Complete analysis of the surface-enhanced Raman scattering of pyrazine on the silver electrode on the basis of a resonant charge transfer mechanism involving three states

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(Received 26 May 1999; accepted 14 December 1999)

A new general procedure to interpret surface-enhanced Raman scattering (SERS) spectra has been developed in order to clarify the controversy concerning the relevant enhancement mechanism of this type of spectra. The analysis consists of detecting the presence of the charge transfer (CT) enhancement mechanism by correlating the most enhanced SERS bands with the ab initio calculated geometries (ΔQ) and vibrational frequencies (Δν) of the isolated molecule and its radical anion. This CT mechanism is assumed to be identical to that of resonance Raman between the electronic ground state of the metal–adsorbate complex and charge transfer excited states. We consider that these excited states arise when one electron is transferred from the metal to pyrazine. For this reason, they have been labeled from the point of view of pyrazine on the basis on the symmetry of the doublet states of its radical anion. The SERS spectra of pyrazine recorded on silver surface at several electrode potentials have been analyzed on the basis of the Franck–Condon and Herzberg–Teller contributions related to 2B_{3u}^{-1}A_{g} and 2A_{u}^{-1}A_{g} transitions. A great deal of experimental facts related to the relative enhancement of in-plane A_{g}, B_{3g}, and B_{1u} modes as well as out-of-plane B_{3u}, B_{2g}, and A_{u} vibrations has been explained. Likewise, it is possible to account for the observation of Raman inactive fundamentals as well as the influence of the forbidden 2A_{u}^{-1}A_{g} transition on the SERS spectra if the symmetry of the metal–adsorbate complex and the nonplanarity of the 2A_{u} state are taken into account. All the results point out that the CT mechanism is mainly responsible for the SERS features of this molecule studied here.

I. INTRODUCTION

In order to account for the selective enhancement of some bands in surface-enhanced Raman scattering (SERS) as well as for its rather complex dependence on the experimental conditions, a series of selection rules have been proposed over the last 20 years on the basis of different mechanisms which up to date have explained only partially the observed facts. Nowadays, it is widely accepted that SERS is a very complex phenomenon which has its origin in two main contributions, the so-called electromagnetic (EM) mechanism and the charge transfer (CT) mechanism. That classification is rather arbitrary and should be understood only as a simplification to study the problem until a unified model, able to put together both mechanisms, is available. Anyway, we have followed the usual approach separating these two kinds of mechanisms although, as we shall see later, the SERS band of pyrazine assigned to mode 1;ν_{ring} is a relevant example showing that both contributions should be taken into account as a whole. In this paper the term “EM mechanism” should be understood as involving all the non-CT contributions to the enhancement of the Raman bands, including the enhancement of the electromagnetic field in the interphase which determine only the absolute Raman intensity, not the relative intensities which are the subject of this work.

Both mechanisms produce selection rules able in principle to explain the observed selective enhancement independently, therefore, a particular SERS spectrum may be analyzed on the basis of each one. Nevertheless, the choice of the relevant selection rules is rather arbitrary given that up to date there is not a trivial way to know the relative contribution of each mechanism in a particular experiment. For instance, in the selective enhancement of 6a, 8a, and 9a fundamentals of pyridine both CI (Ref. 3) and EM (Ref. 4) selection rules have been alternatively applied. Consequently, it is not at all evident which kind of information can be got when the relative SERS intensities of a particular spectrum are analyzed: either the relative orientation of the adsorbate with respect to the metal surface (EM) (Refs. 2, 5) or instead some properties related to the electronic states involved in a charge transfer process (CT).1,6

The CT mechanism has been proposed by Lombardi et al.7 amongst others and assumes that the transfer of an electron from the Fermi level of the metal to an unoccupied molecular orbital of the adsorbate or vice versa is possible depending on the energy of the photon and the electric potential of the interphase. It has been shown that the transfer takes place from the metal to the molecule in pyridine and...
related compounds as well as that the amount of charge transferred should be one electron given that the results from EELS experiments on benzene under resonance conditions agree with those of the SERS spectra recorded on silver or sodium.\textsuperscript{2,9} In both types of experiments the molecule remains vibrationally excited with respect to the same set of fundamentals. Under such experimental conditions the transient state in SERS should be analogous to the radical anion of the adsorbate molecule.\textsuperscript{2} Unfortunately, the proposed selection rules\textsuperscript{10} for EELS under resonance conditions have been developed on the basis of symmetry considerations and are restricted almost exclusively to benzene, the analysis by Creighton of the spectrum of pyridine being one of the very few cases where these qualitative CT rules have been successfully applied to interpret a SERS spectrum.\textsuperscript{3}

A SERS-CT mechanism similar to a resonance Raman (RR) process between the electronic ground state of the adsorbate and charge transfer levels has been proposed.\textsuperscript{2,12} Therefore, the potential energy surfaces (PES) of the involved states will determine the relative intensities of the SERS bands, just as occurs in RR and other types of electronic spectroscopies. Usually, one consider that the most enhanced Raman lines under resonance conditions correspond to totally symmetric modes related to the displacement of the minima of the PES of the two involved states. This simple rule is derived from the $A$-term in RR scattering\textsuperscript{13} and gives rise to Tsuboi’s Rule\textsuperscript{14} that allows for the deduction of the molecular geometry of the excited states from the Raman excitation profiles (REP). It is by application of this RR rule to the CT mechanism that we have recently analyzed the enhancement of the totally symmetric fundamentals in the SERS of pyrazine,\textsuperscript{15,16} pyridine,\textsuperscript{15,17} and 2-methylpyridine [Ref. 16(b)] recorded on a silver electrode. For this, we have assumed that the excited state corresponds to the radical anion of the adsorbate which is denominated as the $D_0$ state provided that it is a doublet in its electronic ground state and then the $ab$ $initio$ optimized geometries have been computed at several levels of theory. The differences between the equilibrium geometries of the anion and the neutral molecule in their respective ground states, $D_0$ and $S_0$, have been quantified by means of the $\Delta Q$ vector that represents the displacement of the minima in the PES of the respective states along each normal mode. For instance, using these $ab$ $initio$ results it has been possible to give account of the following facts: (1) why the bands assigned to the 6a, 1, 9a, and 8a vibrations can become very strong in the SERS of pyrazine and why the 2$\omega$ (CH), $A_g$ mode is very weak; (2) why these same vibrations show a similar enhancement in the SERS of pyridine in spite of the fact that this molecule has lower symmetry and therefore possesses a greater number of totally symmetric vibrations, and (3) why the enhancement of this set of fundamentals is observed at more negative electrode potentials in pyridine than in pyrazine. In both molecules the 6a, 1, 9a, and 8a fundamentals are the only ones that show significant $\Delta Q$ values for which we have proposed that these displacements can be used as semi-quantitative selection rules for the CT mechanism.\textsuperscript{15}

In this work we have discussed the origin of the activity of all the observed bands in the SERS of pyrazine, $A_g$, $B_{3g}$, $B_{1g}$, $B_{2g}$, and $A_u$ vibrations, and we understand that this is the first complete analysis of the SERS activity of the vibrations of a molecule on the basis of the CT mechanism. Concerning the totally symmetric vibrations, it has been possible to separate the EM and CT contributions by taking as a reference for measuring the relative intensities a vibration for which a small $\Delta Q$ value is calculated. In this way, the effect of the charge transfer will be more evident and the EM contribution to the relative intensities of a spectrum can be estimated in order to allow comparison of the experimental and the theoretical SERS-CT intensities calculated from the peti- colas’ equation.\textsuperscript{17} This approximate equation allows for the estimation of the relative intensities in resonance Raman for those $A$-term active vibrations with significant $\Delta Q$ values. Moreover, this work contains novel contributions to the systematic analysis of a SERS spectrum; first, a second excited state is taken into account in the discussion of the results and second, the activity of a fundamental in a SERS-CT process is related to the displacements of the equilibrium minima of the PES ($\Delta Q$) as well as to the shifts of the vibrational frequencies ($\Delta \nu$) in the different states involved. On this basis, it is possible to explain a great deal of details in the SERS of pyrazine amongst which one can emphasize the activity of several fundamentals usually much weaker than the totally symmetric modes. In this respect, it is important to stress the observation of silent modes in Raman, for instance the 16a vibration of $A_u$ symmetry, whose activity could be explained on the basis of nonradiative processes, that hypothesis being alternative or complementary to the previously reported ones,\textsuperscript{1,2} based either on the existence of an electric field gradient in the interphase or on the descent in symmetry caused by the formation of a surface complex.\textsuperscript{18} Finally, our analysis has been carried out on the basis of $ab$ $initio$ calculations which in turn constitute the first systematic study on the molecular structure and the force field of the pyrazine anion in its electronic ground state ($D_0$) and in its first excited doublet ($D_1$).

