Resonant charge transfer on the nanoscale: studying doublet states of adsorbates by surface-enhanced Raman scattering


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This paper summarizes a series of results where the main role of the charge-transfer (CT) mechanism in the surface-enhanced Raman scattering (SERS) of aromatic molecules is demonstrated. This mechanism consists on a photoinduced CT process between nanostructures of the metallic surface and the adsorbed molecules, giving rise to the transient formation of a radical anion of the adsorbate. A general methodology to detect the CT process in SERS is described. It is demonstrated that the SERS features are determined by the differences between the electronic properties of the neutral and the anionic molecular species. On the basis of these results, we propose to use SERS as a tool to characterize such doublet states. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: surface-enhanced Raman scattering; nanoparticles; charge transfer; electron transfer; doublet states

INTRODUCTION

Twenty-eight years after the discovery of surface-enhanced Raman scattering (SERS),¹,² it is generally accepted that the enormous enhancement of the Raman signal is due mainly to the electromagnetic (EM) and the chemical or charge-transfer (CT) mechanisms.¹–³ Both of them produce selection rules able, in principle, to explain the observed selective enhancement independently, but there is not yet a trivial way to establish their relative contributions in a particular experiment. For this reason, it is not at all clear which kind of information can be deduced when analyzing a SERS spectrum, namely the relative orientation of the adsorbate with respect to the metal surface (EM)²,⁴ or some properties of the electronic states involved in a resonant CT process.¹,⁵

This paper summarizes the results of studies aimed at detecting and analyzing the presence of CT processes in SERS.⁶–¹⁰ The experimental and theoretical backgrounds can be found in the original papers, where the main role of the CT mechanism in the SERS of pyridine, pyrazine and analogues is demonstrated. This mechanism can be considered similar to a resonance Raman (RR) process between the ground electronic state of the surface complex and excited levels arising from CT between the metallic nanocluster and the adsorbed molecule. Therefore, it involves the transient formation of the corresponding radical anion of the adsorbate, the reason why SERS could become a powerful tool to study charge transfer on the nanoscale.²¹ Radical anions are indeed doublet electronic states, whose properties are not experimentally well known, and this is why we present here the advantages of using ab initio calculations to analyze SERS spectra and to detect CT processes.

SOME SELECTED SERS

SERS is a very complex phenomenon. One of its most important characteristics is the marked dependence of the overall and the relative enhancement of the bands on the particular experimental conditions. We shall focus attention on the relatives SERS intensities of the following selected examples.

Figure 1 shows the region between 200 and 1700 cm⁻¹ of the Raman spectrum of a 0.2 M aqueous solution of 3,5-dimethylpyridine and the SERS spectra recorded on a silver electrode at potentials ranging between 0.00 and −1.40 V versus saturated Ag/AgCl/KCl.⁸ The most striking fact observed when the Raman and SERS spectra are compared is the strong enhancement shown by the band recorded at
Figure 1. Raman spectrum of an aqueous solution and SERS spectra of 3,5-dimethylpyridine recorded on silver at several electrode potentials vs the saturated Ag/AgCl/KCl reference electrode. Excitation at 514.5 nm. SERS-CT calculated intensities from Eqn (2) by using the respective RHF and UHF/3–21G geometries in the $S_0$ and $D_0$ states.

ca 1590 cm$^{-1}$ in SERS, assigned to mode 8a, which increases as the electrode potential becomes more negative. This band becomes the strongest one in the SERS spectrum recorded at $-1.20$ or $-1.40$ V, whereas it is a very weak band in the Raman spectrum of the aqueous solution. Another striking fact is the strong intensity always shown by the band recorded at 1000 cm$^{-1}$ assigned to mode 12, especially in the Raman spectrum of the aqueous solution and in the SERS spectrum recorded at 0.00 V. Therefore, vibrations 8a and 12 exhibit a distinct behaviour and the SERS at 0.0 and $-1.20$ V seems to contain different enhancement contributions.

Figure 2 shows the Raman spectrum of an aqueous solution of pyrazine and its SERS spectra recorded on silver at electrode potentials ranging between 0.0 and $-0.75$ V. All of them are again dominated by the enhancement of vibration 8a, but vibration 1 shows different intensities depending on the nature of the metal. The trace on gold in Fig. 3 looks like the SERS spectrum on silver at $-0.25$ or $-0.5$ V in Fig. 2.

