ABSTRACT: Several key issues concerning surface-enhanced Raman scattering (SERS) are discussed, especially the surface orientation of the adsorbate, the enhancement mechanism relevant in a particular experiment, and the dependence of SERS frequencies and intensities on the electrode potential. It is shown that ab initio calculations of energies, geometries, and vibrational frequencies are essential in order to understand the complex behavior displayed by SERS spectra, particularly calculations dealing with radical anions of adsorbates. The main conclusion is the confirmation of the presence of resonant charge transfer processes in SERS of aromatic molecules. Such resonant mechanism involves the transient formation of the radical anion of adsorbates such as pyrazine, pyridine, and derivatives.

Key words: Raman; SERS; nanoparticles; charge transfer; doublet states

Introduction

Surface-enhanced Raman scattering (SERS) consists of the enormous enhancement of the Raman signal of a molecule when it is adsorbed on surface nanostructures of some selected metals, especially silver [1, 2]. This complex as well as wonderful phenomenon allows us to detect, under favorable circumstances, the Raman photons emitted by a single molecule, what requires an enhancement factor of \(10^{14}\) [3, 4]. However, 30 years after the discovery of SERS [5–7], the origin of the enhancement is still not well understood.

One of its most important features is the noticeable dependence of both the overall and the relative enhancements of the bands under specific experimental conditions. Two different mechanisms, i.e., electromagnetic (EM) [1, 2, 8] and charge-transfer (CT) mechanisms [1, 2, 9–11], have been proposed to account for the experimental behavior. Both mechanisms produce selection rules that are able, in principle, to explain the observed selective enhancement independently, but there is not yet a
simple way to know their relative contributions in a particular experiment. For this reason, the type of information that can be deduced when analyzing a SERS spectrum is not at all clear, either the relative orientation of the adsorbate with respect to the metal surface (EM) [2, 8] or some properties of the electronic states that are involved in a resonant charge-transfer process (CT) [2, 11, 12].

The challenge is to know which mechanism(s) take part in SERS. The aim of the present work is to show the usefulness of ab initio estimations of energies, geometries, and vibrational frequencies to explain the complex behavior observed in SERS of aromatic adsorbates. In this respect, one objective is to establish the lowest level of theory sufficient to account for the experimental results. The theoretical backgrounds and experimental details can be found in the original papers in which the principal role of the CT mechanism in SERS of pyridine, pyrazine, and their analogues has been demonstrated [11–23].

Surface Orientation: Vibrational Shifts Versus EM Selection Rules

EM SELECTION RULES

The EM enhancement mechanism is based on the resonant response of the metal. The laser photons excite the surface plasmons that amplify and concentrate the EM field on the interphase [1, 2]. The existence of adsorption is the basic hypothesis of the so-called EM propensity rules, which predict the selective enhancement of those normal modes vibrating in a direction perpendicular to the surface [8]. In planar molecules, the relative enhancement of out-of-plane modes should indicate a parallel orientation of the adsorbate with respect to the metal, while a perpendicular orientation should be deduced when in-plane modes show stronger enhancement.

These simple EM selection rules have been widely used to derive surface orientation of the adsorbate from the differences observed between the relative intensities of the Raman and the SERS spectra. However, simultaneous enhancements of in-plane and out-of-plane modes are observed in many SERS. This is the case of the spectra of pyrazine (Pz) (1,4-azobenzene) shown in Figure 1, where the Raman spectrum of the aqueous solution can be compared with its SERS records on silver at electrode potentials ranging between 0.0 and −0.75 V vs. saturated Ag/AgCl/KCl [12, 13, 22]. The Raman is dominated by the strong band assigned to mode 1, but the totally symmetric $A_g$ in-plane modes 6a, 1, 9a, and especially 8a, are strongly enhanced in all SERS records. Besides the large

FIGURE 1. Raman spectrum of an aqueous solution of pyrazine (Pz) and its SERS spectra recorded on silver at several electrode potentials vs. the saturated Ag/AgCl/KCl reference electrode (514.5-nm excitation). SERS-CT calculated intensities from the CASSCF/6-31G* geometries of Pz in the $S_0$ and $D_0$ levels, and SERS recorded on silver by Huang et al. [31].
intensity of these $A_g$ vibrations, several out-of-plane fundamentals are observed, especially the $16a$ and $16b$ Raman forbidden fundamentals of $A_u$ and $B_{3u}$ symmetry, respectively, which means the breakdown of the mutual exclusion principle. The SERS intensities of these vibrations reach their maxima at $-0.50 \text{ V}$, except the band recorded at $-355 \text{ cm}^{-1}$ corresponding to the $16a;\tau_{\text{ring}} A_u$ fundamental, which is not observed at more positive potentials. On the basis of the above-mentioned EM propensity rules, the simultaneous enhancement of in-plane and out-of-plane vibrations could be interpreted by supposing either a tilted orientation or the presence of molecules with both perpendicular and parallel orientations. Nevertheless, these conclusions have to be discarded, given that the SERS frequencies are only compatible with a perpendicular orientation [23], as we shall show later.