II. EXPERIMENT

The chemical reagents (Aldrich) were of the highest available purity and pyrazine was purified at reduced pressure in a Büchi GKR-51 distillator. IR spectra were obtained on a Perkin–Elmer 1760 X FTIR spectrophotometer and Raman spectra were recorded in the 4000–100 cm$^{-1}$ range with a Jobin–Yvon U-1000 spectrometer fitted with a cooled Hamamatsu 943-03 photomultiplier. SERS spectra were recorded on a pure silver electrode (Metals Preciosos) mounted in an electrochemical cell with a platinum counter electrode (Metals Preciosos) at different potentials measured vs a saturated Ag/AgCl/KCl reference electrode (Prin- centon Applied Research, PAR K0260), to which all the electrode potentials are referred to. A PAR model 173 potentiostat and a PAR model 175 programmer have been used to control the electrode potentials. Previous to the recording of the SERS, the working electrode was polished with 1.00, 0.30, and 0.05 µm alumina ( Büeler) and then electrochemically roughened by maintaining it at a potential of $-0.50$ V and then subjecting it to ten 2 s pulses at $+0.60$ V in a KCl.
(1.0 M) aqueous solution. Once the surface had been activated, the SERS spectra have been obtained from an aqueous solution of pyrazine (0.1 M) and KCl (1.0 M) in degassed, deionized, and triply distilled water using the 514.5 nm exciting line from a Spectra Physics 2020 Ar⁺ laser with an effective power of 30 mW reaching the sample.

III. THEORY

A. Analysis of the SERS on the basis of a resonant charge-transfer model

Besides the presence of any CT mechanism in SERS is still under discussion, its nature is in addition an open question which has been the subject of several proposals. Amongst all of them we shall discuss two different CT mechanisms.

1. A Raman resonance charge transfer mechanism (RR-CT) involving the formation of a surface metal–adsorbate complex strong enough as to have to consider both subsystems as a whole. The resonance takes place between the electronic ground state of the complex and new excited CT states equivalent to those observed in inorganic complexes. The vibrational frequency shifts observed in SERS support this mechanism as well as the detection of these new CT transitions of the complex in solid–gas interphases. The trouble is that the CT states are not characterized at all, and this is why it is assumed the hypothesis that in benzenelike molecules those states arise from the donation of one electron from the metal for the adsorbate.

2. Let us suppose that pyrazine is complexed to a lone silver atom on the metal surface, as established in Otto’s adatom model. The ground state of this system is a doublet given that silver atom possesses one unshared electron which is completely transferred to the adsorbate to give doublet CT excited states in turn. This RR-CT process is exclusively photonic and therefore electronic transitions should obey the electric dipole selection rules as occurs in RR, preserving the multiplicity of the systems ($\Delta S=0$). If we accept that the unshared electron is located on the silver atom in the ground state of the complex, while it is located on the adsorbate in the CT excited states. Then, from the point of view of the adsorbate, the electronic transition takes place between the neutral molecule ($S_0$ electronic ground state of the adsorbate) and its anion ($D_0$ electronic ground state of the adsorbate). When the manuscript establishes that $D_0 - S_0$ transitions are allowed or not by the electric dipole selection rules, it has to be understood that in this RR-CT mechanism, the transitions occurring in the complex have been labeled from the point of view of the adsorbate. In this context, whether a particular transition is either allowed or forbidden must be determined only by the orbital part of the symmetry of the $D_i$ and $S_0$ states of the adsorbate, the multiplicity being ignored.

3. The second of the proposed CT mechanism contains nonradiative steps, and it is termed NR-CT. It looks like the RR-CT mechanism but now the metal and the adsorbate do not link as a complex and they have to be seen as two independent subsystems. Under such conditions, the formation of pyrazine radical anion involves necessarily two nonradiative steps to allow for the transfer of one electron. Obviously, in this mechanism, the formation of the radical anion ($D_0$ state) from the neutral molecule ($S_0$ state), in other words, the $D_0 - S_0$ transition, do not obey the electric dipole selection rules. For instance, multiplicity is not preserved. This NR-CT mechanism is shown schematically in Fig. 1 in five steps. (a) First, the incident laser photon is annihilated exciting an electron in the Fermi level (FL) of the metal. (b) The second step corresponds to a nonradiative process (NR$_1$) in which the electron is transferred to vacant levels in the adsorbate. The combined effect of the energy of the photon together with that of the Fermi level in the metal, which can be regulated by controlling the electric potential of the interphase, acts in a similar way to the tunable source of electrons in an EELS experiment, what explains that the results of these two types of spectroscopy under resonance conditions are comparable. When the electron is transferred to a vacant orbital of the neutral molecule such as pyrazine, the corresponding radical anion is formed (step c1), on whose PES the system transitorily remains (step c2) until the electron returns to the metal by another nonradiative process (NR$_2$). If the neutral molecule appears to be vibrationally excited (step c3) the annihilation of the electron–hole ($e^-h$) pair in the metal gives rise to a Raman photon (step d).

Both mechanisms involve the formation of pyrazine radical anion, which is a necessary condition derived from experimental evidences. In both mechanisms that formation of the anion is related to the $D_0 - S_0$ transition in pyrazine, but in the RR-CT mechanism both states must be considered states of the metal-adsorbate complex, although termed from the point of view of the adsorbate. In spite of the similarity of both CT mechanisms, it is necessary to take into account the influence of the adsorption on the molecular structure in the RR-CT mechanism, this may be the cause for the symmetry point group in SERS-CT does not match with that of the isolated molecule relevant in the analysis of its Raman or RR spectra, and the dual character of the NR-CT mechanism given the presence of both radiative (steps a and e of Fig. 1) and nonradiative processes (steps b and c) that can give rise to the violation of the Raman and/or the electronic selection rules.

Although the vibrational selection rules in RR can be
applied only to the RR-CT mechanisms, some quite similar rules based on Franck–Condon (A-term) and Herzberg–Teller (B-term) factors have been involved to analyze vibrational activity in EELS experiences of benzene under resonant conditions, that experiment being essentially equivalent to the NR-CT mechanism. Just as occurs in RR, the excitation to a stationary state in a SERS-CT process gives rise to the enhancement of the Raman spectrum which selectively affects certain bands. According to the formalism of Albrecht for resonance Raman scattering between the electronic ground state $|g\rangle$ and the excited state $|e\rangle$ the transition polarizability can be written as the sum of four terms of which the first two, namely, the A-term and B-term, are the most important ones.

1. A-term

It is generally accepted that this is the most commonly found contribution, and in order to be nonzero the dipole transition moments associated with the electronic transition $|e\rangle - |g\rangle$ and the products of the vibrational overlap integrals $\langle n'_k|v'_k|v_k|m\rangle$. Franck–Condon factors must be nonzero. This last condition gives rise to the selective enhancement of certain bands in RR, and in order to guarantee nonorthogonality one of the following two conditions must be fulfilled at least: first, there exists a displacement along a given normal coordinate of the minima in the PES of the two states involved in the transition ($\Delta Q_\alpha \neq 0$). Usually, it is accepted that this condition is the most important factor in strengthening a Raman band under resonance conditions and our previous works on the enhancement of the 6α, 8α, and 9α vibrations of pyrazine and pyridine have been based exclusively on these $\Delta Q_\alpha$ displacements. The second condition for the overlap integrals being nonzero is that there is a change in the curvature of the PES, i.e., the fundamental $k$ has different vibrational frequencies in the two states ($\Delta v_k \neq 0$).

2. B-term

Another factor that can affect the electronic structure and therefore the PES of the two states is the existence of vibronic coupling (Herzberg–Teller contribution) of the excited state $|e\rangle$ with another excited state $|s\rangle$ or with several excited states, giving rise to the B-term. Generally speaking, one considers that the effect of the B-term is smaller than that of the A-term and in order that this term is non-zero the transition from the ground state $|g\rangle$ to the $|e\rangle$ and $|s\rangle$ excited ones must be allowed by the electric dipole mechanism selection rules. The symmetry of these coupling modes $\langle \Gamma' \times \Gamma' \rangle = \Gamma^\prime_\alpha$ is such that when the molecule is distorted with respect to these coordinates the states $|e\rangle$ and $|s\rangle$ belong to the same symmetry species and their PES repeat, this repulsion gives rise to a change in the shape of the respective PES and therefore, in the vibrational frequencies. The strength of the coupling is inversely proportional to the energy gap between the coupled states $|e\rangle$ and $|s\rangle$ and three cases of weak, strong and very strong vibronic coupling can be seen in the Fig. 2 where the unperturbed and perturbed PES have been drawn as broken and solid lines, respectively; the coupling in the case c is so strong that the curvature of the PES is inverted in the lower state and a double minimum appears; under these circumstances a descent in symmetry is produced if the coordinate $Q_k$ is nontotally symmetric and therefore, these Herzberg–Teller factors can affect the vibrational frequencies ($\Delta v_k \neq 0$) and in extreme cases, the location of the minima of the PES ($\Delta Q_k \neq 0$).

