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Atomically precise graphene-supported Pt₁₂ clusters: an experimental and theoretical NEXAFS study

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Atom-precise Pt₁₂ clusters deposited on a graphene surface have been investigated experimentally by means of Pt N₅-edge NEXAFS spectroscopy. NEXAFS spectra were also calculated within the TDDFT scalar-relativistic framework. Four different structures, corresponding to different energy minima, have been considered. The experimental profile was in remarkably fine agreement with the calculated one of one of the four optimized structures. DOS analysis showed that the feature at lower energy is strongly correlated with the number of Pt atoms with low coordination number, identifying a relationship between spectra features and geometrical structure.

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1. Introduction

Small metal clusters represent a class of systems with unique properties, which can differ substantially from those of the corresponding bulk material. This originates not only from their high surface/volume ratio, an intrinsic structural characteristic of finite size particles, but also from quantum effects, such as quantum confinement, which can profoundly modify the electronic structure upon size reduction. These effects typically emerge when the size falls below a few nanometers, depending on the chemical nature of the system, in the regime of sub-nanometer clusters (SNC). Therefore, it is not surprising that SNC are often more active catalysts or display non-conventional optical properties. In this context platinum plays a pivotal role^{1,2} being a common, albeit expensive, catalyst in many industrial processes.^{3–6} To improve the catalytic activity, band more generally to design materials with tailored properties, it is essential to understand not only the electronic

structure of such systems, but also their atomic geometry. Determining the equilibrium structure of these systems is particularly challenging because numerous structural isomers often lie within a narrow energy window. Moreover, their intrinsic fluxionality enables continuous interconversion among low-lying isomers, making the identification of the experimentally relevant structure especially difficult.⁷ For this reason, the most common strategy to study the structure of platinum clusters is the molecular dynamics (MD) global optimization,⁸ eventually followed by a more accurate DFT local optimization.^{9–11} Despite size and shape effects, there are also other degrees of freedom to play with, in order to modify the properties of metal clusters in general and platinum in particular. From the chemical point of view, the possibility to employ ligands to stabilize the clusters and modify their properties is appealing.^{12,13} Another very powerful strategy consists in the alloying of the clusters. Indeed, alloying has been shown that such effect can have dramatic consequences on the electronic structure as well as magnetic and catalytic properties.¹⁴ Optical properties are even more sensitive to alloying, with both the chemical composition and atomic-scale chemical ordering playing a crucial role, in particular for Pt has proven to be as a ‘poison’ for plasmons, for example in Ag-Pt alloys.^{15–17} From a more physical point of view, the charge state of the cluster represents an additional degree of freedom for tailoring Pt cluster properties. In particular, negatively charged Pt clusters (anions) have attracted significant attention due to their distinct electronic structures and properties,¹⁸ which can also be studied experimentally with ionic traps. Moreover, also atom-precise supported platinum

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clusters are interesting for their use in heterogeneous catalysis^{19,20} as well as for the challenging synthesis.²¹

In the present work we studied both experimentally and theoretically Pt₁₂ clusters deposited over a graphene layer epitaxially grown on Ru(0001), by means of X-ray absorption spectroscopy at the Pt 4d N₅ edge. This has been possible due to the availability of the experimental apparatus ENAC (exact number of atoms in each cluster), a cluster source specifically designed to be connected directly to the SuperESCA beamline of the Elettra synchrotron radiation facility to produce, deposit and characterize supported clusters *in situ*, therefore avoiding any contamination or modification induced by air exposure and/or transport. This approach allowed in the past to study the oxidation of pristine clusters of Pt⁶ and other metals.^{22–24} The graphene/Ru(0001) support was chosen for his large corrugation²⁵ with respect to other supports often used to stabilize Pt clusters at high temperature ($T > 500$ K) for catalytic applications, such as Al₂O₃,²⁶ TiO₂ and SnO₂,²⁷ thin oxides. This property allows to limit the cluster mobility while minimizing the modifications on the properties of clusters.

In this context, supported clusters represent prototypes of catalytic active sites. The models of the supported clusters were obtained by DFT calculations starting from their minimum energy configuration in the gas phase and letting them relax on graphene. Four non-equivalent isomers, labeled Pt₁₂-A, B, C and D, were obtained by positioning the clusters on graphene in four different rotational configurations. NEXAFS spectroscopy has the potential to study the electronic structure of molecules and, consequently, their geometric structure even under conditions that go beyond ultra-high vacuum, namely those defined as *in-operando*; for this reason, it is widely used to understand the kinetics of chemical reactions. In the case of isolated size-selected clusters, this type of studies is very difficult to carry out due to the extremely low cluster densities that must be maintained in order to preserve the nuclearity and thus study their properties as a function of atomic size. Techniques based on microscopy, such as transmission electron microscopy, have the potential to observe the spatial distribution of clusters, but they are typically used in this field by depositing the clusters on grids (and not directly on the substrate of interest); the introduction of gases into the measurement columns is typically not possible.