FREQUENCY SHIFTS ORIGINATED BY SOLVATION AND PROTONATION

The vibrational frequency shifts of azines (azo-benzenes) have been used in SERS to deduce how the molecule interacts with the metal [24, 25] by comparing them with the shifts originated by protonation or dilution in water [26, 27]. Aromatic heterocycles, such as Pz and pyridine (Py), can interact with the solvent or the protons or hydrogen ions through the unshared electron pairs of the nitrogen atoms or through the $\pi$-system. In the latter case, the aromatic ring should be weakened because of the bonding nature of the $\pi$-electrons and therefore, the ring stretching vibrations should be red-shifted, as observed in benzene and toluene [25]. In contrast, the aromatic ring is strengthened if the interaction takes place through the heteroatom because of the nonbonding nature of the unshared electron pairs, and therefore causing an increase in the frequencies of the ring stretching fundamentals. The latter type of shift is expected in aqueous solutions because of the hydrogen bonding between the heteroatoms and the molecules of the solvent, and an even stronger effect should be observed in acid aqueous solutions, given that the bonding with the hydrogen ions is, in turn, stronger [27].

The effect of protonation and dilution in water on the vibrational frequencies of Pz has been studied with the help of ab initio RHF/3-21G calculations [26]. The Raman frequencies of pure Pz are blue-shifted in the spectrum of the aqueous solution, especially the $6a$ or $8a$ ring modes, which are shifted by $+20 \text{ cm}^{-1}$. The observed shifts correspond quite well with the calculated ones for Pz, either isolated or coordinated to two molecules of water through both nitrogen atoms (H$_2$O–N), (b) hydrogen ion (H$^+$–N), (c) an Ag$^+$ atom through a nitrogen (Ag$^+$–N), or (d) through the $\pi$-system (Ag$^+$–$\phi$).

FIGURE 2. Correlation between the observed frequency shifts of pyrazine (Pz) caused by dilution on water or in acid aqueous solution and by the adsorption on silver, and the calculated shifts between isolated Pz and coordinated with (a) two water molecules (H$_2$O–N), (b) hydrogen ion (H$^+$–N), (c) an Ag$^+$ atom through a nitrogen (Ag$^+$–N), or (d) through the $\pi$-system (Ag$^+$–$\phi$).
A majority species, even at high HCl concentrations. Moreover, the C₂ᵥ symmetry of that species allows all the fundamentals to be Raman active and can explain why “u” modes, such as 19b, 14, 18a, and 12, are observed.

**FREQUENCY SHIFTS CAUSED BY ADSORPTION ON SILVER**

The differences between the Raman and SERS frequencies have been used to propose surface orientations of the adsorbate independent of the enhancement mechanism [24, 25]. The adsorption of Pz on the metal through the π-system (Ag–Φ) or through the lone electrons of the heteroatom (Ag–N) leads to parallel or perpendicular surface orientations, respectively. The frequencies of the SERS recorded at 0.00 V are comparable to those of the aqueous solution, indicating that it is coordinated in a similar way in both cases, giving an orientation that is approximately perpendicular to the metal. Figure 2(c) demonstrates the good correlation between the frequency shifts observed in the SERS at 0.0 V with respect to the pure liquid Raman and the RHF/3-21G calculated ones from the isolated species and its complex with Ag⁺ (Ag⁺–N) [23]. As can be seen in Figure 2(d), the calculated results for the Ag⁺–Φ complex do not correlate at all with the experimental shifts, and therefore the parallel orientation has to be discarded.

Moreover, the dependence of the vibrational frequencies on the electrode potential confirms the previous conclusion [23]. Figure 3(a) shows the shifts of the SERS frequencies recorded at electrode potentials of 0.0, −0.25, −0.50, and −0.75 V, respectively. It can be seen that almost every fundamental shifts toward the red as the electrode potential becomes more negative, i.e., as the negative surface charge excess increases. The back-donation from the silver to vacant levels in Pz can be responsible for the decrease in the vibrational frequencies. These experimental results have been compared successfully with the ab initio computed frequencies (RHF and B3-LYP calculations with the 3-21G and LanL2DZ basis sets) for several Ag–Pz complexes with different composition, orientation, and charge of the metallic clusters. All the chosen complexes (Ag⁺–Pz, Ag⁺–Pz, Ag⁺–Pz, and Ag⁺–Pz) are closed-shell systems, and the metallic clusters have linear structures oriented along the axis C₂(z).
(Ag–N) or C$_3$(x) (Ag–Φ), modeling perpendicular or parallel surface orientations, respectively. Such complexes permit us to simulate the change in the electrode potential and, therefore, the change in the surface charge excess on the metal.

The surface complex is formed by charge donation from Pz to the metallic cluster, which is controlled by the charge of the silver atom directly bonded to pyrazine (Ag$_1$), i.e., by the electrode potential. The calculated shifts for the complexes Ag$^+$/N, Ag$^+$/N, Ag$_2$/N, and Ag$_3$/N, where the atom Ag$_j$ supports a charge amounting to $+0.83$, $+0.50$, $-0.11$, and $-0.99$, respectively, agree with the experimental results, confirming the perpendicular orientation of Pz [Fig. 3(b)] and discarding the parallel one. The net charges of Pz in the mentioned clusters are 0.172, 0.140, 0.101, and 0.066, respectively.