Taking into account the B-term when analyzing a RR spectrum requires the introduction of a third state into the discussion. This circumstance is almost unavoidable when the excited state in a SERS-CT process corresponds with the radical anion of a molecule like pyrazine, which is structurally quite similar to benzene. The benzene radical anion is one of the most characteristic examples of strong vibronic coupling, since there is no energy gap between the states $|e\rangle$ and $|s\rangle$ given that the LUMO of the neutral molecule is doubly degenerate. Under these circumstances the Jahn–Teller theorem establishes that the benzene must distort in order to remove the degeneracy and these molecular deformations are just those that play an important role in electron impact experiments under resonance conditions as well as in the SERS spectra on silver or sodium, as was noted by Otto.

3. Electronic transitions involved in the SERS-CT process

The presence of heteroatoms in the ring removes the degeneracy in the ground state of the pyrazine anion although the gap between the resolved levels remains small, for which in these cases it is referred to as pseudo-Jahn–Teller effect. If the energy of the $D_0$ state is close to that of the $D_1$ state Franck–Condon and Herzberg–Teller factors related to the two possible transitions $D_0 \rightarrow S_0$ and $D_1 \rightarrow S_0$ should be taken into account, although the role of the $D_1$ excited doublet is going to be qualitatively different if the RR-CT mechanism is relevant in the CT process. The ground electronic state of neutral pyrazine is $S_0 \equiv A_g^0$ whilst the symmetries of the anion in the $D_0$ and $D_1$ states are $2B_{3u}$ and $2A_v$, respectively if the molecular point group remains $D_{2h}$. On this basis, the $2B_{3u} \rightarrow A_g$ transition is allowed by

![Figure 2](image-url)
the electric dipole mechanism selection rules, whilst the \(^3A_u^1A_g^1\) transition is not. Therefore, the influence of the \(D_1\) state in the SERS spectra should be much smaller than that of the \(D_0\) state if the RR-CT is the relevant mechanism, given that nonradiative transitions of the NR-CT mechanism do not seem, in principle, to obey such strict selection rules as the electric dipole ones are. Irrespective of this, the effect of the \(D_1\) in the RR-CT mechanism cannot be discarded because (1) the effects of vibronic coupling that can activate transitions that are, in principle, forbidden by the electronic selection rules, (2) the possibility of a descent in the molecular symmetry in the \(D_1\) states and (3) the effect of the adsorption on the molecular point group.

B. Method of analysis

The lack of data referring to the equilibrium structures or to the vibrational frequencies of the anions of molecules similar to pyrazine makes it necessary to carry out \(ab\ initio\) calculations of the optimized geometries and the force field of the adsorbate in the \(S_0\), \(D_0\), and \(D_1\) states. If the most enhanced SERS bands correspond with those vibrations for which significant \(\Delta Q\) or \(\Delta v\) values have been calculated, we shall be in position to confirm the participation of a resonant charge transfer process given that the \(A_\nu\) as well as the \(B\)-terms can give rise to the same effects, \(\Delta Q \neq 0\) and/or \(\Delta v \neq 0\).

1. Changes in the molecular geometry (\(\Delta Q \neq 0\)) and in the vibrational frequencies (\(\Delta v \neq 0\))

The displacements between the minima of the \(S_0\) and \(D_1\) states are expressed as a function of the normal coordinates of the ground state by the relationship,

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

where \(L^{-1}\) is the inverse of the normal mode matrix of the \(S_0\) state calculated from the corresponding \(ab\ initio\) force field and \(\Delta R\) is a vector that contains the differences between the optimized geometries of the states involved in the \(D_1\rightarrow S_0\) transitions.\(^{15\text{a,b}}\) These \(\Delta Q\) can be used to calculate the relative intensity of a Raman line under resonance conditions due exclusively to changes in the equilibrium structures related to the \(A\)-term by using the Peticolas’ equation,

\[
I_i = K \Delta Q_i^2 v_i^3,
\]

where \(K\) is a constant and \(v_i\) is the vibrational frequency in the \(S_0\) state.

The \(ab\ initio\) force field calculation for the \(S_0\), \(D_0\), and \(D_1\) states will allow for the determination of those normal modes that show significant vibrational frequency shifts derived from the \(A\)- and \(B\)-terms. Given that the fundamentals of different electronic states will be compared, we have calculated the Duschinski matrix\(^{27}\) from the \(L\)-matrices of neutral pyrazine (\(S_0\)) and its anion in the \(D_0\) and \(D_1\) states. This matrix relates the fundamentals of the two electronic states and its elements account for the mode mixing that occurs,

\[
D = L^{-1}(D_1) L(S_0).
\]

2. \(ab\ initio\) calculations

Calculations have been carried out using the \textsc{gaussian} 94 (Ref. 30) program at several levels of theory in order to establish the minimum level needed to explain the experimental results. In this work we will compare the CASSCF/3-21G, 6-31+G, and 6-31+G* calculations for the neutral molecule with those of the anion in its \(D_0\) and \(D_1\) states; the active space includes the six \(\pi\)-type valence molecular orbitals (2\(B_3g\), 2\(B_2g\), 1\(A_u\), and 1\(B_1g\)\(^{25}\)) with six or seven electrons in the neutral molecule or its anion, respectively. Likewise, UHF calculations of the geometries of the anion in the \(D_0\) and \(D_1\) states have been carried out with the aforementioned basis sets and with the 6-311+G** one and such results have been compared with the respective RHF ones of the neutral molecule.\(^{31}\) The force field for the \(S_0\), \(D_0\), and \(D_1\) states have been also calculated at the same levels of theory used for the geometry optimizations. Finally, it must be mentioned that the difference between the \(ab\ initio\) energies of the \(S_0\), \(D_0\), and \(D_1\) states in different molecules can be particularly useful in order to foresee the range of electrode potentials over which it will be possible to detect the CT mechanism in a SERS (\(\Delta E(D_0\rightarrow S_0)\)) and the relative influence of the \(D_1\) state (\(\Delta E(D_1\rightarrow D_0)\)).

IV. RESULTS AND DISCUSSION

A. Assignment of the vibrational spectrum of neutral pyrazine in the electronic ground state (\(S_0\))

In order to obtain a reliable assignment of the vibrational spectrum we have used the RHF/3-21G force field according to the scaled quantum mechanical force field methodology (SQMFF) of Pulay et al.,\(^{32}\) since it has been confirmed that this level of theory is sufficient for this kind of molecule.\(^{33}\) A figure with the internal coordinates and two tables, one with the independent internal coordinates and refined scale factors for the RHF/3-21G force field and the other with the vibrational frequencies of the IR and Raman spectra of pure pyrazine and its aqueous solution and the contributions to the potential energy distribution matrix (PED) have been submitted to EPAPS.\(^{51}\) The assignment derived from the scaled force field can be seen in Table I and basically coincides with that previously proposed by ourselves\(^{34}\) except for the 16\(a^1\); \(\tau_{ring}\) \(A_\nu\) mode whose frequency should be lower than the 16\(b^1\); \(\tau_{ring}\) \(B_{3g}\) vibration in agreement with other authors.\(^{5,35}\)

Usually the off-diagonal force constants are affected in the SQMFF procedure by the geometric mean of the two diagonal scale factors to which it is related to. Nevertheless, in order to adjust the frequencies of the ring stretching vibrations, and especially the 14\(a^1\); \(\tau_{ring}\) \(B_{2u}\) mode, in the case of benzene\(^{37}\) or pyrazine\(^{15a}\) it has been also necessary to adjust independently an off-diagonal factor that affects the coupling of \(v_{ring}\) coordinates in the ortho, meta, and para positions. That is due to the fact that the RHF force field overestimates the coupling that occurs between the ground electronic state and the first \(1B_{2u}\) excited singlet of these two molecules. The RHF/3-21G frequency calculated for the 14\(a^1\) is not adequately corrected by multiplying it by the factor 0.90,\(^{36}\) which gives rise to the need to adjust independently an off-
TABLE I. Frequencies and relative intensities of the Raman bands of pyrazine in aqueous solution and SERS spectra at several electrode potentials.

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<td>366</td>
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| a 1 M aqueous solution.  
 bElectrode potentials measured vs saturated Ag/AgCl/KCl reference electrode.  
 c Frequencies in cm⁻¹.  
 dThe intensities are measured as the height of the bands. The intensity of the vibration 2;ν(CH) has been arbitrarily set equal to 100.  
 e RHF/3-21G scaled frequencies.  
 f 1, stretching; δ and γ, in-plane and out-of-plane bending; τ, torsion.

