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The Influence of the Basis Set Size on DFT Calculations of Surface Complexes for the Assignment of SERS Spectra

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The Influence of the Basis Set Size on DFT Calculations of Surface Complexes for the Assignment of SERS Spectra[#]

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Abstract

Motivation. DFT calculations of surface complex models are able to assist the correct assignment of SERS spectra of compounds strongly chemisorbed on metal surfaces. Till now these calculations have been usually carried out using the LANL2DZ basis set on both the metal and ligand atoms. Due to the reduced size of the LANL2DZ basis set, the frequencies and the normal mode description provided by them are not always accurate. Therefore, the use of a mixed basis set can be a significant improvement in these kinds of calculations. In the present paper we have reported the results of an investigation of the influence of the basis set size on the quality of calculations carried out on surface complex models. The study has been performed on TZ3, because we have already assigned its Raman and SERS spectra in silver colloids with the help of DFT/LANL2DZ calculations.

Method. DFT/BPW91 calculations of the model of the surface complex formed by TZ3 on silver have been carried out with different mixed basis sets varying the size of the basis used on the ligand.

Results. The quality of the calculated results has been critically evaluated on the basis of three important computational parameters: the absolute mean delta, the standard deviation and the maximum delta.

Conclusions. On the basis of the comparison between all the calculations carried out on the model of the surface complex formed by TZ3 on silver, it has been evinced that the best basis set is the LANL2DZ/6–311+G.

Keywords. DFT calculations; mixed basis sets; adsorption models; SERS; silver nanoparticles; triazole.

Abbreviations and notations

SERS, surface enhanced Raman scattering	TZ3, 1,2,3–triazole
DFT, density functional theory	TZ3A, 1,2,3–triazole anion

1 INTRODUCTION

The Surface Enhanced Raman Scattering (SERS) effect is the giant Raman intensity enhancement shown by compounds upon adsorbing on rough metal substrates (usually metals like

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gold, silver and copper). The theoretical explanation of this effect is still a very controversial point, although this technique was discovered more than 30 years ago. However, there is an agreement in the literature that the main enhancement mechanisms are electromagnetic [1] and chemical [2]. According to the first mechanism, the Raman enhancement of a molecule adsorbed on a rough metal substrate is due to the resonance between the excitation wave of the electrons localized at the metal surface and the incident radiation. The induction of an electric field near the metal surface by electron plasma excitation provokes a strong increase of the Raman signal of the molecule adsorbed on the metal surface. On the other hand, the chemical mechanism dictates that the molecular polarizability is strongly increased upon adsorption on the metal surface due to the adsorbate–metal charge transfer.

When the chemical mechanism plays a significant role in the SERS effect, a surface complex is formed and, upon going from the normal Raman to the SERS spectra, some bands undergo sizeable frequency–shifts due to the changes in some force constants of the free molecule, upon bonding to the metal surface. Therefore, these shifts are useful to evaluate the contribution of the chemical effect to the SERS enhancement. In this case, DFT calculations of the vibrational frequencies of surface complexes formed by molecules bound to metal adatoms or adclusters are able to give useful information about the interaction between the adsorbate and the metal surface [3–6]. However, due to the presence of transition metal ions or atoms in these calculations, the LANL2DZ basis set [7] is very often used for all the atoms of the complex. Due to the reduced size of this basis set, the calculated frequencies and the normal mode description are not always accurate. Therefore, the use of a mixed basis set can be potentially a significant improvement. In order to evaluate to what extent the use of mixed basis sets can affect the agreement between experimental and calculated vibrational frequencies, we have planned an investigation on a test molecule, 1,2,3–triazole (TZ3), whose normal Raman and SERS spectra in silver and gold colloids have been completely assigned with the help of DFT/BPW91 (LANL2DZ) calculations [3,4]. We have decided to present here the calculations carried out on the model of the surface complex formed by TZ3 on the silver colloidal nanoparticle surface when no halide anions have been added to the sol [3]. In this case we found that the compound adsorbed on silver in its deprotonated form; therefore the calculations were carried out on the complex constituted by the anion of TZ3 (TZ3A, hereafter) bound to two Ag^+ , because this model provided the best agreement between calculated and experimental frequencies.