The results obtained allow us to deduce that all the bands recorded in SERS, in-plane and out-of-plane vibrations, are caused by only one type of molecule adsorbed with an orientation perpendicular to the surface in the whole range of the studied molecule adsorbed with an orientation perpendicular to the surface. The net charges of Pz in the mentioned clusters are 0.172, 0.140, 0.101, and 0.066, respectively.

The results obtained allow us to deduce that all the bands recorded in SERS, in-plane and out-of-plane vibrations, are caused by only one type of molecule adsorbed with an orientation perpendicular to the surface in the whole range of the studied electrode potentials. Consequently, SERS activity of out-of-plane modes 16b$_u$ and 16a$_u$ cannot be explained by an orientation parallel to the surface, as it should be derived on the basis of the propensity rules of the EM mechanism.

### CT Mechanism: Selection Rules

In addition to all the above-described deficiencies, the EM enhancement mechanism is also unable to explain the relative enhancement of the totally symmetric Ag$^+$ vibrations observed in the SERS of Figure 1 or the dependence of the intensities on the electrode potential [2]. As will be shown later, the activities in SERS of these vibrations are caused by the presence of resonant charge transfer (CT) processes between the metal and the adsorbate [12, 13, 22].

### RR-CT MODEL

The CT mechanism of SERS is considered analogous to a resonance Raman (RR) process. In RR, a molecule A is usually photoexcited up to the first excited singlet $S_1$, and the resonance condition is tuned by the energy of the laser photon ($h\nu$). The position of the maximum ($h\nu_{\text{max}}$) in the Raman excitation profiles (REP: Raman intensity vs. photon energy) relates to the energy of the vertical transition between the $S_1$ and $S_0$ states [$E_{\text{vert}}(S_1–S_0) = h\nu_{\text{max}}$] [28]. However, in the CT mechanism (RR-CT), the transient excited state corresponds to a charge transfer state of the metal–adsorbate complex. Such CT transitions are caused by photoinduced charge donation from the metallic nanocluster to the adsorbate or vice versa, and have been detected in very few cases. Given that the available information regarding these CT states is quite scarce, we have assumed a simplified RR-CT mechanism based on the following steps [11]:

1) **Adsorption:** \[ M + A \rightarrow M–A. \]

The molecule from which the SERS is recorded (A) should be directly linked to the metal (M), which is in turn at a particular electric potential, so giving rise to the surface complex M–A.

2) **Photoinduced charge transfer:**

\[ M–A_S0 + h\nu \rightarrow M^+–A^-;CT. \]

If the energy of the photon matches that of the CT transition [$h\nu = E_{\text{CT}} = E_{\text{vert}}(\text{CT–}S_0)$], where CT and $S_0$ are the excited and the ground states of the surface complex, respectively) a resonant CT process occurs. In pyridine and its analogues, the charge is transferred initially from the metal to the adsorbate [29], yielding the formation of the adsorbate anion in the CT excited level $M^+–A^-$ if the donated charge amounts to a complete electron.

3) **Raman emission:**

\[ M^+–A^-;CT \rightarrow M–A^+_S0 + h\nu'. \]

Finally, a Raman photon can be emitted ($h\nu'$) if the adsorbate remains vibrationally excited ($A^+_S$) when the CT state relaxes to the ground level of the complex. Therefore, it can be assumed that the properties of the adsorbate in the ground (M–A) as well as in the CT state (M$^+–A^-$) of the surface complex are similar to those of the neutral species (A$^+_S$0) and its anion A$^-$, respectively, at any electrode potential. Anion A$^-$ is referred to as the D$_0$ level, given that it is a doublet in its electronic ground state.

Given that the properties of the doublets states of neutral adsorbates such as Pz, Py, and derivatives are not yet well characterized at all, we have proposed a methodology for predicting the SERS rela-
tive intensities under RR-CT conditions (SERS-CT) by using ab initio calculations.

**GEOMETRIES OF THE S₀ AND D₀ STATES**

The previous RR-CT model is strongly supported by the correlation between the relative intensities observed in SERS with the differences between the electronic properties of the neutral molecules (A;S₀) and their radical anions (A⁻;D₀), especially the respective equilibrium geometries [11–22]. According to the A term in RR [28], those vibrations connecting the equilibrium geometries of the two electronic states involved in the resonant process should be the most enhanced ones. The consequences derived from this well-known Tsuboi rule can be quantitatively estimated by the means of the Peticolas equation [30]:

\[ I_i = k\Delta Q_i^2\nu_i, \]  

(1)

where \( I_i \) is the Raman intensity of vibration “\( i \)” under resonant CT conditions (SERS-CT), \( \Delta Q \) is a vector containing the differences between the equilibrium geometries of both resonant states (D₀ and S₀) along each normal mode, \( \nu_i \) is the vibrational frequency corresponding to the \( i \)th-normal mode in the S₀ state, and \( k \) is an arbitrarily adjusted constant. These \( \Delta Q \) displacements contain the enhanced vibrations via Franck–Condon factors and can be obtained from the geometric differences between both states if expressed as a function of the internal coordinates \([\Delta R = R(D_0) - R(S_0)]\) through the transformation:

\[ \Delta Q = L^{-1}\Delta R, \]  

(2)

where \( L^{-1} \) is the inverse of the normal mode \( L \)-matrix in the S₀ state.