B. Raman and SERS intensities

The region between 100 and 1700 cm⁻¹ of the Raman of the 0.1 M aqueous solution of pyrazine can be seen in Fig. 3. This spectrum is dominated by the strong band corresponding to 1;ν(CH) mode whilst the remaining bands have very weak intensities. The same figure shows also the SERS spectra recorded between 0.00 and −0.75 V which have been shown as is usual for this type of work in such a way that the strongest band exhibits the same height in all of them. The most enhanced SERS spectra are those recorded at −0.50 and −0.25 V showing the best signal/noise ratio, while at more positive or negative electrode potential this ratio decreases. The broad SERS band at ~240 cm⁻¹ could be alternatively assigned to the stretching of Ag—Cl or Ag—N bonds since very close frequencies have been proposed for both of these vibrations. Three SERS bands are also recorded at about 600, 1200, and 1600 cm⁻¹, that are clearly the most enhanced SERS spectra are those recorded at 0.0 V, 0.25 V and 0.50 V. The region between 100 and 1700 cm⁻¹ of the Raman of the 0.1 M aqueous solution of pyrazine can be seen in Fig. 3. This spectrum is dominated by the strong band corresponding to 1;ν(CH) mode whilst the remaining bands have very weak intensities. The same figure shows also the SERS spectra recorded between 0.00 and −0.75 V which have been shown as is usual for this type of work in such a way that the strongest band exhibits the same height in all of them. The most enhanced SERS spectra are those recorded at −0.50 and −0.25 V showing the best signal/noise ratio, while at more positive or negative electrode potential this ratio decreases. The broad SERS band at ~240 cm⁻¹ could be alternatively assigned to the stretching of Ag—Cl or Ag—N bonds since very close frequencies have been proposed for both of these vibrations. Three SERS bands are also recorded at about 600, 1200, and 1600 cm⁻¹, that are clearly enhanced with respect to the Raman spectrum of the aqueous solution at whatever electrode potential. These bands correspond with the totally symmetric 6a;δ_2g, 9a;δ(CH) and 8a;ν_2g modes, respectively, and the band at 1200 cm⁻¹ is split into two components because of a Fermi resonance which will be discussed later. These three fundamentals together with the 1 mode are the strongest ones of the SERS spectra but their intensities have a different behavior upon varying the electrode potential. The most outstanding feature of the SERS in Fig. 3 is the intensity of the band at about 1600 cm⁻¹ assigned to the 8a mode that becomes the strongest band in the spectra recorded at −0.25 and −0.50 V. The band assigned to the 6a mode seems to be enhanced as the electrode potential is made more negative, whilst the 1 vibration is the strongest one at the potentials of 0.00 and −0.75 V. On the other hand, the component of lower fre-
quency of the band at 1200 cm$^{-1}$ becomes weaker at more negative potentials while the behavior of the higher frequency component is just the opposite.

In this respect, it is to be stressed the importance of the way of showing the relative intensities since the study of their changes is just the main objective of this work and the behavior can apparently be different depending on the choice of the band used as a reference. In Raman or RR an internal standard can be used to adequately refer to the intensities, but in SERS the situation is much more complex given that, for instance, the absolute intensity depends, besides other factors, on the method of preparation of the surface as well as on its hysteresis, on the coverage that in turn depends on the electrode potential, etc. For these reasons, and provided that one of the aims is to detect the presence of the SERS-CT mechanism, we propose the use of the band corresponding to that one of the aims is to detect the presence of the SERS-CT mechanism, we propose the use of the band corresponding to the $2\nu(CH), A_g$ mode as an intrinsic standard to refer to the relative intensities. Table I shows the Raman and SERS intensities referred to that mode, measured as the heights of the relative intensities, the presence or absence of charge transfer in SERS can be detected from the plot of these relative intensities vs the electrode potential. Figure 4 shows the relative intensities of the strongest SERS bands with respect to mode 2 vs the electrode potential; this is equivalent to the Raman excitation profiles (REP) where the variable is the energy of incident photon. Whilst in Fig. 3 the $A_g$ fundamentals show a complex behavior, in Fig. 4 all of these vibrations depend on the potential in very similar way, since all of the profiles show a maximum at approximately $-0.50$ V. As these plots can be considered as SERS-CT profiles it is deduced that the range of electrode potentials studied is approximately centered in relation with the charge transfer band whose absorption maximum should be located close to $-0.50$ V. Therefore, the silver-pyrazine system is an especially favorable case since the CT band is centered in the potential range in which the SERS are usually recorded.

Apart from the large intensity of the $A_g$ vibrations, other features of the SERS spectra related to the behavior of the nontotally symmetric fundamentals can be highlighted: (1) these vibrations are weak with the exception of the band at 1520 cm$^{-1}$ assigned to the $6b; \nu_{ring}, B_{3g}$ mode that in the spectra at more negative potentials reaches an intensity comparable with that of the 9a vibration; (2) as in other published works on the SERS of pyrazine some bands of “$u$” symmetry ($B_{1u}, B_{2u}$, and $A_u$) are observed, which means the breakdown of the mutual exclusion principle; (3) in the low frequency region ($<800$ cm$^{-1}$) several out-of-plane fundamentals are observed. From Table I it can be deduced that the relative intensities of these vibrations also reach their maxima at $-0.50$ V except the band recorded at about 355 cm$^{-1}$ corresponding to the $16a; \tau_{ring}A_u$ mode that is not observed at the more positive potentials and exhibits relative intensities of 36 and 47 at $-0.50$ and $-0.75$ V, respectively.

C. Raman and SERS vibrational frequencies

The vibrational frequencies recorded in the Raman of pure pyrazine are blue-shifted in the spectrum of the aqueous solution, especially those of the ring fundamentals such as the $6a$ or $8a$ modes that are shifted up to 20 cm$^{-1}$. This well known behavior in the azines is due to the formation of...
hydrogen bonds between the nonbonding electron pairs on the nitrogen atoms and the solvent molecules.\textsuperscript{35,38} On the same basis, the changes between the vibrational frequencies of the Raman and SERS spectra have been used to propose surface orientations of the adsorbate independently of the enhancement mechanism.\textsuperscript{39} If a molecule such as pyrazine is adsorbed on the metal in a SERS experience by the \( \pi \) system or by the lone electrons on the heteroatom it gives rise to surface orientations that are parallel or perpendicular to the metal, respectively. The adsorption through the \( \pi \) system would have the effect of reducing the frequencies of the ring vibrations due to the bonding character of these electrons.\textsuperscript{39(b)}

The frequencies of the SERS recorded at 0.00 V are comparable to those of the aqueous solution, indicating that pyrazine is coordinated in a similar way in both cases, giving an orientation approximately perpendicular to the metal. Moreover, the dependence of the vibrational frequencies on the electrode potential points out that the molecule is in contact with the metal. Given that all of the bands shift in the same way without splitting one can assume that there exist only one type of surface orientation. As the electrode potential is made more negative all of the frequencies shift towards the red, becoming more similar to those of the pure liquid although, for instance, the 6a mode is still some 20 cm\(^{-1}\) higher in the SERS recorded at −0.75 V than in the Raman. As the metal charge becomes more negative, the backdonation from the silver to vacant levels in pyrazine can be responsible for the decrease of the vibrational frequencies. For these reasons the possibility that the relevant symmetry in SERS is that of the metal–adsorbate complex (\( C_{2v} \)) and not that of the isolated molecule (\( D_{2h} \)) cannot be discarded.

### D. \textit{Ab initio} energies of the \( S_0 \), \( D_0 \), and \( D_1 \) states

The \textit{ab initio} calculated energies of the \( S_0 \), \( D_0 \), and \( D_1 \) states of pyrazine can be seen in Table II. The difference in the \( D_0-S_0 \) energies is related to the resonance condition for the SERS-CT process and the influence of the \( D_1 \) state will depend on the gap between the \( D_0 \) and \( D_1 \) states.

#### 1. \( \Delta E(D_0 - S_0) \)

This difference is always positive independently of the level of theory and this result is not in agreement with the experimental fact that the anion is more stable than the neutral molecule.\textsuperscript{17} This is a well known behavior of the Hartree–Fock methods\textsuperscript{40} and in spite of this fact it has been argued that it is possible to calculate reasonable structural results for the anions even when they incorrectly represent that the electron is unbound.\textsuperscript{41} In our case the quality of the calculated geometries and the frequencies will be tested by their capability to explain the SERS results.

By comparing the RHF and UHF results it can be confirmed that the gap between the two states decreases upon increasing the size of the basis set (1.37 and 0.67 eV for 3-21G and 6-31+G basis sets, respectively) although the inclusion of the first set of polarization functions increases the difference (0.81 eV for the 6-31+G\(^*\) basis set). The CASSCF calculations destabilize the anion by approximately 1 eV with respect to the previous results, whilst the effect of the basis set is identical to that already mentioned. The CASMP2 energies have been calculated as well in order to partially account for the effect of dynamical electron correlation for the corresponding optimized CASSCF geometries and are included in the same Table II. These differences are still positive although they are lower than the CASSCF results especially with the 6-31+G and 6-31+G\(^*\) basis for which \( \Delta E \) of 0.39 and 0.25 eV are obtained, respectively.

