of the modes.

4.4. Substrate induced charge concentration over normal modes

The dipole moment is a property that can be calculated from atomic and bond contributions, and serves for partitioning of molecular properties into atomic contributions [21]. The Atomic Polar Tensor (APT) of an atom i, defined as first derivative of dipole moment of molecule with respect to Cartesian coordinates of the atom, *i*, gives the molecular charge partitioned on the atom and is called as APT charge, q_i (Eq. (9)) [21]. The present study measures change in APT charge of the ligand atom as a result of binding to the cluster and divides the resultant value with normal coordinate atoms (Cartesian displacement vectors of atoms) involved in a mode of vibration. This is numerically equal to substrate induced charge concentrated per unit displacement of the atom in a mode of vibration. We called the resultant as substrate induced charge of an atom over a normal mode, Δq_{ir} (*r*: *x*, *y*, *z*). Atoms that show larger magnitudes of Δq_{ir} are the sites for greater charge polarization during a vibrational mode and contribute significantly for chemical Raman enhancement.

Tables S9 and S10 show magnitudes of APT charges of atoms in all the species and Figs. S4–S6 show the charge profiles. Cartesian displacement vectors of atoms in all vibrational modes are given in Tables S11–S13. Magnitudes of Δq_{ir} of atoms in the three modes of the species are shown in Tables S14–S16. Cartesian displacement vectors greater than 0.01 are considered for the calculation of Δq_{ir} . The following discussion validates the proposed property of the descriptor.

Observation of APT charge profiles of ligand atoms in isolated ligand geometry and complex geometries (See Figs. S4–S6) reveals that most of the atomic charges in all the species of molecular charge -1 are greater in magnitude than that in the neutral state. Change of atomic charges for ligand atoms of neutral (anionic) complex geometry is calculated with respect to atoms in ligand with molecular charge 0 (-1). A few ligand atoms of Zn₃Se₃:SPyr (0,2) show change in sign of atomic charge compared to that of related atoms in isolated ligand. While atom, C1 changed to negative from positive charge, the atoms S1 and C2, became positive in charge. In all other cases, charge of ligand atoms decreases with no change in sign of the charge (See Figs. S4–S6). The descriptor, Δq_{ir} , locates the atomic sites where change in the atomic charge during vibrational motion is significant. We are interested in finding such atomic regions of vibrational modes to understand trends with observed surface enhanced Raman activity.

Mode ν_1 : Following are the atoms involved in the ring breathing mode, ν_1 mode of all the complex geometries: N1, C2, H2, C5, and H5 (See Figs. 1 and 3).



Fig. 2. Schematic representation of various modes of ligand (Row 1). Here, ν_1 : Symmetric ring breathing by the atoms N1, C2 and C5, ν_2 : Symmetric ring breathing by the atoms, C1, C3 and C4 and ν_3 : Symmetric C-H wagging by the atoms, C2, C3, C4, C5, H2, H3, H4 and H5. Raman activities of the modes in -SPyr, -SPyr^{-(Row 2)}, complex geometries, Zn₃Se₃:SPyr, Zn₃Se₃:SPyr^{-(Row 3)}, Zn₂MSe₃:SPyr, Zn₂MSe₃:SPyr⁻ (M: Ag, Cu) (Row 4 and 5). Raman Activity is in Å⁴/amu, EF: enhancement factor, ρ : depolarization ratio.

Magnitude of Δq_{ix} for C2 of Zn₃Se₃:Spyr is significantly larger than that of its charged counterpart (See Fig. 4). Both x and y-components of the descriptors for all other atoms are comparable between the uncharged and charged systems of Zn₃Se₃:Spyr. We infer from the measurements that atom C2 is responsible for observed enhancement factor of the mode, ν_1 of Zn₃Se₃:Spyr.

Both the metal substituted clusters show enhanced Raman activity in charged state. The profiles of Δq_{ir} agree with the result. Relatively higher magnitudes for Δq_{iy} of N1, Δq_{iz} of C2 and Δq_{ix} of H5, belonging to charged Zn₂AgSe₃:Spyr substantiate the observed enhanced Raman activity with EF = 2.3. The Δq_{iy} component of N1 for charged Zn₂CuSe₃:Spyr is superior to that in uncharged Zn₂CuSe₃:Spyr. The descriptor for other atoms is comparable in both uncharged and charged states of the Cu substituted complex geometry. We attribute the EF = 2.2 of the mode in Zn₂CuSe₃:Spyr⁻ to N1.