By comparing the calculated optimized geometry (R) of the neutral molecule in its S₀ state with that of the anion in its D₀ state, we are able to foresee which fundamentals will be the most enhanced through this RR-CT mechanism. In order to detect the presence of CT processes in the SERS of Pz, the CASSCF/3-21G, 6-31+G, and 6-31+G* optimized geometries have been calculated, the active space including six \( \pi \)-type valence molecular orbitals with six or seven electrons in the neutral molecule or its anion, respectively. Likewise, UHF calculations of the geometries of the anion have been carried out with the above-mentioned basis sets and with the 6-311++G** one and compared with the respective RHF structures of the neutral molecule [12, 13, 22]. The force field for the S₀ states have also been calculated in each case to obtain the \( L \)-matrix and to carry out the transformation (2). The level of theory and the size of the basis set do not meaningfully affect the relative \( \Delta Q \) values on which the relative SERS-CT intensities depend. All the calculations point out that the 6a;\( \delta \)r (1;\( \nu \)r (9a;\( \delta \)(CH) and 8a;\( \nu \)r modes have comparable \( \Delta Q \) values, explaining their activity in the SERS of Figure 1, while the 2;\( \pi \)(CH) mode has a much lower value, in agreement with the very weak intensity of this vibration.

As an example, Figure 1 shows the SERS-CT calculated intensities from the CASSCF/6-31G* geometries of Pz in the S₀ and D₀ levels [22]. The theoretical spectrum compares very well with the SERS recorded on Ag by Huang et al. [31] (Fig. 1); we deduce that this spectrum contains only CT contributions (SERS-CT). In contrast, mode 1 in the SERS recorded from 0.0 to \(-0.75\) V in Figure 1 shows an enhancement stronger than expected, therefore it should contain also some non-CT (SERS-EM) contribution [22].

**DETECTING CT PROCESSES**

The agreement between the experimental behavior and the theoretical SERS-CT intensities allows us to confirm the participation of the RR-CT mechanism in a particular spectrum [11, 12]. Figure 4 displays the Raman spectrum of an aqueous solution of 3,5-dimethylpyridine (3,5-DMPy) and its SERS recorded on a silver electrode at potentials ranging between 0.00 and \(-1.40\) V [15]. The most striking fact is the strong SERS enhancement shown by the band recorded at \(-1590\) cm\(^{-1}\) assigned to mode 8a, as compared with the very weak intensity in the Raman of the aqueous solution. Another striking fact is the strong intensity of the band recorded at \(1,000\) cm\(^{-1}\) assigned to mode 12, especially in the Raman spectrum of the aqueous solution and in the SERS recorded at 0.00 V. Therefore, vibrations 8a and 12 exhibit a distinct behavior and the SERS at 0.0 and \(-1.20\) V appear to be produced by different mechanisms. The SERS recorded at \(-1.2\) V should be visualized as a sum of that recorded at 0.0 V plus some other else characterized by the strong intensity of mode 8a. Figure 4 also shows the theoretical SERS–CT spectrum calculated from the HF/3-21G geometries. The theoretical intensities demonstrate the presence of CT processes.
in those SERS where vibration 8a is enhanced, and that vibration 12 contains exclusively EM contributions. Furthermore, the calculated SERS-CT and the experimental intensities of 2-methylpyrazine recorded at −0.25 V are shown in Figure 5 [16]. These examples demonstrate the usefulness of simple RHF (S₀ state) and UHF/3-21G (D₀ state) calculations [18–21] in predicting SERS-CT intensities.

As can be seen, the enhancement of the band at ~1600 cm⁻¹ assigned to the 8a;ᵦₗ ring mode is the main feature of the CT mechanism in the SERS of these benzene-like molecules. This mode is related to the differences between the structures of the neutral molecules and their anions. When the trans-

**FIGURE 4.** Raman spectrum of an aqueous solution of 3,5-dimethylpyridine and its SERS spectra recorded on silver at several electrode potentials vs. the saturated Ag/AgCl/KCl reference electrode (514.5-nm excitation). SERS-CT calculated intensities from respective RHF and UHF/3-21G geometries in the S₀ and D₀ states.

**FIGURE 5.** SERS intensities of 2-methylpyrazine recorded on silver at −0.25 V vs. the saturated Ag/AgCl/KCl reference electrode (514.5-nm excitation) and SERS-CT calculated intensities from the respective RHF and UHF/3-21G geometries in S₀ and D₀ states.