In the present manuscript, a critical comparison between the calculated data obtained by varying the size of the basis set used on the atoms of TZ3A is reported in order to find the best compromise between accuracy and computational time in the calculations of surface complex models.

2 MATERIALS AND CALCULATIONS

The calculations of $[\text{TZ3A}(\text{Ag})_2]^+$ (see Figure 1) were carried out using GAUSSIAN 03 package [8]. Optimized geometries were obtained at the density functional level of theory with the Becke's 1988 exchange functional [9] in combination with the Perdew–Wang 91 gradient–corrected correlation functional [10] denoted BPW91. Calculations with this hybrid functional provided a satisfactory agreement between calculated and experimental vibrational frequencies, without using scaling factors, as found in other cases [3,4]. By allowing that all the parameters could relax, the calculations converged to optimized geometries, which corresponded to true energy minima, as revealed by the lack of imaginary values in the vibrational mode calculations.

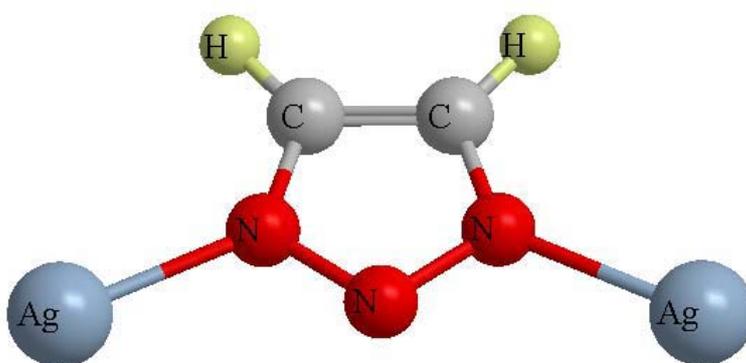


Figure 1. Optimized structure of the $[\text{TZ3A}(\text{Ag})_2]^+$ complex calculated with the mixed basis set constituted by LANL2DZ on Ag atoms and 6–311G+ on the atoms of TZ3A.

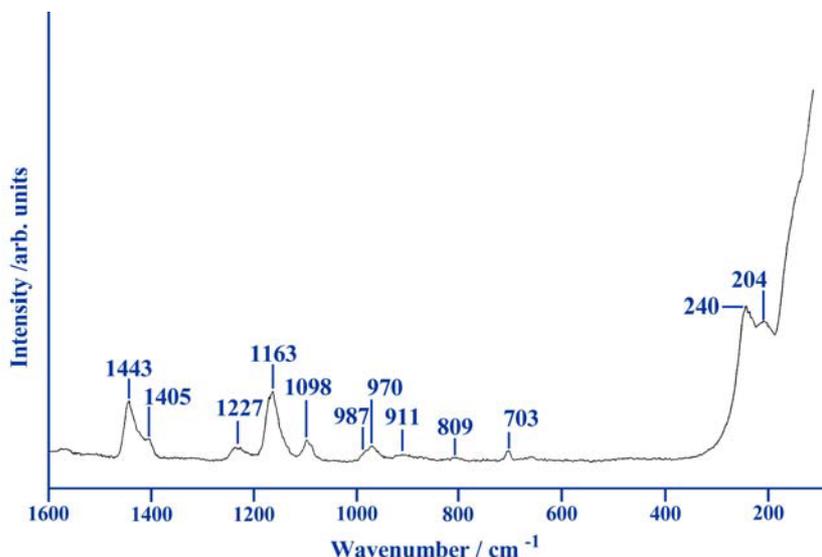


Figure 2. SERS spectrum of TZ3 adsorbed on Ag sols.

The harmonic vibrational frequencies were calculated at the same level of approximation using the parameters corresponding to the structure obtained from the optimization step. Force constants

in internal coordinates, which were calculated according to the procedure described elsewhere [11], were used for a standard zero-order GF-matrix treatment from which vibrational frequencies and potential energy distributions (PEDs) were obtained. In Figure 2 the SERS spectrum of TZ3 in silver colloid without addition of halide anions is displayed. SERS data compared with the calculated results are reported in Table 1. The table of the PEDs is not reported here, but it can be provided by authors upon request.