The Raman and SERS spectra of pyridine recorded on a silver electrode are shown in Fig. 4. Vibrations 1 and 12 are strong or very strong in the Raman spectrum of the aqueous solution and in the SERS spectra, whereas vibrations 6a, 9a and 8a are only enhanced at $-0.5$ or $-0.75$ V. The relative intensities of this set of vibrations at $-0.5$ V are very similar to those of pyrazine in the SERS spectra in Figs 2 and 3, but the 8a band in pyridine does not become the strongest one.

As in the case of 3,5-dimethylpyridine, the SERS spectra of pyridine at 0.0 V (or $-0.25$ V) and $-0.50$ V (or $-0.75$ V) seem to be enhanced by different mechanisms. The SERS record at $-0.5$ V could be considered as a sum of that recorded at 0.0 V plus some other one characterized by the strong intensity of mode 8a as the SERS spectra of pyridine recorded on nickel by Huang et al. show (Fig. 5).

How can we rationalize these results?

THE CT MECHANISM

In an RR experiment, a molecule $A$ is photoexcited up to a stationary state ($A'$), usually the first excited singlet $S_1$. The
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Figure 3. SERS spectra of pyrazine on several metals reported by Huang et al.\textsuperscript{22} Excitation at 632.8 nm.

Figure 4. Raman spectrum of an aqueous solution and SERS spectra of pyridine recorded on silver at several electrode potentials vs the saturated Ag/AgCl/KCl reference electrode. Excitation at 514.5 nm.

The CT mechanism of SERS is considered to be analogous to the RR mechanism (RR-CT), but in the latter the transient excited state corresponds to a CT state of the metal–adsorbate complex similar to that observed in some inorganic CT complexes.\textsuperscript{2} In SERS, such new electronic CT transitions consist of photoinduced charge donation from the metallic nanocluster to the adsorbate or vice versa, and have been detected in very few cases.\textsuperscript{25–30} Given that the available information about these CT states is scarce, we have assumed a simplified RR-CT mechanism based on the following steps:\textsuperscript{20}

**Step 1:**

\[ M_V + A \rightarrow M_V - A \]

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 (M\textsubscript{V}), so giving rise to the surface complex M\textsubscript{V} - A.

**Step 2:**

\[ M_V - A; S_0 + h\nu \rightarrow M_V^+ - A^-; CT \]

if \[ h\nu = E_{CT} = E_{\text{ver}}(CT - S_0) \]

If the energy of the photon energy matches with that of the CT transition [\( h\nu = E_{\text{ver}}(CT - S_0) \)], where CT and S\textsubscript{0} are the excited and the ground states of the surface complex, respectively) a resonant CT process occurs. In pyridine and analogues the charge is transferred initially from the metal to the adsorbate,\textsuperscript{31} yielding the formation of the adsorbate anion in the CT excited level M\textsubscript{V} - A\textsuperscript{−} if the donated charge amounts to a complete electron.

**Step 3:**

\[ M_V^+ - A^-; CT \rightarrow M_V - A^-; S_0 + h\nu' \]

Finally, a Raman photon can be emitted (h\nu') if the adsorbate remains vibrationally excited (A\textsuperscript{−}) when the CT state relaxes.

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to the ground level of the complex. Therefore, we assume that the properties of the adsorbate in the ground \((M_V - A)\) and also in the CT state \((M_V^+ - A^-)\) of the surface complex are similar to those of the neutral species \((A_S^0)\) and its anion \(A^-\) (named \(D_0\) level given that it is a doublet in its electronic ground state), respectively, at any electrode potential.

**PREDICTING RR-CT RELATIVE INTENSITIES**

The steps and hypothesis mentioned in the RR-CT model are supported by several experimental facts, the main one being that the relative intensities observed in the SERS of several adsorbates are strictly compatible with the differences between the electronic properties of the neutral molecules \((A_S^0)\) and their respective radical anions \((A^-;D_0)\). We have proposed a general methodology for predicting the RR relative intensities under RR-CT conditions: according to the A-term in RRR, those vibrations connecting the equilibrium geometries of the two electronic states involved in the resonant process should be the most enhanced. Since these doublets of neutral adsorbates such as pyrazine, pyridine and derivatives are not well characterized, we used \(ab\) initio calculations in order to gain information on these chemical species.