#### 2. \( \Delta E(D_1-D_0) \)

The SERS band at 1600 cm\(^{-1}\) in the spectrum of pyrazine recorded at 0.00 V already shows an intensity comparable to that of the 1 mode, therefore, one can deduce that at this potential the system is in resonance or near-resonance with the \( D_0 \) state. The differences between the \textit{ab initio} energies of the \( D_0 \) and \( D_1 \) states can be seen also in Table II and are in the order of or less than 1 eV for which the influence of the \( D_1 \) state in the SERS spectrum recorded at −0.75 V cannot be discarded. An approximate scheme of the relative energies of the states involved has been plotted in Fig. 5. In this situation it is to be expected that the spectra recorded at the most negative potentials show the combined effect of the \( D_0-S_0 \) and \( D_1-S_0 \) transitions whose relative participation will depend on their allowed or forbidden character on the basis of the RR-CT mechanism, as previously mentioned. The calculated values for the \( \Delta E(D_1-D_0) \) differences are much more dependent on the level of theory than the \( \Delta E(D_1-S_0) \) are. Now, upon increasing the size of

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**Table II.** Calculated \textit{ab initio} energies of pyrazine in the \( S_0 \), \( D_0 \), and \( D_1 \) states.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>State ( S_0 ) method</th>
<th>State ( S_0 ) energy (hartrees)</th>
<th>States ( D_0 ) method</th>
<th>( \Delta E ) (eV) ( D_0-S_0 )</th>
<th>( \Delta E ) (eV) ( D_1-D_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
<td>RHF</td>
<td>−261.197 50</td>
<td>UHF</td>
<td>1.37</td>
<td>0.87</td>
</tr>
<tr>
<td>6-31+G</td>
<td>RHF</td>
<td>−262.564 01</td>
<td>UHF</td>
<td>0.67</td>
<td>0.97</td>
</tr>
<tr>
<td>6-31+G(^*)</td>
<td>RHF</td>
<td>−262.690 48</td>
<td>UHF</td>
<td>0.81</td>
<td>1.03</td>
</tr>
<tr>
<td>6-31++G**</td>
<td>RHF</td>
<td>−262.744 52</td>
<td>UHF</td>
<td>0.77</td>
<td>1.04</td>
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<tr>
<td>3-21G</td>
<td>6( \times )6 CASSCF</td>
<td>−261.283 53</td>
<td>7( \times )6 CASSCF</td>
<td>2.26</td>
<td>0.72</td>
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<tr>
<td>6-31+G</td>
<td>6( \times )6 CASSCF</td>
<td>−262.651 45</td>
<td>7( \times )6 CASSCF</td>
<td>1.68</td>
<td>0.78</td>
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<tr>
<td>6-31+G(^*)</td>
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<td>−262.772 01</td>
<td>7( \times )6 CASSCF</td>
<td>1.79</td>
<td>0.83</td>
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<td>6( \times )6 CASMP2(^a)</td>
<td>−261.868 24</td>
<td>7( \times )6 CASMP2(^a)</td>
<td>1.72</td>
<td>0.75</td>
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<td>6-31+G</td>
<td>6( \times )6 CASMP2(^a)</td>
<td>−263.053 67</td>
<td>7( \times )6 CASMP2(^a)</td>
<td>0.39</td>
<td>1.11</td>
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<tr>
<td>6-31+G(^*)</td>
<td>6( \times )6 CASMP2(^a)</td>
<td>−263.463 86</td>
<td>7( \times )6 CASMP2(^a)</td>
<td>0.25</td>
<td>1.18</td>
</tr>
</tbody>
</table>

\(^a\)CASMP2 energies calculated for the optimized CASSCF geometries.
the basis set, the gap increases although only to a small degree; from RHF and UHF calculations, values of 0.87 and 1.03 eV are obtained with the 3-21G and 6-31+G* basis sets, respectively, whilst the respective CASSCF results are in turn somewhat less: 0.72 and 0.83 eV, respectively. The CASMP2 results are the opposite to that found for the $D_0$–$S_0$ differences, the gap increasing upon the size of the basis set increases with values somewhat greater than 1 eV.

**E. Vibrations of $A_g$ symmetry ($A$-term, $\Delta Q \neq 0$)**

The factor that determines the relative intensities of the totally symmetric vibrations is the difference between the equilibrium geometries of the $S_0$ and $D_0$ states.

**TABLE III. Calculated $\Delta Q^*$ displacements between the ab initio optimized structures of pyrazine in the $S_0$; $^1A_g$ state and its radical anion in the $D_0$; $^2B_{3u}$ and $D_1$; $^2A_u$ states.**

<table>
<thead>
<tr>
<th>Basis set</th>
<th>3-21G</th>
<th>3-21G</th>
<th>6-31+G</th>
<th>6-31+G</th>
<th>6-31+G*</th>
<th>6-311++G**</th>
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</thead>
<tbody>
<tr>
<td>State $S_0$:</td>
<td>RHF</td>
<td>CAS$^b$</td>
<td>RHF</td>
<td>CAS</td>
<td>RHF</td>
<td>CAS</td>
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<tr>
<td>State $D_0$:</td>
<td>UHF</td>
<td>CAS$^c$</td>
<td>UHF</td>
<td>CAS</td>
<td>UHF</td>
<td>CAS</td>
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<tr>
<td>$2\alpha;\nu(CH)$</td>
<td>0.016</td>
<td>0.017</td>
<td>0.010</td>
<td>0.011</td>
<td>0.011</td>
<td>0.013</td>
</tr>
<tr>
<td>$8\alpha;\nu_{\text{ring}}$</td>
<td>−0.183</td>
<td>−0.131</td>
<td>−0.164</td>
<td>−0.123</td>
<td>−0.165</td>
<td>−0.126</td>
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<tr>
<td>$9\alpha;\delta(CH)$</td>
<td>−0.172</td>
<td>−0.140</td>
<td>−0.149</td>
<td>−0.120</td>
<td>−0.155</td>
<td>−0.128</td>
</tr>
<tr>
<td>$1\alpha;\nu_{\text{ring}}$</td>
<td>−0.197</td>
<td>−0.144</td>
<td>−0.190</td>
<td>−0.136</td>
<td>−0.149</td>
<td>−0.106</td>
</tr>
<tr>
<td>$6\alpha;\delta_{\text{ring}}$</td>
<td>−0.332</td>
<td>−0.326</td>
<td>−0.262</td>
<td>−0.236</td>
<td>−0.264</td>
<td>−0.268</td>
</tr>
</tbody>
</table>

$D_1$–$S_0$ transition

| State $S_0$: | RHF | CAS$^b$ | RHF | CAS | RHF | CAS | RHF |
| State $D_1$: | UHF | CAS$^c$ | UHF | CAS | UHF | CAS | UHF |
| $2\alpha;\nu(CH)$ | 0.002 | 0.004 | −0.001 | 0.001 | 0.001 | 0.001 | −0.003 | −0.003 |
| $8\alpha;\nu_{\text{ring}}$ | 0.157 | 0.136 | 0.141 | 0.122 | 0.131 | 0.113 | 0.132 | 0.129 |
| $9\alpha;\delta(CH)$ | 0.097 | 0.118 | 0.072 | 0.088 | 0.061 | 0.074 | 0.061 | 0.058 |
| $1\alpha;\nu_{\text{ring}}$ | −0.248 | −0.177 | −0.241 | −0.174 | −0.250 | −0.192 | −0.257 | −0.251 |
| $6\alpha;\delta_{\text{ring}}$ | −0.064 | −0.036 | −0.039 | −0.010 | −0.029 | −0.000 | 0.032 | 0.031 |
| $17\alpha;\gamma(CH)$ | 0.016 | 0.332 | 0.262 | 0.236 | 0.264 | 0.268 | 0.262 |
| $16\alpha;\tau_{\text{ring}}$ | 0.195 |

$^a$Displacements in amu$^{-1/2}$ Å.

$^b$6×6 CASSCF.

$^c$7×6 CASSCF.

$^d$6-311++G** calculations with the planar $D_{2h}$ structure.

$^e$6-311++G** calculations with the nonplanar $D_2$ structure (state $D_1; ^2A$).

**1. Geometries of the $S_0$ and $D_0$ states**

When an electron is transferred to pyrazine to form the anion in a SERS-CT process the nuclei are displaced from their equilibrium positions depending on the shape of the LUMO; $B_{3u}$ molecular orbital that accepts it [Fig. 6(a)]. These geometrical changes are just those shown by the optimized geometries of the $S_0$ and $D_0$ states, presented in a table submitted to EPAPS, and it have been used to obtain the $\Delta R$ vector from the RHF and UHF or 6×6 and 7×6 CASSCF geometric parameters, respectively. Then, the corresponding $\Delta Q$ displacements have been obtained by using the transformation (1) by employing the calculated $L^{-1}$-matrix of the $S_0$ state for each level of theory and are shown in Table III. It can be confirmed that all of the calculations point out that the 6a, 1, 9a, and 8a modes have comparable $\Delta Q$ values, explaining their activity in SERS, whilst the 2; $\nu(CH)$ mode has a much lower value, in agreement
TABLE IV. Comparison between the calculated\(^a\) and experimental relative\(^b\) intensities of the totally symmetric vibrations of pyrazine.