Table 1. SERS data, calculated frequencies with different basis sets for [TZ3A(Ag)₂]⁺ surface complex model

$\tilde{\nu}^a_{\text{obs.}}$	LANL2DZ	LANL2DZ/ 6-31G	LANL2DZ/ 6-311G	LANL2DZ/ 6-311+G	LANL2DZ/ 6-311G*	LANL2DZ/ 6-311+G*	LANL2DZ/ 6-311++G**
1443	1441	1447	1439	1434	1467	1464	1459
1405	1362	1377	1370	1372	1392	1390	1386
1227	1195	1206	1195	1196	1230	1226	1225
1163	1166	1164	1155	1157	1159	1186	1185
1098	1119	1123	1117	1115	1087	1086	1084
987 (sh)	1015	1001	1003	1002	1074	1071	1071
970	957	971	968	969	976	972	971
911	950	957	956	956	956	953	952
809	861	869	865	857	823	827	834
703	659	671	672	669	684	682	682
240	274	273	276	270	267	261	261
204	188	190	190	185	185	180	180

3 RESULTS AND DISCUSSION

In quantum mechanics calculations, the use of larger basis set is not always a guarantee of better results: one of the most important thing to achieve is the correct balancing between the method used and the basis set dimension. In the case of calculations of complexes, the problem is worsened by the difficulty of describing the core space and the relativistic effect of heavy atoms. A workaround is the use of an ECP (Effective Core Potential) basis set: the core electrons are modeled by a suitable potential function, and only the valence electrons are explicitly treated. One of the most widely basis used is the LANL2DZ, which describes the core space by Los Alamos ECP [12] and a DZ quality basis set for the valence space [13–15].

The problem encountered when using the LANL2DZ basis in the calculations of complexes is the poor quality of the basis set that has to be used for the light atoms, if compared with the larger bases used nowadays. In order to mitigate this problem, it is possible to carry out calculations using the ECP basis set for heavy atoms and larger basis sets for first–second row elements.

As stated before, one of the most important thing in the calculations is the balance among different factors: in the case of mixed basis set calculations, it is not sure that the use of larger basis sets in part of the complex will lead to better results, because the difference in the quantum mechanics description of heavy and light atoms increases more and more, getting to an unbalanced situation. In order to investigate the basis set size dependence of frequency calculation quality, we

have taken into account six different bases improved over the simple DZ quality basis set used in the LANL2DZ case.

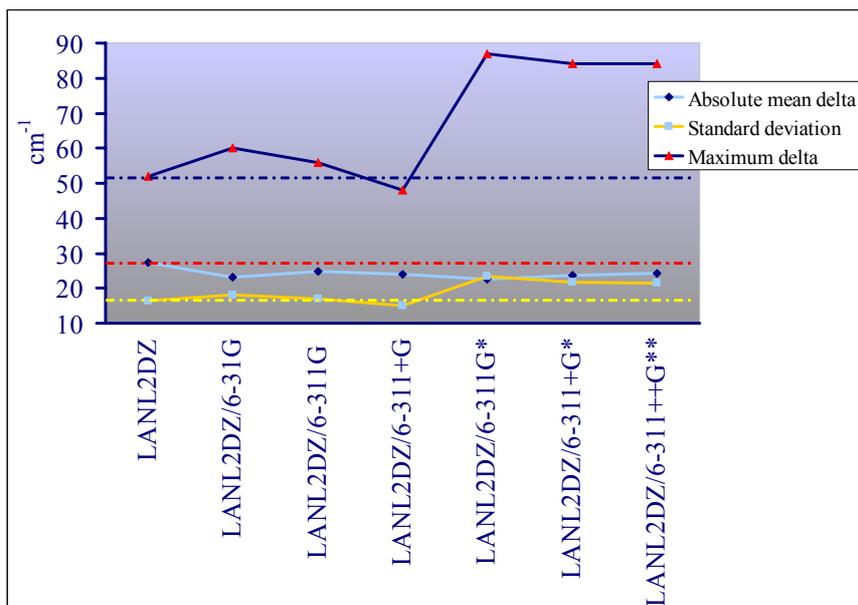
The basis sets used to carry out the DFT/BPW91 calculations are: LANL2DZ, the standard DZ quality basis set, used in all cases for the silver atoms; 6–31G, a basis set that roughly has the same quality as the LANL2DZ in both the core and valence space; 6–311G, a TZ basis that slightly improves over the 6–31G; 6–311+G, introducing d–type orbitals in both the core and valence space; 6–311G*, introducing a diffuse function for the first row elements; 6–311+G*, that introduces the two improvements over the 6–311G reported above; 6–311++G**, that is the largest basis set used, having d–type and diffuse orbitals on both hydrogen and first row elements.