By comparing the calculated optimized geometry of the neutral molecule in its \(S_0\) state with that of the anion in its \(D_0\) state we are able to predict which fundamentals will be the most enhanced through this resonant CT mechanism. These geometric differences \(\Delta R = R(D_0) - R(S_0)\) expressed as a function of the selected internal coordinates can be related to the normal modes of vibration \(\Delta Q\) through the transformation:

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

where \(L^{-1}\) is the inverse of the normal mode \(L\)-matrix in the \(S_0\) state and \(\Delta Q\) is a vector containing the amplitudes along each normal mode connecting the equilibrium geometries of both resonant states. These \(\Delta Q\) displacements contain the enhanced vibrations through a resonant CT mechanism via Franck–Condon factors and represent the shift between the minima of the potential energy surfaces of the involved electronic states \((D_0\) and \(S_0)\) along each normal coordinate. Moreover, these \(\Delta Q\) can be used to estimate the intensity of the bands in an RR process according to Peticolas et al.'s equation:

\[
I_i = k \Delta Q_i^2 v_i^3
\]

where \(v_i\) is the wavenumber corresponding to the \(i\)th normal mode in the \(S_0\) state and \(k\) can be adjusted to assign an arbitrary relative intensity to a selected fundamental when the exciting laser line is fixed.

**DETECTING CT PROCESSES**

The agreement between the experimental behavior and the theoretical RR-CT intensities will allow the confirmation of the participation of the CT mechanism in the SERS recorded under any particular experimental conditions.

Figure 6 shows the RR-CT intensities calculated from the CASSCF/6–31 + \(G^*\) optimized geometries of pyrazine in the \(S_0\) and \(D_0\) levels. The theoretical spectrum of pyrazine compares very well with its SERS spectrum recorded on Ag or Cu (Fig. 3), and we therefore deduce these spectra contain only CT contributions (SERS-CT). In contrast, mode 1 in the SERS spectra in Fig. 2 and in the spectrum recorded on Au (Fig. 3) shows an enhancement stronger than calculated for a pure CT mechanism (Fig. 6), hence it should also contain non-CT (either EM or effects derived from the chemisorption) contributions.

The predicted RR-CT intensities for pyridine and pyrazine (Fig. 6) are almost identical, therefore the SERS of pyridine recorded by Huang et al. on Ni should contain only CT contributions (Fig. 5). In contrast, the spectrum of pyridine at 0.0 V in Fig. 4 is exclusively enhanced by the EM mechanism (SERS-EM), and the bands assigned to modes 1 and 12 in the record at −0.5 V would contain EM contributions.

The calculated RR-CT intensities for 3,5-dimethylpyridine can also be seen at the top of Fig. 1. The theoretical spectrum is dominated by the strong intensity of mode 8a and shows the usefulness of simple RHF \((S_0)\) and UHF/3–21G \((D_0)\) calculations in order to predict SERS-CT features. The very weak RR-CT calculated intensity for vibration 12 indicates that this strong SERS band contains exclusively EM (non-CT) contributions. On this basis, one can deduce that the SERS spectrum of 3,5-dimethylpyridine recorded at 0.0 V can be considered as SERS-EM and the SERS spectrum recorded at −1.2 V can be visualized as a sum of that recorded at 0.0 V plus the theoretical RR-CT spectrum characterized by the strong intensity of mode 8a.

Summarizing, a particular SERS can be enhanced through either only CT, only EM or both mechanisms. In this more complex case, EM and CT bands can coexist but there is also the possibility that one band contains both kinds of

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Figure 6. Theoretical SERS-CT intensities estimated from Eqn (2) by using the optimized CASSCF/6–31 + \(G^*\) geometries of pyrazine and pyridine in the respective \(S_0\) and \(D_0\) levels.
contributions. As can be seen, the enhancement of the band at ca 1600 cm$^{-1}$ assigned to the 8a, $v_{\text{ring}}$ mode is related to the presence of the CT mechanism in the SERS of these benzene-like molecules. These $v_{\text{ring}}$ coordinates are just the ones related to the differences between the structures of the neutral molecules and their anions because the transferred electron is located in the LUMO of the adsorbate. In the case of pyrazine, this gives rise to lengthening of the CN bonds and shortening of CC bonds, as seen in Fig. 7.