The NEXAFS spectrum of the Pt 4d N₅ edge was considered to characterize the supported cluster. According to the atomic electric-dipole selection rules, these core excitations probe the p and f atomic contributions to the virtual states. In practice, however, the f contribution is negligible, and the spectrum primarily reflects the character of the unoccupied states. This information is therefore extremely useful for correlating the X-ray absorption features with the electronic structure of the system.

2. Experimental and computational details

2.1. Experimental setup

The near-edge X-ray absorption fine structure (NEXAFS) measurements were performed *in situ* at the SuperESCA beamline at

Elettra - Sincrotrone Trieste, Italy. The Ru(0001) single crystal was mounted on a sample manipulator with four degrees of freedom. The sample was heated by electron bombardment from hot tungsten filaments mounted close to the sample back. The temperature of the sample was monitored by means of two K-type thermocouples directly spot-welded on the back of the specimen. The surface was cleaned by repeated cycles of Ar⁺ sputtering and annealing in O₂ atmosphere between 600 and 1000 K. The residual oxygen was removed by a final flash annealing at 1570 K. The surface long-range order and cleanliness were checked by low energy electron diffraction, which exhibited a sharp (1 × 1) pattern with low background intensity, and by high-resolution XPS which show the characteristic first- and second-layer core level shifted components in the Ru 3d_{5/2} components.^{28,29}

Graphene was grown by thermal decomposition of ethylene (C₂H₄) at 1100 K. The precursor pressure was initially set to 5×10^{-9} mbar and successively increased up to 5×10^{-8} mbar to ensure that entire surface was covered by graphene.^{26,30}

Positively charged Pt₁₂⁺ clusters were produced using the cluster source ENAC (exact number of atoms in each cluster). This cluster source is based on the laser ablation of a metal target and on mass-selection performed by quadrupole mass analyzer, which is capable of selecting cluster with masses up to to 16 000 amu with atomic precision. A more detailed description of the source is reported elsewhere.³¹ The clusters were deposited *in situ* and at $T = 80$ K on a freshly grown graphene/Ru(0001) (Gr/Ru) substrate, on which they are electrically neutralized. The amount of deposited clusters was monitored by directly measuring the ion current collected at the sample. A positive bias voltage was applied to the substrate to decelerate the incoming clusters, thereby reducing their kinetic energy E_k below the threshold required for soft landing ($E_k < 1$ eV per atom).³² To prevent cluster sintering, the Pt atomic coverage was limited to 0.5% of a monolayer (ML) calculated with respect to the Ru(0001) substrate. The temperature was maintained at 80 K both during deposition and throughout the measurement. A mass spectrometer is aligned along the trajectory of the clusters leading from the ablation region to the soft-landing region, and possesses the dual functionality of filtering clusters with different masses, selectable at will by the experimenter. The use of a high-sensitivity radio-frequency mass quadrupole is the principal method used in all machines producing mass-selected clusters. At the beginning of each experiment, once the ablation and transport conditions are set, it is possible to acquire a mass spectrometer scan which exhibits peaks corresponding to clusters of size. The quadrupole acts as a filter, allowing the transport of masses only within a range chosen by the experimenter.

In the present experimental conditions several conformations of Pt₁₂ cluster can exist on the graphene substrate, depending on the azimuthal and polar soft-landing angles. Also the contribution of the interaction with the substrate can modify the structure of the clusters themselves. In the following, we will consider four different cluster configurations, corresponding to non-equivalent orientations with respect to

the substrate, on the basis of the calculated lowest-energy models, as described in the 2.2 paragraph.

The near-edge X-ray absorption fine structure (NEXAFS) measurements were performed *in situ* at the SuperESCA beam-line at Elettra-Sincrotrone Trieste, Italy. The base pressure during the spectrum acquisition was 1×10^{-10} mbar and the temperature was kept at 80 K. The absorption spectrum was collected in Auger yield by monitoring the intensity of the Auger signal at 152 eV as a function of the photon energy. The Pt N₅-edge spectrum was normalized by a background spectrum acquired in the same conditions and on the same sample in an area outside of the cluster spot. The NEXAFS spectrum is the sum of 100 scans for a total data acquisition time of about 5800 s.

The monochromator was calibrated using, as absolute energy references in the photon-energy range relevant to the present work, the gas-phase Ar L_{2,3} absorption edge at 244.3 eV and the N K absorption edge at 400.85 eV. At higher photon energies, the Ne K absorption edge at 867 eV was used as an additional absolute reference. In addition to these three reference points, further calibration points were obtained using narrow core-level features at lower binding energies, such as the Ir 4f_{7/2} and Ta 4f_{7/2} levels. The complete set of calibration points was then fitted with a fourth-order polynomial. The resulting calibration curve is used to convert the desired photon energy into the corresponding command value for the monochromator, whose motion is controlled according to its nominal theoretical energy scale. Importantly, the calibration does not consist of applying a simple constant offset to the nominal monochromator scale. Rather, each photon-energy value is recalculated individually using the polynomial calibration function, thereby accounting for the non-linear deviation of the actual photon-energy scale from the nominal one.