Table 2. Absolute mean delta, standard deviation and maximum delta values obtained with different mixed basis sets for $[\text{TZ3A}(\text{Ag}_2)]^+$ and TZ3A

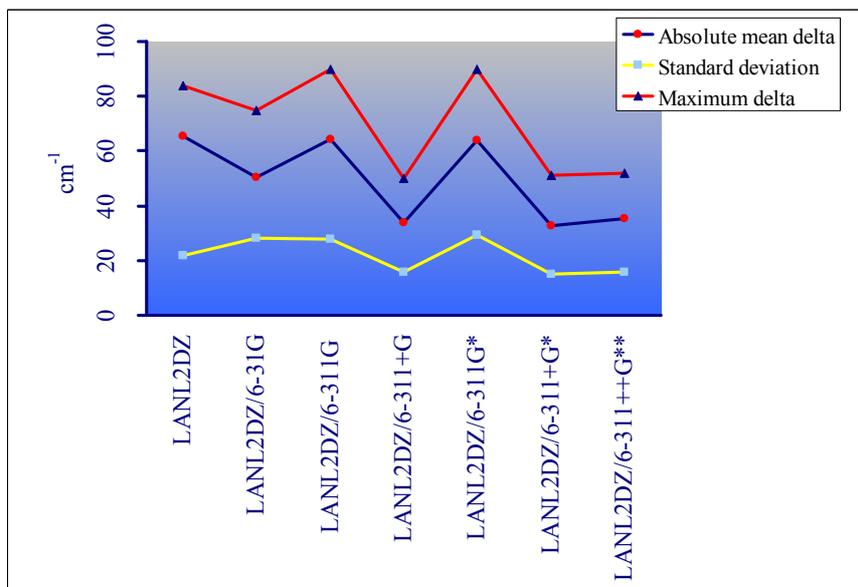
$[\text{TZ3A}(\text{Ag}_2)]^+$	LANL2DZ	LANL2DZ/ 6–31G	LANL2DZ/ 6–311G	LANL2DZ/ 6–311+G	LANL2DZ/ 6–311G*	LANL2DZ/ 6–311+G*	LANL2DZ/ 6–311++G**
Abs. Mean Delta	27	23	25	24	23	24	24
Std. Dev.	16	18	17	15	23	22	22
Max. Delta	52	60	56	48	87	84	84
TZ3A	LANL2DZ	LANL2DZ/ 6–31G	LANL2DZ/ 6–311G	LANL2DZ/ 6–311+G	LANL2DZ/ 6–311G*	LANL2DZ/ 6–311+G*	LANL2DZ/ 6–311++G**
Abs. Mean Delta	65	50	64	34	64	33	35
Std. Dev.	22	28	28	16	29	15	16
Max. Delta	84	75	90	50	90	51	52

The three benchmarks used to define the quality of the calculated frequencies are: the absolute mean delta (a measure of the calculation accuracy), the standard deviation (a measure of the calculation precision) and the maximum delta. All of them have to be considered to determine the overall quality of a basis set in the current calculations, because they describe different aspects of the agreement between experiment and theory. We carried out a step–by–step analysis by comparing the LANL2DZ results to those obtained by means of all other basis sets (see Table 2). A diagram of the trends of the absolute mean delta, standard deviation and maximum delta versus the different basis sets in the case of the $[\text{TZ3A}(\text{Ag}_2)]^+$ complex is reported in Figure 3a. It can be observed that upon going from the LANL2DZ basis set to LANL2DZ/6–31G, the mean absolute delta is improved but the maximum delta and the standard deviation are worsened. Since these two DZ basis sets are of comparable quality (with a better description of core orbitals by the LANL2DZ) the contrasting results are not surprising. Upon changing the basis set to the TZ quality, the 6–311G basis improves the results over the 6–31G basis set, but the overall result is still contrasting with respect to LANL2DZ. When the 6–31G basis set is changed to 6–311G, it can be observed that the increasing in the basis set size is too small to produce a significant improvement in all the three benchmarks. On the contrary, an overall improvement is reached by the introduction of diffuse functions in the 6–311+G basis set. In particular, the standard deviation and the