<table>
<thead>
<tr>
<th>State (S_0):</th>
<th>(\text{RHF~CAS}^d)</th>
<th>(\text{RHF~CAS}^d)</th>
<th>(\text{RHF~CAS}^d)</th>
<th>(\text{RHF~CAS}^d)</th>
<th>(\text{RHF~CAS}^d)</th>
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<td>3-21G</td>
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<td>6-31+G</td>
<td>6-31+G*</td>
<td>6-31+G*</td>
</tr>
<tr>
<td>(2\nu(CH))</td>
<td>6</td>
<td>12</td>
<td>3</td>
<td>6</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>(8\nu;\nu_{\text{ring}})</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(9\nu;\delta(CH))</td>
<td>42</td>
<td>54</td>
<td>39</td>
<td>45</td>
<td>42</td>
<td>44</td>
</tr>
<tr>
<td>(1\nu_{\text{ring}})</td>
<td>31</td>
<td>32</td>
<td>36</td>
<td>33</td>
<td>22</td>
<td>19</td>
</tr>
<tr>
<td>(6\nu;\delta_{\text{ring}})</td>
<td>18</td>
<td>34</td>
<td>14</td>
<td>20</td>
<td>14</td>
<td>25</td>
</tr>
</tbody>
</table>

\(^a\)Calculated intensities from the \(\Delta Q\) of the \(D_2h-S_0\) transition by using Eq. (2).
\(^b\)The intensity of the vibration \(8\nu;\nu_{\text{ring}}\) has been arbitrarily set equal to 100.
\(^d\)6×6 CASSCF.
\(^e\)4×6 CASSCF.
\(^f\)1 M aqueous solution Raman spectrum.
\(^g\)SERS recorded at \(-0.50\) V vs Ag/AgCl/KCl saturated reference electrode.

\(^h\)Estimated SERS-CT experimental intensities from Eq. (4).

with the very weaker intensity of this vibration in SERS, which supports its choice as a reference band for the plot of the SERS-CT profiles in Fig. 4.

The size of the basis set and the level of theory does not meaningfully affect the relative \(\Delta Q\) values on which the relative SERS-CT intensities depend; the results obtained from the RHF and UHF calculations with the 3-21G basis set for the 6a, 1, 9a, and 8a modes are \(-0.332, -0.197, -0.172,\) and \(-0.183\) amu\(^{1/2}\) Å, respectively, and with the 6-31+G basis set are \(-0.262, -0.190, -0.149,\) and \(-0.164\) amu\(^{1/2}\) Å. The polarization functions of the 6-31+G* basis set almost exclusively affect the 1 mode decreasing its \(\Delta Q\) value (\(-0.149\) amu\(^{1/2}\) Å), whilst the results obtained with the 6-311+G** basis set are almost the same as those from 6-31+G*. The \(\Delta Q\) values obtained from the CASSCF geometries are systematically smaller than the previous ones except for the 6a mode that shows similar values in both cases and the effect of basis set size for this type of calculations is similar to that already mentioned for the HF results.

As can be seen, the observed intensities in SERS are not noticeably proportional to the \(\Delta Q\) values since the band due to the 6a mode does not become the strongest one in spite of showing the largest \(\Delta Q\) value.

2. SERS-CT intensities for the \(D_2h-S_0\) transition

The SERS-CT intensities calculated from the Peticolas’ equation can be seen in Table IV where it is appreciated that the dependence on the cube of the vibrational frequency corrects, at least partially, the lack of direct correlation between the relative intensities and the \(\Delta Q\) values. All of the results indicate that (1) the band corresponding to the 8a mode should be the strongest one for which it has been used as a reference in this table, (2) the \(2\nu(CH)\) mode should be much weaker than the remaining totally symmetric fundamentals, and (3) the 6a, 1, and 9a modes should have similar intensities and smaller than 50% of that of the 8a band. The calculated intensities qualitatively reproduce the experimental results since in the SERS spectra it can be seen that the 2 mode is much weaker than the remaining \(A_g\) fundamentals, whilst in the Raman spectrum of the solution it is strong; moreover, the band assigned to the 8a mode is the strongest one in the SERS recorded at \(-0.25\) and \(-0.50\) V. The calculated intensities are compared in Table IV with those recorded in the Raman solution and the SERS recorded at \(-0.50\) V which is chosen since it corresponds to the maximum of the profiles in Fig. 4, and it can be seen that the theoretical intensities do not exactly reproduce the experimental behavior; for instance, the intensity of the 1 mode is very much weakened on going from the Raman of the solution (1109) to the SERS (89), but the latter figure is still about three or four times greater than the calculated one, which range from 36 to 19.

3. EM and CT contributions to the intensity of a SERS spectrum

These disagreement between the calculated and experimental intensities could be due to the fact that we are comparing calculated intensities for a SERS-CT process with those measured in a spectrum that can have contributions from both types of enhancement mechanism. If the previously mentioned hypothesis is fulfilled, i.e., the EM mechanism does not significantly affect the relative SERS intensities and additionally, the 2 mode is not enhanced by the SERS-CT mechanism, the EM and CT contributions can be estimated by using a particular spectrum in which the CT mechanism does not take place. Given that all of the SERS of pyrazine in Fig. 3 exhibit SERS-CT features, there is no other possibility that using the intensities of the pure liquid Raman or still better the aqueous solution spectrum,

\[
I_{\text{SERS-CT}} = I_{\text{SERS-EXP}} - I_{\text{SERS-EM}} = I_{\text{SERS-EXP}} - I_{\text{SOLUTION}}.
\]  

(4)

All the involved intensities here should be referred to the \(2\nu(CH)\) mode as occurs in Table I. This procedure affects specifically the bands that are very strong in the Raman of the solution for which in the case of pyrazine only the relative intensity of the 1 mode is affected, as can be noticed from the column headed SERS-CT in Table IV. According to these results, two-thirds of the intensity of this band are due to the EM mechanism and this significant EM contribution gives rise to the anomalous profile of the 1 mode in the more positive potentials region in Fig. 4.

It can be noticed that the agreement between the calculated SERS-CT intensities (8, 100, 49, 19, and 25 for...
vibrations 2, 8a, 9a, 1, and 6a, respectively, from CASSCF/6-31+G* results) and the SERS-CT experimental ones (0, 100, 30, 26, and 41, respectively) is very good, especially when keeping in mind the differences between the relative SERS intensities reported in the literature,\(^\text{15a}\) all the approximations introduced as well as that the intensities have been calculated without adjusting any parameter as is usual in RR.

### 4. Influence of the D\(_1\) state on the intensities of the A\(_g\) modes

In this work we have followed the opposite way to what normally is done in RR, where the \(\Delta Q\) are obtained from the experimental relative intensities recorded in preresonance conditions in order to reduce the influence of other excited states on the relative intensities.\(^\text{42}\) As the SERS-CT calculated intensities correlate very well with those of the maximum of the SERS-CT excitation profile at \(-0.50\) eV, it is concluded that the influence of the D\(_1\) state on the SERS intensities is very weak, in spite of the small energy gap between both doublets states, due to the fact that the D\(_1\)–S\(_0\) transition is forbidden by the electric dipole selection rules in the RR-CT mechanism. In our opinion, an effect of this type could be the reason why the 8a profile in Fig. 4 decays much more quickly than the others as the electrode potential is made more negative. At these potentials the interference would become more important since the system is excited to energy levels much closer to the D\(_1\) state.

The differences between the bond lengths and angles of the equilibrium structures of the S\(_0\) and D\(_1\) states are determined by the shape of the LUMO + 1; A\(_g\) orbital drawn in the Fig. 6(b). The C–C lengths should increase in the D\(_1\) state due to the antibonding interaction of the \(\pi\)-orbitals of the 2–3 and 5–6 pairs of atoms whilst the ring angles do not undergo so important changes as in the D\(_0\) state, the only significant changes in the D\(_1\) optimized parameters being the C–C bond lengths that increase between 0.06 and 0.08 Å in the D\(_1\) state. The corresponding \(\Delta Q\) values obtained with the optimized geometrical parameters of the S\(_0\) and D\(_1\) states can be seen in Table III and it can be confirmed that if the SERS-CT intensities are calculated with these displacements then the agreement with the experimental ones is much worse than for the D\(_0\)–S\(_0\) transition; for instance, the \(\Delta Q\) values for the 6a vibration are much smaller than the previous ones and are in the order of those corresponding to the 2\(_v\)(CH) mode, a non-SERS-CT active fundamental.