**FIGURE 6.** Pictorial representation of the LUMO:B₃u and LUMO+1:A_u of pyrazine related to the D₀;²B₃u and D₁;²A_u states of its anion and approximate distortions originated by the 16b;B₃u and 16a;A_u out-of-plane vibrations.
ferred electron is located in the lowest unoccupied molecular orbital (LUMO) of the adsorbate, the molecular structure of Pz is deformed lengthening the CN bonds and shortening CC bonds [22] (Fig. 6) as mode 8a does [32]. In summary, a specific SERS can be enhanced by either CT alone (SERS of Pz recorded by Huang et al. [31]) (Fig. 1), or EM alone (SERS of 2,3-DMPy recorded at 0.0 V; Fig. 4), or by both contributions. In this more complex case, EM and CT bands can coexist (modes 12 and 8a in the SERS of 2,3-DMPy at \( V = 1.2 \) V; Fig. 4), but there is also the possibility that a band contains both types of contributions (mode 1 in the SERS of Py recorded between 0.0 and \(-0.75\) V; Fig. 1).

**ROLE OF THE ELECTRODE POTENTIAL**

Figures 1 and 4 show the marked sensitivity of the SERS relative intensities on the electrode potential, given that the energy of the CT transition \( E_{\text{CT}}(V) = E_{\text{vac}}(\text{CT} - S_0) \) depends on the electric potential of the interphase [11]. If the energy of laser photons is kept constant, the role of the electrode potential is just to tune the energy of the CT transition \( E_{\text{CT}} \):

\[
\Delta E_{\text{CT}}(\Delta V) = e\beta \Delta V.
\]

When the electrode potential is changed from \( V \) to \( V' = V + \Delta V \) the CT level \( M^+ - A^- \) stabilizes as much as \( e\beta \Delta V \) [Fig. 7(a)]. The physical meaning of \( \beta \) can be found in Ref. [11] and quantifies the effectiveness of the electrode potential to shift the energy of the CT transition. Therefore, the resonance condition in the RR-CT model can be achieved by tuning the electrode potential. The origin of the SERS-CT profiles (SERS intensity vs. electrode potential) [Fig. 7(b)] should be similar to that of REP, but the variable is the electrode potential instead of the energy of the photon. For a particular potential \( V_{\text{max}} \) the resonant CT condition is achieved \( E_{\text{CT}}(V_{\text{max}}) = h\nu \) and the SERS-CT profiles show a maximum (Fig. 7).

Figure 7(c) shows the intensity of the vibration 8a of Pz vs. the electrode potential by using the \( \nu\text{(CH)} \) band as an intrinsic standard to refer to the intensities, given that these modes are not involved in the resonant CT process [22]. The profile shows a maximum at approximately \( V_{\text{max}} = -0.50 \) V as in the case of methylpyrazine [16], being found that it shifts toward more negative values as the number of methyl-substituents attached to the pyrazine ring increases [11]. In the case of 3,5-DMPy, the electronic CT band is centered at \( \sim -1.0 \) V [Fig. 7(c)] as occurs in pyridine [11, 14], 2,6-dimethylpyridine [19], or 2,4,6-trimethylpyridine [20].

**ENERGIES OF THE S_0 AND D_0 STATES**

These results can be understood by comparing the relative stability of the respective radical anions. On the basis of the RR-CT model, it is possible to relate the \( V_{\text{max}} \) of two different molecules, A and B, obtained under the same experimental conditions to their electron affinities as follows [11]:

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\( \text{FIGURE 7.} \) (a) Dependence of the energy of the \( M^+ - A^-; \text{CT} \) level of the surface complex \( (E_{\text{CT}}) \) on the electrode potential, and (b) the origin of the SERS-CT profiles (intensity vs. electrode potential). (c) SERS-CT profiles of mode 8a of pyrazine (Pz) and 3,5-dimethylpyridine (DMPy).
Moreover, if no experimental data on EA are available, ab initio energy calculations can be used in order to estimate the relative stability of anions with respect to the neutral molecule $E_{\text{ver}}(D_0-S_0)$ [33]:

$$EA_A = -E_{\text{ver}, A}(D_0-S_0).$$

The good correlation between the calculated energies (HF/6-31+$G$) of the vertical transitions between the $D_0$ and $S_0$ states [$E_{\text{ver}} = E_{\text{ver}}(D_0-S_0)$] and the experimental electron affinities (EA) of benzene and selected diazines [11]:

$$(EA_A - EA_B) = e\beta(V_{\text{max}, A} - V_{\text{max}, B}).$$  \hspace{1cm} (4)$$

Moreover, if no experimental data on EA are available, ab initio energy calculations can be used in order to estimate the relative stability of anions with respect to the neutral molecule $E_{\text{ver}}(D_0-S_0)$ [33]:

$$EA_A = -E_{\text{ver}, A}(D_0-S_0).$$  \hspace{1cm} (5)$$

The ground state of benzene anion is doubly degenerate, so the $D_1$ excited state of the anions of analogous molecules such as pyrazine has to be taken into account. Therefore, the analysis of the SERS can be completed by considering a second doublet state of the adsorbate ($D_1$), which requires taking into account two electronic transitions, $D_0-S_0$ and $D_1-S_0$, in the discussion. Moreover, the activity of a vibration in RR, or SERS-CT, cannot be caused only by the displacements of the equilibrium minima of the potential energy surfaces ($\Delta Q \neq 0$) but also by the shifts of the vibrational frequencies ($\Delta \nu \neq 0$) in the different electronic states involved [28]. So the force field in the $S_0$, $D_0$, and $D_1$ states have to be computed. This changes in the frequencies are originated by Franck–Condon and Herzberg–Teller contributions, which, in turn, are related to the most important A- and B-terms in RR.