THE ROLE OF THE ELECTRODE POTENTIAL

The SERS spectra in Figs 1, 2 and 4 show the marked sensitivity of the relative intensities to the electrode potential. Obviously, the energy of the CT transition [$E_{\text{CT}} = E_{\text{CT}}(V) = E_{\text{CT}}(V) = E_{\text{CT}}(V)$] depends on the electric potential of the interphase given that the $M^+ - A^-$;CT level involve charged species. Negative electrode potentials stabilize the species $M^+$ and destabilize the species $A^-$. 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 $E_{\text{CT}}$:

$$\Delta E_{\text{CT}}(\Delta V) = e\beta \Delta V = e\Delta V / S$$

with $\beta = S^{-1}$. When the electrode potential is changed from $V$ to $V' = V + \Delta V$, $\Delta V$ equals the change in the polarizable electrode, and the CT level $M^+ - A^-$ stabilizes as much as $e\beta \Delta V$. The physical meaning of $\beta$ (or $S^{-1}$) has been described in Ref. 20 and quantifies the effectiveness of the electrode potential to shift the energy of the CT transition. It may depend in a complex way on the electrode potential and a wide range of values have been reported for pyridine on different conditions. Therefore, one can achieve the resonance condition in the RR-CT model by tuning the electrode potential. The origin of the SERS-CT profiles is shown in Fig. 8: the plot of the intensity of a SERS band versus the electrode potential should be similar to REP, but the variable is the electrode potential instead of the energy of the photon. The electrode potential of the maximum of these SERS-CT profiles ($V_{\text{max}}$) must be related to the energy of the vertical CT transition. The particular situation where the electrode potential has been selected to achieve the resonance condition [$E_{\text{CT}}(V_{\text{max}}) = hv$] can be seen in Fig. 8(b).

Figure 9 shows the relative intensities of the strongest SERS bands of pyrazine with respect to the electrode potential by using the $v$(CH) band as an intrinsic standard to refer to the intensities given that it is not involved in the resonant process. The profiles show a maximum at $V_{\text{max}} \approx -0.50$ V as in the case of methylpyrazine, it being found that the maximum shifts towards more negative values as the number of methyl substituents attached to the pyrazine ring increases.

The SERS-CT excitation profiles of 3,5-dimethylpyridine are shown in Fig. 10. Two distinct behaviors can be realized. Vibration 12, which contains an important EM contribution, shows two maxima at $-0.25$ and ca $-1.2$ V. The electronic CT band is centered at this last potential where the CT-active mode 8a has its maximum. In the SERS spectra of pyridine, 7,20 2,6-dimethylpyridine 12 and 2,4,6-trimethylpyridine 13, the maximum of the mode 8a is reached at similar values.

![Figure 8. Dependence of the energy of the CT level on the electrode potential in the RR-CT mechanism of SERS.](image-url)
IMPROVING THE ANALYSIS

The analysis of SERS spectra can be improved in three ways.\textsuperscript{17,18} First, by taking into account a second doublet state of the adsorbate (D\textsubscript{1}) in the discussion of the results, which requires to consider two electronic transitions, D\textsubscript{0}–S\textsubscript{0} and D\textsubscript{1}–S\textsubscript{0}, in order to analyze the spectra. Second, by relating the activity of a vibration in SERS-CT not only to the displacements of the equilibrium minima of the potential energy surfaces (\(\Delta Q \neq 0\)) but also to the shifts of the vibrational wavenumbers (\(\Delta \nu \neq 0\)) in the different electronic states involved; hence force fields in the S\textsubscript{0}, D\textsubscript{0} and D\textsubscript{1} states have to be calculated. Third, by including the metal in the theoretical calculations. We have calculated the electronic properties of the silver–pyrazine complex finding two excited CT states of the complex, CT\textsubscript{0} and CT\textsubscript{1}, where the properties of pyrazine look similar to those of the D\textsubscript{0} and D\textsubscript{1} levels of its anion.\textsuperscript{18}

In this way, a great deal of fine detail of the SERS spectra of pyrazine can be explained, amongst which one can emphasize the activity of several fundamentals of B\textsubscript{3\gamma}, B\textsubscript{1u}, B\textsubscript{2u}, B\textsubscript{2g} and A\textsubscript{g} symmetries, usually much weaker than the totally symmetric modes.