Mode ν_2 : The Δq_{ir} profiles for the mode is shown in Fig. S7. The atom C4 of Zn₃Se₃:SPyr; atoms C1, C4, C3 and H3 of Zn₂AgSe₃:SPyr⁻; and atoms C1, C4, H4 and C3 of Zn₂CuSe₃:SPyr⁻ show larger magnitudes of Δq_{ir} compared other atoms in their respective counterparts, for the mode ν_2 (See Fig. S7). The measurements agree well with the

Table 1

Change in total polarizability components δa^{mn} (Bohr³) due to adsorption of ligand on nanoclusters and magnitudes for change in polarizability components with normal mode, $\frac{\partial a^{mn}}{\partial Q}$, (Bohr³/a.u.) for modes of vibrations, ν_1 , ν_2 and ν_3 of complexes geometries. Note: Relatively larger magnitudes of components of $(\partial a^{mn}/\partial Q)$, are shown in bold.

Species	$\delta \alpha^{xx}$	$\delta lpha^{yy}$	$\delta \alpha^{zz}$	Mode	$\frac{\partial \alpha^{XX}}{\partial Q}$	$\frac{\partial \alpha^{yy}}{\partial Q}$	$\frac{\partial \alpha^{ZZ}}{\partial Q}$
Zn ₃ Se ₃ :SPyr(0,2)	458.4	36.1	-9.3	$ \nu_1 $ $ \nu_2 $	16.7 77.1	16.0 8.8	2.8 3.9
Zn ₃ Se ₃ :SPyr ⁻ (-1,1)	67.6	-11.6	-5.0	$ \nu_{3} \\ \nu_{1} \\ \nu_{2} \\ \nu_{3} $	24.3 22.5 6.0	2.3 8.4 11.1 1.3	1.2 2.3 3.5 2.5
Zn ₂ AgSe ₃ :SPyr (0,1) Zn ₂ AgSe ₂	-192.5	2.4	51.6		12.6 15.6 5.2 21.5	7.4 9.4 4.8 6.8	8.4 10.6 2.4 10.3
:SPyr ⁻ (-1,2)	-105.0	55.5	03.7	ν_1 ν_2 ν_3	26.5 12.3	7.3 0.7	12.6 3.8
Zn ₂ CuSe ₃ :SPyr (0,1)	23.8	-120.4	42.3	$ \begin{array}{c} \nu_1 \\ \nu_2 \\ \nu_3 \end{array} $	17.5 22.1 6.5	3.2 4.2 0.5	9.0 11.7 1.0
Zn ₂ CuSe ₃ :SPyr (-1,2)	12.5	- 67.3	56.3	$ \begin{array}{l} \nu_1 \\ \nu_2 \\ \nu_3 \end{array} $	22.2 26.8 13.5	6.1 6.9 1.9	9.1 11.0 2.3

Raman activity trends described in the previous section.

Mode ν_3 : The Δq_{ir} profiles for the mode is shown in Fig. S8. The atoms C2 and C4 of Zn₃Se₃:SPyr; C3, H2 and C5 of Zn₂AgSe₃:SPyr⁻; and H3, C2, H5 and C4 of Zn₂CuSe₃:SPyr⁻ show larger magnitudes of Δq_{ir} compared to other atoms in the respective geometric counterparts of the systems. The observed trends infer that relatively higher Raman enhancements of modes in species come from the atomic regions that have larger magnitudes of Δq_{ir} .

We report that the APT charge based descriptor is a tool for description of chemical Raman enhancement of vibrational modes of 4MPy adsorbed on the semiconducting nanoparticles.