maximum delta are the best among all the basis sets. Moving to larger basis sets, *i.e.*, 6–311G*, 6–311+G* and 6–311++G**, the mean absolute delta is not improved, but, in contrast, there is a sharp worsening in the maximum delta, and a consequential rising in the standard deviation. This behavior is due to a very poor description of the SERS band at 987 cm^{-1} , assigned to a normal mode with noticeable contributions from the $\text{N}_1\text{--N}_2$ and $\text{N}_2\text{--N}_3$ stretching modes. Being N_1 and N_3 the molecular sites bound to the Ag^+ ions in the complex, the observed larger delta could be due to an unbalanced description of the molecule–silver system.



(a)



(b)

Figure 3. Diagrams of the trends of the absolute mean delta, standard deviation and maximum delta versus the different basis sets, in the case of $[\text{TZ3A}(\text{Ag}_2)]^+$ (a) and TZ3A (b). The horizontal dotted lines in Figure 3a indicate the parameter values in the case of LANL2DZ basis set.

For the sake of completeness, all the calculations with the same basis sets were also carried out for the free TZ3A (see Table 2 and Figure 3b). In this case, the 6–311+G basis is again confirmed to be the best overall choice, and not surprisingly the diffused basis set are fundamental for the correct description of an anionic molecule (as seen in the 6–311+G and 6–311+G* cases). It is to be noted that the use of larger basis sets, such as 6–311+G* and 6–311++G**, leaves almost unchanged the calculation quality, but the computational time undergoes a significant increase.

4 CONCLUSIONS

For the first time an investigation on the influence of the basis set size on the quality of the calculated vibrational frequencies has been carried out for surface models able to mime the interaction of an organic ligand with a silver surface. Due to the widespread use of quantum mechanics calculations for the vibrational assignment of SERS spectra, the quality of the calculated data for surface complexes is a very crucial point. Therefore, the need of continuously improving the agreement between calculated and experimental data leads to use mixed basis sets, *i.e.*, the traditional LANL2DZ basis set for metal atoms and a larger basis set for the atoms of the ligand. Since the LANL2DZ basis is the best for heavy metals, we can only change the basis set on the atoms of the ligand in order to obtain the best agreement between experimental and calculated frequencies. But the choice of the basis set on the ligand is not a simple point, because it is not sure that the use of larger basis sets will lead to better results. In fact, instead of an improvement, even a worsening can be obtained, if the difference in the quantum mechanics description of the metal and the atoms of the ligand increases too much. Another problem is to find the best compromise between the quality of the calculated data and the CPU time needed (a fundamental parameter in the case of larger molecules).

In the present work we have reported the results of an investigation carried out on the model of the surface complex formed by TZ3 on silver colloidal surface. We carried out DFT calculations using mixed basis sets with different sizes and the results have been critically evaluated on the basis of three fundamental benchmarks: the absolute mean delta, the standard deviation and the maximum delta. Despite the molecule studied is quite simple, it represents a good test for calculations of silver complexes: the results obtained have to be taken into account in order to choose the best mixed basis set. It is shown that the use of larger and larger basis sets may lead to degradation in the spectrum calculation, as well as an increasing in the CPU time needed. The 6–311+G basis set has proven to be the best compromise. Future investigations on larger molecules will be able to confirm or not if the use of the 6–311+G basis set on the ligand can be a guarantee of improvement in the calculated frequencies.