From the complete analysis of the SERS of pyrazine it is possible to draw the following conclusions:\textsuperscript{17,18}

1. Activities of the B\textsubscript{3\gamma} modes (\(\Delta \nu \neq 0\)). The SERS activity of vibration 8b, B\textsubscript{3\gamma}, is related to Herzberg–Teller factors\textsuperscript{24} corresponding to the vibronic coupling between both D\textsubscript{0}–B\textsubscript{3\gamma} and D\textsubscript{1}–A\textsubscript{u} CT states [\(\Gamma(D_0) \times \Gamma(D_1) = B_{3\gamma} \times A_u = B_{3\gamma}\)]

2. Activity of the B\textsubscript{1u} modes (\(\Delta Q \neq 0\)). The activity of vibration 12 is explained by assuming a decrease in molecular symmetry from D\textsubscript{2h} to C\textsubscript{2v} due to the formation of the surface complex. On this basis, B\textsubscript{1u}(D\textsubscript{2h}) vibrations become A\textsubscript{1} under C\textsubscript{2v} and have non-zero \(\Delta Q\) in a surface complex, so that the breaking of the mutual exclusion principle appears as a natural conclusion.\textsuperscript{18}

3. Activities of the out-of-plane modes (\(\Delta \nu \neq 0\)). The SERS enhancement of the out-of-plane modes is not due to a planar orientation of pyrazine with respect to the metal, given that such possibility has been discarded.\textsuperscript{19} Vibrations B\textsubscript{3u}, B\textsubscript{2g} and A\textsubscript{u} show wavenumber shifts closely related to the electronic structure of the LUMO+B\textsubscript{3u} and LUMO +1:A\textsubscript{u} antibonding orbitals of pyrazine, where the transferred electron is located in the CT\textsubscript{0} and CT\textsubscript{1} states, respectively. The observation in SERS of the vibration 16a of A\textsubscript{u} symmetry, a silent mode in both IR and Raman spectra, confirms the participation of the D\textsubscript{1}–S\textsubscript{0} transition given that it is related to the non-planar structure of the anion of pyrazine in the D\textsubscript{1} state.

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:\textsuperscript{20}

\[ (EA_A - EA_B) = c \beta (V_{\text{max},A} - V_{\text{max},B}) \]  \hspace{1cm} (4)

If no experimental data on EA are available, \textit{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):\textsuperscript{36}

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

The correlation between the electron affinities and the \(V_{\text{max}}\) of a set of molecules can be found in Ref. 20.
CONCLUSION

In this work, the relevance of the CT mechanism in the SERS spectra of aromatic molecules is demonstrated, which allows this technique to be used to study CT processes and to establish the electronic properties of adsorbates in their doublet states, such as relative stabilities, geometries and vibrational wavenumbers.

It has been confirmed that the vibrational activity in SERS-CT depends on the same factors as in other types of spectroscopy such as RR, absorption or fluorescence, namely Franck-Condon and Herzberg-Teller contributions related to the A- and B-terms in RR. Moreover, the previous discussion shows the usefulness of simple "ab initio" calculations to understand the complex and differentiated behaviors observed in SERS. A more detailed discussion of the usefulness of "ab initio" calculations in order to understand SERS results can be found in Ref. 37.

These conclusions shed some light on the origin of the SERS enhancement and on some still open questions related to single-molecule detection by using SERS experiments. It supports the hypothesis that the large anti-Stokes intensities observed in the SERS spectra of several molecules is due to resonance or near-resonance processes involving CT states of the adsorbate surface complex and negates other alternatives based on uncommonly large Raman cross-sections or very intense local fields.

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