Raman Intensity $\alpha \frac{\partial \alpha}{\partial Q}$ $\frac{\partial \alpha}{\partial Q}$ = Difference between polarizability of equilibrium (EQ) and distorted (D) geometries for a mode of vibration

 $\alpha \rightarrow$ Charge distribution

APT Charge

$$q_i = \frac{1}{3} \left(\frac{\partial \mu_x}{\partial x_i} + \frac{\partial \mu_y}{\partial y_i} + \frac{\partial \mu_z}{\partial z_i} \right)$$

$$\Delta q_i = \frac{q_{ic} - q_{il}}{r_{i0} - r_i}$$

5. Conclusions

We performed B3LYP/6-31 + G(d) (LANL2DZ for Ag atom) level of density functional theory based calculations on neutral and anionic forms of deprotonated 4-Mercaptopyridine (-SPyr) bound to Zn_3Se_3 , Zn_2AgSe_3 , Zn_2CuSe_3 nanoclusters. Changes in binding energy and Raman spectral properties with variation of molecular charge of the system Zn_3Se_3 :SPyr are different from that of Zn_2MSe_3 :SPyr (M: Ag, Cu).

While change of molecular charge from 0 to -1 increases the binding energy of the system, Zn_3Se_3 :SPyr from -24.9 to -53.4 kcal/mol, the energy is nearly same for both neutral and anionic forms of Zn_2AgSe_3 :SPyr (-37.5 kcal/mol). The energy decreases slightly for Zn_2CuSe_3 :SPyr from -48.7 to -45.6 kcal/mol on change of the state from neutral to anionic form. The increase in binding energy on varying the molecular charge is reflected as short bond length between ligand atom, sulphur, and a cluster atom involved in bonding. The NBO analysis of ground state charge transfer interactions between lone pair sulphur atom of the ligand to the various delocalized non-Lewis orbitals of the cluster substantiate the observed binding energy variations. Increase in magnitudes of these interactions, in Zn_3Se_3 :SPyr with change of charge from 0 to -1 is greater than that observed in metal substituted clusters. Systems of larger binding energy show greater flow of charge from the ligand atom to the nanocluster.

The study focuses on two different ring breathing modes (named, ν_1 and ν_2) and one symmetric C-H wagging mode (ν_3) for Raman activity. Except in neutral state of Zn₃Se₃:SPyr the modes with depolarization ratio less than 0.75, show Raman enhancement with enhancement factor greater than 1. The ligand bound to the Zn₃Se₃ with overall charge 0 shows greater Raman enhancement of the modes compared to its anionic counterpart. On the other hand, the ligand bound to the metal substituted clusters in anionic form show relatively high surface Raman enhancement of the modes compared to their corresponding neutral states. We attributed the observed trends with Raman enhancement profiles to change in total molecular polarizability components of systems and change of polarizability components with normal coordinates of modes of the vibrations. While variation of the molecular polarizability, for metal substituted complexes the magnitudes increase

Fig. 3. Left: A schematic representation for the ligand geometries in equilibrium and the states distorted along the normal coordinates of the modes ν_1 , ν_2 and ν_3 , used to calculate the change in molecular polarizability with respect to normal coordinate of the vibrational modes. Note: All the geometries are bound to the semiconducting nanoclusters as shown in Fig. 1. The cluster geometries are not shown. Right: Relation between the Raman intensity of a mode and the APT charge based descriptor is shown. Here, *a* is polarizability, Q: Normal coordinate of mode of vibration, μ_m : *m*th component of dipole moment, q_{ic} : APT charge of atom *i* of ligand adsorbed on a cluster, q_{il} : APT charge of atom *i* of isolated ligand, $r_{i0} - r_i$: Spatial extent of vibrating atom in a mode.



with change of molecular charge from 0 to -1. Raman enhancement of the modes is high in complexes associated with greater values of $\frac{\partial \alpha}{\partial \Omega}$.

APT charge based descriptor identified the atomic sites of ligand where substrate induced charge concentration over a normal mode is high. Comparison of magnitudes of the descriptor between charged and uncharged complex geometries lead to the conclusion that modes with greater chemical Raman enhancement are associated with atomic sites for which the descriptor value is relatively high.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.vibspec.2020.103019.

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Fig. 4. Substrate induced charge concentration on atoms of ligand, over normal mode, ν_1 in neutral and anionic complex geometries of Zn₃Se₃:SPyr and Zn₂MSe₃:SPyr (M: Ag, Cu), calculated using APT atomic charges. Charges on neutral (anionic ligand) geometry are reference for calculation of induced charge on ligand atoms neutral (anionic) complex geometry. The charge concentration, Δq_{ir} is in Coulomb/unit displacement of normal coordinate.

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