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5 REFERENCES

- [1] E. Burstein, S. Lundqvist and D. L. Mills, *Surface Enhanced Raman Scattering*, R. K. Cheng, T. E Furtak, eds., Plenum press, New York and London, 1982, pp.67–87.
- [2] J. R. Lombardi, R. L. Birke, T. Lu and J. Xu, Charge–transfer theory of surface enhanced Raman spectroscopy: Herzberg–Teller contributions, *J. Chem. Phys.* **1986**, *84*, 4174–4180.
- [3] B. Pergolese, M. Muniz–Miranda and A. Bigotto, Study of the adsorption of 1,2,3–triazole on silver and gold colloidal nanoparticles by means of Surface Enhanced Raman Scattering, *J. Phys.Chem B* **2004**, *108*, 5698–5702.
- [4] B. Pergolese, M. Muniz–Miranda and A. Bigotto, SERS investigation of the halide anion effect on the adsorption of 1,2,3–triazole on silver and gold colloidal nanoparticles, *J. Phys. Chem. B* **2005**, *109*, 9665–9671.
- [5] B. Pergolese, M. Muniz–Miranda and A. Bigotto, Adsorption Models of Bipyrazine on Silver Colloidal Nanoparticles: a Computational Study, *Internet Electron. J. Mol. Des.* **2005**, *4*, 249–255.
- [6] B. Pergolese, M. Muniz–Miranda, G. Sbrana and A. Bigotto, Surface–Enhanced Raman Scattering investigations of 4–nitro(pyridine N–oxide) and 4,4'–azobis(pyridine N–oxide) adsorbed on silver colloidal nanoparticles, *Faraday Discussions* **2006**, *132*, 111–120.
- [7] P. J. Hay and W. R. Wadt, *Ab initio* effective core potentials for molecular calculations. Potential for the transition metal atoms Sc to Hg, *J. Chem. Phys.* **1985**, *82*, 270–283.
- [8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al–Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- [9] A. D. Becke, Density–functional exchange–energy approximation with correct asymptotic behavior, *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [10] J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electron–gas correlation energy, *Phys. Rev. B* **1992**, *45*, 13244–13249.
- [11] B. Pergolese, A. Bonifacio and A. Bigotto, SERS investigations of the adsorption of guanine derivatives on gold colloidal nanoparticles, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3610–3613.
- [12] T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry: Methods of Electronic Structure Theory*, Ed. H. F. Schaefer III, Vol. 3 (Plenum, New York, 1976) 1–28.
- [13] P. J. Hay and W. R. Wadt, *Ab initio* effective core potentials for molecular calculations. Potentials for the transition metal atoms scandium to mercury, *J. Chem. Phys.* **1985**, *82*, 270–283.
- [14] W. R. Wadt and P. J. Hay, *Ab initio* effective core potentials for molecular calculations. Potentials for main group elements sodium to bismuth, *J. Chem. Phys.* **1985**, *82*, 284–298.
- [15] P. J. Hay and W. R. Wadt, *Ab initio* effective core potentials for molecular calculations. Potentials for potassium to gold including the outermost core orbitals, *J. Chem. Phys.* **1985**, *82*, 299–310.

Biographies

Barbara Pergolese is post–doc researcher in the field of vibrational spectroscopy at the Department of Chemical Sciences of the University of Trieste (Italy). She received a PhD degree in chemistry from the University of Trieste with a thesis in the SERS field. Her research has been devoted to experimental and theoretical SERS studies of heterocyclic

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Domenico Marchesan received a PhD degree in chemistry from the University of Trieste with a thesis in theoretical chemistry. His research has been devoted to the development and application of methods for the accurate determination of molecular properties that rationalize the interaction between molecular systems and electromagnetic fields.

Maurizio Muniz Miranda is senior researcher at the Department of Chemistry of the University of Firenze (Italy). Recently, his research has been devoted to experimental and theoretical studies on SERS of molecules adsorbed on metallic and non–metallic surfaces, on non–linear effects of polymeric monolayers and on the preparation of novel nanostructured materials.

Adriano Bigotto is full professor at the Department of Chemical Sciences of the University of Trieste (Italy). His studies have been devoted to experimental and theoretical IR and Raman studies. More recently his research activity has been focused on SERS spectroscopy.