### F. Vibrations of B\(_{3g}\) symmetry (\(B\)-term, \(\Delta v\neq0\))

The enhancement of the B\(_{3g}\) symmetry modes, especially the 8b fundamental, in the SERS of pyrazine is due to vibronic coupling between the D\(_0\) and D\(_1\) states of the radical anion ([\(\Gamma_{D0}\times\Gamma_{D1}\)] \(\rightarrow\) 6 \(B\_{3g}\) mode, that has a frequency of \(\approx1700\) cm\(^{-1}\) (RHF) in the S\(_0\) state and 979 cm\(^{-1}\) (UHF) with the 3-21G basis set or \(\approx1100\) cm\(^{-1}\) with more extended basis sets in the D\(_0\) state, which means about a 40% decrease of its vibrational frequency. When the molecule bends according to a B\(_{3g}\) vibration the molecular symmetry reduces from D\(_{2h}\) to C\(_{2v}\), in such a way that both doublets states show the same symmetry (\(\Gamma_{A_g}\) in C\(_{2v}\)) and their surfaces repel giving rise to a similar situation to case b in Fig. 2. The Duschinski’s matrices indicate that the D\(_0\) fundamentals with UHF/3-21G, 6-31+G, 6-31+G*, and 6-311++G** frequencies of 979, 1102, 1123, and 1117 cm\(^{-1}\), respectively, should be related to the 8b mode in the electronic ground state; the corresponding biggest D\(_{ij}\) elements are 0.86, 0.88, 0.88, and 0.89, respectively, indicating that a noticeable amount of mode mixing exists. The 6\(\times6\) and 7\(\times6\) CASSCF calculated frequencies show the same behavior that has been discussed.
2. Vibrational frequencies in the \(S_0\) and \(D_1\) states

The calculated frequencies for the \(D_1\) state indicate once again that is coupled to the \(D_0\) state through the \(8b\) mode. The most important UHF result is that a fundamental is calculated with an imaginary frequency at 1245 \(\text{cm}^{-1}\) with the 3-21G, 6-31+G*, and 6-311+G** basis sets, respectively, that correlate with the 8b mode in the \(S_0\) state since the \(D_{ij}\) coefficients are 0.94, 0.96, 0.97, and 0.97, respectively. This is the only imaginary frequency that is calculated with the first three basis sets, indicating that the \(D_{2a}\) molecular structure for the \(2A_g\) configuration does not correspond with a minimum in the PES, for which this is a similar situation to the lower surface in Fig. 2(c), but all of the attempts to optimize the geometry following the direction of the eigenvector of the imaginary frequency have systematically converged on point \(a\) of Fig. 7, the minimum of the \(2B_{3u}\) surface that is the absolute minimum of the lower PES of the pyrazine anion.

The CASSCF frequencies related to the \(8b\) mode are real instead of imaginary in \(D_1\); 8419, 2862, and 2783 \(\text{cm}^{-1}\) with the 3-21G, 6-31+G, and 6-31+G* basis sets, respectively. This increase in the vibrational frequency is what is to be expected for the upper state in the \(b\) and \(c\) cases in Fig. 2 indicating that the CASSCF minima of the \(2B_{3u}\) (point \(a\)) and \(2A_u\) (point \(b\)) surfaces must be located at the same side of the crossing point with respect to the \(X\) coordinate (Fig. 7). The different behavior of the \(8b\) mode at CASSCF and UHF levels is due once again to the \(8b\) crossover of both surfaces (point \(c\)), which explains why small changes in the calculation method affect so noticeably its frequency.\(^{33}\) The Duschinski’s matrices indicate that the \(8b\) mode is mixed with the \(3\delta(\text{CH})\) fundamental in the doublet states; for instance, \(D_{ij}\) coefficients of 0.33 or 0.47 are obtained for both transitions from RHF and UHF/3-21G calculations. In spite of this result, we have not detected the \(\delta(\text{CH})\) mode in our SERS spectra, but we did detect the \(6b; \delta_{\text{ring}}, B_{3g}\) mode instead.\(^{44}\) The activity of the \(6b\) fundamental must be due to the significant participation of the related \(\delta_{\text{ring}}\) internal coordinate in the PED of the \(8b\) mode in the different electronic states, while \(\delta(\text{CH})\) internal coordinates do not contribute so noticeably.

Summarizing, the different force fields calculated indicate that the activity of the \(8b; \nu_{\text{ring}}, B_{3g}\) vibration in the SERS of pyrazine is due to Herzberg–Teller contributions, but that band always shows a lower intensity than the totally symmetric modes which indicates that the \(B\)-term has less importance than the \(A\)-term in the SERS of this molecule.\(^{45}\) On the contrary, when the Raman spectrum of pyrazine is recorded under near-resonance conditions with the first excited singlet the strongest band is the out-of-plane 10\(a\); \(\gamma(\text{CH}), B_{1g}\) being responsible for the vibronic coupling between the \(S_1; 1B_{3u}\) and \(S_2; 1B_{2g}\) states of the neutral molecule. The fact that the effect of vibronic coupling in the SERS of pyrazine is not so important as in RR, seems to confirm again that the RR-CT mechanism is the relevant one in the SERS-CT process because the \(D_{1} - S_0\) transition is forbidden by the electric dipole selection rules whilst in RR both transitions, \(S_1 - S_0\) and \(S_2 - S_0\), are allowed.

G. Vibrations of \(B_{3u}\) and \(B_{2g}\) symmetry (A-term, \(\Delta\nu \neq 0\))

From the shape of the LUMO [Fig. 6(a)] it can be deduced that a displacement of the nitrogen atoms above or below the plane defined by the four carbon atoms decreases the antibonding interactions between the nitrogen and the contiguous carbon atoms and therefore, the \(B_{3u}\) and \(B_{2g}\) out-of-plane related vibrations will have a lower frequency in \(D_0\) than in \(S_0\). This effect should be more important for the ring torsion modes than for the \(\gamma(\text{CH})\) since the transferred electron locates essentially in the ring. Just as can be expected, the modes \(16b; \tau_{\text{ring}}, B_{3u}\) and \(4; \tau_{\text{ring}}, B_{2g}\) fundamentals exhibit the greatest relative shifts between the RHF and UHF out-of-plane frequencies of the \(S_0\) and \(D_0\) states, amounting to some 35% and 15% of their vibrational frequencies, respectively (Table V) explaining its activity in the SERS spectra and why the \(16b\) mode is the most enhanced out-of-plane vibration. The activity of the \(11; \gamma(\text{CH}), B_{3u}\) mode could be due to mixing with the \(16b\) fundamental in the \(D_0\) state although the calculated Duschinski matrices do not show a noticeable degree of mode mixing. The \(ab\) initio calculated frequencies of the out-of-plane modes of the \(S_0\) and \(D_0\) states depends very little on the basis set size, especially if relative shifts are concerned; the main difference is that the relative shifts of the CASSCF frequencies are some 10% smaller than those corresponding to the HF calculations.

Besides the bands assigned to totally symmetric fundamentals, the strongest SERS band is the one recorded very close to that assigned to the \(9a\) mode, at about 1220 \(\text{cm}^{-1}\) (see Fig. 3 and Table I), that has independently been assigned by Brolo and Irish\(^{37}\) and by ourselves\(^{15(a),34}\) to the \(11 + 16b; A_g\) combination. The unexpected intensity of this band could be due to a Fermi resonance with the \(9a\) fundamental\(^{15(a),37}\) since this effect is very sensitive to the frequencies of the involved vibrations that in turn depend on the electric potential of the surface.\(^{48}\) Anyway, the enhancement of this combination band should be related with the
TABLE VI. Relevant symmetries related with the isolated or complexed pyrazine.

<table>
<thead>
<tr>
<th>Molecular symmetry:</th>
<th>Isolated planar</th>
<th>Isolated nonplanar</th>
<th>Complexed planar</th>
<th>Complexed nonplanar</th>
</tr>
</thead>
<tbody>
<tr>
<td>State $S_0$:</td>
<td>$1A_g$</td>
<td>$1A$</td>
<td>$1A_1$</td>
<td>$1A$</td>
</tr>
<tr>
<td>State $D_{1h}$:</td>
<td>$2B_{1u}$</td>
<td>$2B_3$</td>
<td>$2B_1$</td>
<td>$2B$</td>
</tr>
<tr>
<td>State $D_1$:</td>
<td>$2A_g$</td>
<td>$2A$</td>
<td>$2A_2$</td>
<td>$2A$</td>
</tr>
</tbody>
</table>

Electronic activity$^b,c$

- $D_0 \rightarrow S_0$ transition: $a$ $a$ $a$ $a$
- $D_1 \rightarrow S_0$ transition: $a$ $a$ $a$ $a$

Raman activity$^b$

- $g$-modes in $D_{2h}$: $a$ $a$ $a$ $a$
- $u$-modes in $D_{2h}$: $a$ $a$ $a$ $a$

$^a$Preserving the $C_3(z)$ axis.
$^b$Active; $i\sigma$, inactive.
$^c$Activity in the electric dipole radiation mechanism on the basis of the RR-CT mechanism.

activity of the 11 and 16b modes in the SERS of this molecule that are in turn related with the discussed frequency shift in the $D_0$ state.$^{50}$