Table I summarizes the HF and CASSCF calculated vibrational frequencies of those modes of Pz from the computed ab initio energies of the $S_0$ and $D_0$ states.

**VIBRATIONAL FREQUENCIES IN THE $S_0$, $D_0$, AND $D_1$ STATES**

The vibrational frequencies in the $S_0$, $D_0$, and $D_1$ states are calculated at the HF/6-31+$G$ level of theory in pyrazine and methylpyrazines [11].

**FIGURE 8.** Correlation between the calculated energies (HF/6-31+$G$) of the vertical transitions between the $D_0$ and $S_0$ states [$E_{\text{ver}} = E_{\text{ver}}(D_0-S_0)$] and the experimental electron affinities (EA) of benzene and selected diazines [11].
showing a significant change in the considered electronic states [13, 22]. The red shifts of the 16b and 16a out-of-plane modes in the D0 and D1 states, respectively, account for their activity in SERS. The symmetry of each vibration, B3u and Au, respectively, coincides with that of the D0 and D1 states as well as with that of the acceptor molecular orbital involved in the CT process (Fig. 6). From the shapes of the LUMO or the LUMO/H11001 one can deduce that the 16b and 16a out-of-plane deformations decrease the antibonding interactions in the respective orbitals and therefore, they will show a lower frequency in D0 or D1 than in S0. The mode 16b; H9270 ring,B3u exhibits the greatest relative shifts between the calculated out-of-plane frequencies of the S0 and D0;2B3u states, which explains its activity in the SERS spectra and why it is the most enhanced out-of-plane vibration.

Finally, the SERS activity of the vibration 8b;B3g is related to the Herzberg–Teller factors [24] corresponding to the vibronic coupling between both, D0;2B3u and D1;2Au CT states; Γ(D0) × Γ(D1) = B3u × Au = B3g. Both electronic levels are coupled through mode 8b; H9263 ring,B3g given that it is the only in-plane vibration for which a significant frequency shift is calculated, as can be deduced from the ab initio calculations (Table I). This vibration shows an RHF frequency of ~1700 cm⁻¹ in the S0 state, and a UHF/3-21G frequency of ~979 cm⁻¹ or ~1100 cm⁻¹ with more extended basis sets in the D0 state, which means about a 40% decrease of that frequency. When the molecule bends according to a B3g vibration the molecular symmetry descends from D2h to C2h, in such a way that both doublet states have the same symmetry (2Au in C2h) and their potential energy surfaces repel [22, 35].

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<th>Table I: Calculated vibrational frequencies (cm⁻¹) of fundamentals of isolated pyrazine and of complexed pyrazine.</th>
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- a Isolated pyrazine (Pz) shows significant frequency shifts between the S0;1Ag state (RHF, CASSCF) and the D0;2B3u and D1;2Au states (UHF, CASSCF) of its radical anion.
- b Complexed pyrazine (Ag2–Pz) shows significant frequency shifts between the ground S0;1A1 state (RHF) and the excited CT0;1B1 and CT1;1A2 charge-transfer states (CIS).
- c Experimental frequencies.
- d 6 × 6 and 7 × 6 CASSCF calculations for the S0 and D1 states, respectively.
- e Imaginary frequency obtained with the 6-311++G** basis set.
CASSCF calculated frequencies exhibit the same behavior. This is the origin of the UHF imaginary frequencies calculated for mode 8b in the D1 state at 1245i, 1911i, 4288i, and 4438i cm\(^{-1}\) with the 3-21G, 6-31+G, 6-31+G*, and 6-311++G** basis sets, respectively. The CASSCF frequencies calculated for this vibration in D1 state with the 3-21G, 6-31+G, and 6-31+G* basis sets are real instead of imaginary, amounting to 8419, 2862, and 2783 cm\(^{-1}\), respectively. The different behavior of 8b mode at CASSCF and UHF levels is due to the vicinity of the minimum of the \(^2\)A\(_{1}\) state to the crossover of both D\(_0\) and D\(_1\) surfaces, which explains why small changes in the calculation method affect the vibrational frequency so noticeably [22].

Electronic Properties of the Nanocluster–Adsorbate System

**CT STATES OF THE SURFACE COMPLEX**

The previous RR-CT mechanism resembles an electron impact experiment under resonance conditions, in which the transfer of a complete electron is involved in step II. But the formation of the radical anion of the adsorbate is only a hypothesis, given that any intramolecular charge redistribution different to a complete electron is possible in a complex. In order to clarify all this, we have studied the electronic properties of the silver–pyrazine complex in its ground electronic state, as well as in its excited states, to confirm the existence of charge transfer levels and to compare their properties with those of the corresponding radical anion of the adsorbate [12]. When we have carried out CIS/3-21G calculations of the properties of singlet states of the Ag\(_2\)–N complex of Pz, using a 3-21G as well as LanL2DZ basis sets, two excited levels, i.e., CT\(_{0}\)\(^1\)B\(_1\) and CT\(_{1}\)\(^1\)A\(_2\), have been found lying at 3.43 and 4.31 eV over the ground state, respectively, which can be considered real charge transfer states. Pyrazine has a net charge in its S\(_0\)\(^1\)A\(_1\) ground state amounting to either +0.05 or +0.10 with LanL2DZ or 3-21G, respectively, but shows net charges amounting to −0.75 or −0.63 in the 2\(^1\)B\(_1\) state and −0.84 or −0.79 in the 1\(^1\)A\(_2\) state, by using these basis sets, respectively. This means a charge transfer from the metal cluster to Pz amounting to −0.80 or −0.73 in the 2\(^1\)B\(_1\) state and −0.89 in the 1\(^1\)A\(_2\) state, respectively. In the remaining levels, the charge transfer is <0.13.

Provided that CIS calculations systematically overestimate the electronic transition energies [36], it is evident that the CT\(_0\) and CT\(_1\) states at 3.14 and 4.31 eV are in an energy range in which a resonant mechanism is possible, using the standard 5145 or 4880 Å (~2.5 eV) exciting lines from an Ar\(^{+}\) laser.

The symmetry of both excited CT states of the complex, B\(_1\) and A\(_2\) in a C\(_{2v}\) point group, matches those of the D\(_{0}\)\(^2\)B\(_{3u}\) and D\(_{1}\)\(^2\)A\(_u\) states of the radical anion when descending in symmetry from D\(_2\)\(_{h}\) to C\(_{2v}\). The likeness of the respective CT\(_{0}\)\(^1\)B\(_1\) and CT\(_{1}\)\(^1\)A\(_2\) states of the complex and the respective D\(_0\) and D\(_1\) states of the radical anion is demonstrated when the respective geometries and vibrational frequencies are compared [12].

**RELATING GEOMETRIES OF THE RADICAL ANION AND THE CT STATES OF THE SURFACE COMPLEX: SERS ACTIVITIES OF A\(_g\) AND B\(_{1u}\) VIBRATIONS**

The geometric differences between the ground S\(_0\)\(^1\)A\(_1\) and the CT\(_{0}\)\(^1\)B\(_1\) state of the surface complex determine the most relevant characteristic of the SERS spectra of Pz, namely, the enhancement of modes 6a, 1, 9a, and mainly mode 8a (Fig. 1). Figure 10 shows the agreement between the experimental and the calculated [Eq. (1)] SERS-CT intensities corresponding to the transition D\(_0\)\(^2\)B\(_{3u}\)–S\(_0\)\(^1\)A\(_1\) of isolated Pz (UHF and RHF/3-21G and LanL2DZ, respectively), as well as the CT\(_{0}\)\(^1\)B\(_1\)–S\(_0\)\(^1\)A\(_1\) one of the Ag\(_2\)–Pz complex (CIS and RHF/3-21G and LanL2DZ, respectively) [12]. This proves the similarity between the CT\(_{0}\)\(^1\)B\(_1\) state of the complex and the D\(_0\)\(^2\)B\(_{3u}\) level of radical anion and the involvement of the RR-CT mechanism in SERS.

Moreover, the inclusion of the metal in the theoretical model allows us to explain in a straightforward way the violation of the mutual exclusion rule observed in the SERS spectrum of Pz where some Raman inactive “u” vibrations are recorded. This explains the appearance of silent modes in Raman without to resort to effects related to electric field gradient in the interphase [1, 2]. The activities in SERS of the B\(_{1u}\) vibrations are explained by assuming a descent in symmetry from D\(_{2h}\) to C\(_{2v}\) due to the formation of the surface complex. On this basis, B\(_{1u}\) (D\(_{2h}\)) vibrations become totally symmetric, A\(_{1}\), under C\(_{2v}\). Therefore, B\(_{1u}\) modes of Pz have nonzero ΔQ in the complex, so that breaking the mutual exclusion principle appears as a natural conclusion. The estimated SERS-CT intensities for the B\(_{1u}\) modes 12, 18a, and 19b are weak as expected (Fig. 10), given that the respective ΔQ values are significantly smaller than those obtained for the previous A\(_g\) vibrations. The
choice of basis set is found to affect these small $\Delta Q$, given that there is some uncertainty in estimating the intensities of vibrations with small $\Delta Q$. Moreover, this problem is more important for mode 12 due to the proximity with mode 1, as is the case for pyridine, where both fundamentals belong to the same symmetry species [17].