H. Vibrations of $A_u$ symmetry ($A$-term, $\Delta \nu \neq 0$ and $\Delta Q \neq 0$)

The same arguments that explain the activity of the $B_{3u}$ and $B_{2g}$ modes can account for the enhancement of the 16a; $\tau_{\text{ring}}, A_u$ vibration in the SERS of pyrazine. If the shape of the LUMO $\rightarrow 1A_u$ orbital is taken into account, the antibonding interactions between the 2-3 and 5-6 pairs of carbon atoms decrease when the planes defined by the 6-1-2 and 3-4-5 atoms rotate around the $C_2(z)$ axis in opposite direction [Fig. 6(b)]. This out-of-plane deformation of $A_u$ symmetry is similar to the 16a mode which shows the most important shifts of the ab initio vibrational frequencies in the $D_1$ state, with UHF frequencies calculated at 311, 160, 22, and 731 cm$^{-1}$ with the 3-21G, 6-31+G, 6-31+G*, and 6-311++G** basis sets, respectively (Table V). According to the latter level of theory, the $A_u$ PES of pyrazine exhibits two different directions of negative curvature in point b of Fig. 7; the one with $B_{3g}$ symmetry already discussed, and the other with $A_g$ symmetry which looks like to the 16a; $\tau_{\text{ring}}$ mode. Following the latter eigenvector of imaginary frequency it is possible to find a stationary point with $D_2$ symmetry only 42 J mol$^{-1}$ more stable than the planar $D_{2h}$ structure, where the imaginary frequency becomes real amounting 100 cm$^{-1}$ what gives an insight of how planar is the PES in the vicinity of point b along that coordinate. If this stationary point is associated with the $D_1$ state, then the $D_1 \rightarrow S_0$ electronic transition remains forbidden by the electric dipole selection rules ($\gamma A \rightarrow -1 A$) in the RR-CT mechanism (Table VI), explaining why the 16a,b pair of vibrations shows a similar enhancement in the SERS spectra in spite of the fact that the 16a show greater changes than the 16b mode; from the 6-311++G** results, $\Delta Q = 0.195$ amu$^{1/2}$ Å and $\Delta \nu = 320$ cm$^{-1}$ values are obtained for the 16a mode associated with the forbidden $D_1 \rightarrow S_0$ transition whilst the 16b mode is only characterized by a $\Delta \nu = 165$ cm$^{-1}$, but related to the allowed $D_0 \rightarrow S_0$ transition, always in the RR-CT mechanism.

Although the 17a and 16a vibrations show high $\Delta Q$ values considering the nonplanar $D_2$ structure, $-0.123$ and $0.195$ amu$^{1/2}$ Å, respectively, for the $D_1 \rightarrow S_0$ transition (Table III, only the 16a mode is observed. It is possible that the 17a band is not observed due to the strong intensity of the 1 mode in all of the SERS. Finally, it is important do not forget that the 16a is the only fundamental which is stronger in the SERS at $-0.75$ V than at more positive potentials. This latter observation confirms the influence of the $D_1$ state at the electrode potentials of $-0.75$ and $-0.50$ V.

I. Vibrations of $B_{1u}$ symmetry

The agreement between the results obtained with both techniques EELS and SERS, supports the hypothesis that a similar mechanism are involved in both types of experiments and therefore, nonradiative processes (NR-CT) could play an important role in the SERS-CT mechanism. This could be responsible for the breakdown in SERS of the electric dipole selection rules or for the observation in Raman of inactive vibrations of '"u"' symmetry, but other alternative possibilities also exist if RR-CT is the relevant mechanism: for instance, we have seen that the descent in the molecular symmetry in the $D_1$ state from $D_{2h}$ to $D_2$ does not upset the forbidden character of the $D_1 \rightarrow S_0$ transition but changes the Raman activity of these fundamentals which become active if the symmetry is $D_2$ as can be seen in Table VI.

Analogous results are reached if one consider that the operating symmetry in SERS is that of the metal–adsorbate complex. If it is assumed that pyrazine adsorbs with orientation perpendicular to the metal through one of the two heteratoms of the ring, the system will belong to the $C_{2v}$ point group. Under these conditions the $D_1$ level will still be dark since its symmetry will be $\gamma A_2$ but all of the vibrations will be Raman active as before (Table VI). As a consequence of the descent from $D_{2h}$ to $C_{2v}$ the $B_{1u}$ vibrations become totally symmetric and can be SERS-CT active through Franck-Condor factors. The $12; \delta_{\text{ring}}, B_{1u}$ and $19a; \delta(CH), B_{1u}$ modes are observed in the SERS with very weak intensity and it would appear reasonable to suppose that the activity of these $B_{1u}$ fundamentals is due to the formation of a surface complex sufficiently strong to assume that these vibrations, and especially the $12$ mode, could be considered as totally symmetric.

Finally, if the formation of the surface complex as well as the non-planar nature of the $D_1$ state are put together it is possible to explain the observation of '"u"’ fundamentals and the participation of the $D_1$ state in the SERS on the basis of the RR-CT mechanism. Under these circumstances the subset of common symmetry operations of the $S_0$, $D_0$, and $D_1$ states are only those generated by the $C_{2}(z)$ axis, and the operating symmetry reduces to $C_2$ (Table VI). Therefore, all of the modes are Raman actives as occurs in $D_2$ or $C_{2v}$ point groups, but now the $D_1 \rightarrow S_0$ transition ($\gamma A \rightarrow -1 A$) is allowed in the RR-CT mechanism by the electric dipole mechanism selection rules. However, the $D_0 \rightarrow S_0$ transition would certainly play a much more important role in the RR-CT process than
the $D_1-S_0$ one since the molecular properties vary very little when pyrazine is distorted along the normal coordinate with an imaginary frequency of $A_u$ symmetry.

V. SUMMARY AND CONCLUSIONS

In this work we have presented the most complete analysis reported up to date of the SERS spectra of a molecule on the basis of a CT model. We have found proofs enough to confirm the presence of the CT mechanism in the here analyzed SERS spectra of pyrazine and it is confirmed that the activity of the fundamentals in SERS depends on the same factors than other types of spectroscopy such as RR, absorption, fluorescence or EELS experiments under resonance conditions; Franck-Condon and Herzberg–Teller contributions related with the $A$- and $B$-terms in RR. This conclusion has been derived on the basis of the agreement between the observed experimental behavior and that which would be expected for a SERS-CT process similar to that of resonance Raman by using the \textit{ab initio} geometry optimization and force field calculations for the neutral molecule as well as for the radical anion, that in the RR-CT mechanism should be equivalent to the transient excited state in RR.

Using the SERS-CT relative intensities we have found that the maximum of the charge transfer band of the silver-pyrazine system is located at about $-0.50$ V when the 514.5 nm exciting line is used. Besides, the electronic transition that originates that band should involve the electronic ground state. This result can be explained in the RR-CT mechanism given that the $D_0-S_0$ transition is forbidden by the electric dipole selection rules; but if the symmetry of the metal--adsorbate complex is taken into account together with the possibility that the $D_1$ state is nonplanar it is possible to explain the breakdown of the Raman selection rules and the observation of effects related with the $D_1$ state in the SERS on the basis of the RR-CT mechanism without resorting to electronic field gradient arguments or to the participation of nonradiative processes (NR-CT) in the CT mechanism.

If future works confirms that the SERS relative intensities of this type of molecules are determined by CT processes it will be necessary to reinterpret many of the already analyzed spectra on the basis of the EM selection rules. Finally, it has to be established that the confirmation of the SERS-CT mechanism in the SERS spectra is going to mean a greater complexity when analyzing the results but it could give rise to a renaissance of this technique if it is used for the systematic study of charge transfer processes or for the characterization of electronic properties of the radical ions of the adsorbate.

ACKNOWLEDGMENT

This research has been supported by the Spanish DGICYT through Project No. PB 96-0697.

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The effect of the spin contamination in the UHF results is not expected to be large given that the eigenvalues of the \( \langle S^2 \rangle \) operator lie between 0.829 and 0.866. This range can be considered as moderate when compared to the value of 0.75 for a pure doublet wave function (Ref. 15).


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45 At point b in Fig. 7 the \( ^1B_{1u} \) and \( ^2A_1 \) UHF/6-311++G** surfaces are separated by 36.3 kJ mol\(^{-1}\) while the gap amounts to 348.9 kJ mol\(^{-1}\) in point a; this indicates that point b should be closer to the crossover and explains why the coupling is so strong that the curvature of the PES respect to the \( F;B_{1g} \) direction becomes negative at this point.

46 In other published works on the SERS of pyrazine the appearance of the 3 mode has been reported although always with weak intensity and weaker than the 6b mode. See Refs. 5, 37, and G. R. Erdheim, R. L. Birke, and J. R. Lombardi, Chem. Phys. Lett. 69, 495 (1980).

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51 See EPAPS Document No. E-JCPSA6-112-709010 for one figure and five tables. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.