**RELATING THE VIBRATIONAL FREQUENCIES OF THE RADICAL ANION AND THE CT STATES OF THE SURFACE COMPLEX: SERS ACTIVITIES OF B$_{3u}$, A$_u$, AND B$_{3g}$ VIBRATIONS**

It is possible, again, to appreciate the likeness between the properties of Pz in the CT states of the complex and that of its radical anion by comparing the calculated frequencies for the isolated molecule and for the Ag$_2$-Pz system in the relevant electronic states [12] (Table I). The CT states are the only ones that show significant changes in the vibrational frequencies for some specific modes. With respect to the in-plane vibrations, mode 8b is the only one for which the shift is significant. The calculated frequency in the ground state of the complex is 1724 or 1678 cm$^{-1}$, respectively, by using the LanL2DZ or 3-21G basis sets, in agreement with the calculated values of 1728 or 1679 cm$^{-1}$ in isolated pyrazine. In contrast, this fundamental is calculated at 1195 and 2599 cm$^{-1}$ (LanL2DZ) or 1304 and 2924 cm$^{-1}$ (3-21G) in the CT$_{0;1B_1}$ and CT$_{1;1A_2}$ states, respectively. These results are similar to those obtained for the radical anion and support the previous conclusion that mode 8b is responsible for vibronic coupling between both CT states. In this sense, the CIS frequencies for the complex are similar to the CASSCF results of the radical anion.

While the calculated frequency shift for mode 8b in the CT states arises from vibronic coupling, the out-of-plane vibrations show frequency shifts closely related to the electronic structure of the LUMO:B$_{3u}$ and LUMO+1:A$_u$ antibonding orbitals of isolated pyrazine, where the transferred electron is attached in the CT$_0$ and CT$_1$ states, respectively. For instance, the LanL2DZ-calculated frequency for mode 16b;A$_u$, B$_{3u}$ is 513 cm$^{-1}$ in the ground state of the Ag$_2$-pyrazine complex, red-shifted 152 cm$^{-1}$ in the CT$_0$ state, showing the most significant change of its vibrational frequency (~35%) and explaining why it shows the strongest enhancement. Although almost all the out-of-plane fundamentals show a significant red shift in the CT$_1;1A_2$ state, the imaginary frequencies of mode 16a;A$_u$, of 149i or 110i cm$^{-1}$, depending on the basis set used, have to be stressed. These results mean again that the molecule is not planar in this state, as the geometry is distorted along the direction of this normal coordinate. Taking the imaginary frequencies as “negative,” the red shift of mode 16a in the CT$_1$ state should be about 130% of its vibrational frequency [12].

**CONSEQUENCES OF THE ADSORPTION ON THE RELEVANT SYMMETRY**

This 16a;A$_u$ out-of-plane distortion of Pz in the CT$_1$ state of the complex implies a molecular symmetry descent from C$_{2v}$ to C$_2$, becoming mode 16a, inactive in IR and Raman under D$_{2h}$ symmetry,
The transition to this state under D$_{2h}$ or C$_{2v}$ symmetries (A$_u$–A$_g$ or A$_g$–A$_1$, respectively) should be forbidden by the electric dipole selection rules, becoming allowed under C$_2$ symmetry (A–A). In any case, the involving of the CT$_1$ state in the SERS mechanism is of secondary importance, as is demonstrated by the low enhancement observed in modes 16a or 8b. Strictly speaking, the vibronic coupling effect requires that both excited states be accessible from the ground state through the electric dipole mechanism [28]. In contrast, by comparing the SERS intensities of mode 16a with those of the remaining out-of-plane modes, it is easy to see that its activity is much weaker than the expected from the calculated $\Delta\nu$. Finally, the relationship between the activity of vibration 16a and the CT$_1$ state is evident, provided that it is the only fundamental that shows greater enhancement in the SERS recorded at the more negative potentials, that is, at potentials where a greater contribution of the CT$_1$ state is expected.

**Conclusions**

The differences observed when the Raman and the SERS spectra are compared can be understood on the basis of the combined effect of both the molecular adsorption and the selection rules of the enhancement mechanisms involved in any particular experiment. Moreover, both effects are very sensitive to the electrode potential, which determines the presence of resonant CT processes between the metal and the adsorbate. This complex scenario can be rationalized by means of ab initio calculations of energies, geometries, and vibrational frequencies of the adsorbate [11, 13–23] or, improving the approach, the metal–adsorbate system [12]. Quantum chemical calculations have proved useful in deducing the surface orientation of the adsorbate and in detecting the presence of resonant charge transfer processes. In this respect, ab initio calculations are essential to clarify the old controversy about the origin of the SERS enhancement [1, 2, 37–39] or the nature of the CT mechanism [12]. SERS of pyrazine and its analogues are compatible with a resonance Raman mechanism involving the ground state of the surface complex and excited levels arising from charge transfer between the metal and the adsorbate. These conclusions strengthen the relevance of the CT mechanism in the SERS of aromatic molecules, as it is possible to apply this technique to study of the respective radical anions and charge transfer processes on the nanoscale [40].

**References**