2.2. Computational details

The calculations on the minimum energy configurations of the clusters have been performed using density functional theory (DFT) as implemented in the VASP code.³³ The system was described starting from a slab of a freestanding layer of 13×13 unit cell of graphene. The initial cluster geometry was the minimum energy configuration structure that Pt₁₂⁺ adopted in the gas phase.⁶ The Pt₁₂ cluster and the graphene layer were fully relaxed using the rev-vdw-DF2 functional³⁴ until the largest residual force was less than $0.015 \text{ eV } \text{\AA}^{-1}$. We employed the projector augmented method (PAW)³⁵ using PBE³⁶ potentials. The plane wave cutoff was set to 400 eV, and the relaxations were performed by sampling the Brillouin zone using the Γ point only. This process was repeated positioning the minimum-energy gas-phase cluster in four non-equivalent orientations with respect to the substrate, which relaxed into the four unique models Pt₁₂-A, B, C and D. The periodic calculations showed that Pt₁₂-A is the most stable isomer on graphene, while the relative total energy differences of the other Pt₁₂ isomers are +0.40 eV for Pt₁₂-B, +0.82 eV for Pt₁₂-C and +0.87 eV for Pt₁₂-D.

The calculations of the NEXAFS spectra reported in this work were performed by the AMS program³⁷ employing a TZP basis of STO functions included in the AMS database. The core excitations have been calculated as described previously,³⁸ separately for each atom, and then summed up to obtain the spectrum of the cluster. Therefore, we employed the all electron TZP basis only for the atom with the core excitation, for the other ones a frozen core basis set up to the Pt 4f atomic orbitals has been employed. A comment regarding the basis set choice has been reported in the SI. The PBE³⁷ exchange correlation functional has been employed in all the calculations, since it has already proven suitable¹⁵ to describe the electronic structure of Pt clusters. The suitability of PBE to describe both structure and spectroscopy of small platinum carbonyl clusters has been already proven previously, by validation with respect to experimental data.³⁹ The calculated profiles have been reported in the figures without any energy shift. The TDDFT calculation on Pt₁₂ takes about 1 hour using 16 cpu on a HPE ProLiant DL580 Gen10 server. The calculation must be repeated for all the atoms (12) of all the clusters (4), therefore the results for the four clusters are obtained within roughly 2 days. All the calculations were performed employing the zero order regular approximation (ZORA) in order to include relativistic effects at the scalar level.⁴⁰ Due to the rather large Spin Orbit splitting of the Pt 4d_{5/2} and 4d_{3/2} edges which is around 17 eV,⁴¹ in order to reduce the computational effort, we neglected the SO coupling in the calculations. In fact, for such large SO coupling, the two edges would have generated a pair of identical spectra, with an intensity distribution governed by the statistical ratio determined by the threshold degeneracy, that is 3:2 for 4d_{5/2}:4d_{3/2}. For this reason in practice the calculated profiles refer only to the Pt N₅ edge.

The theoretical spectra, consisting of discrete lines, were convoluted with Gaussian functions having different Full Width Half Maximum (FWHM) values (1.2 eV, 1.5 eV, and 2.5 eV) to allow an easier comparison with the experiment (see Fig. S1 in the SI). Although these values are larger than the experimental resolution (50 meV), it should be considered that the intrinsic line width of the spectral features is significantly broader than the experimental contribution in the present case. In fact the N₅ core-hole lifetime broadening of the Pt atom is 3.6 eV⁴² [J. C. Fuggle and J. E. Inglesfield, *Unoccupied Electronic States*, Springer Verlag, Berlin, 1992] therefore it is not surprising that the observed spectral width is much larger than the instrument resolution. From Fig. S1 the best agreement with the experimental data was obtained using a FWHM of 1.5 eV. Therefore the theoretical profiles discussed in the following refer to convolutions with FWHM of 1.5 eV. It is worth mentioning that besides finite basis TDDFT methods there are also other approaches which are widely employed in this field. The most common yet diffuse approach is the multiple scattering, where each atom is considered as a scattering center and the scattering equations can be solved with different degrees of accuracy. For example the typical muffin-tin approximation allows for drastic reduction of computational efforts, allowing the treatment of quite large systems. Important methods

suitable to calculate X-ray spectroscopy are for example Wien2k,⁴³ FEFF⁴⁴ and FDMNES.⁴⁵

3. Results and discussion

The theoretical investigation of the N₅-edge NEXAFS spectra of the Pt₁₂ clusters deposited on graphene is based on four different Pt₁₂ cluster models whose structures have been optimized as previously described. We assumed that the free clusters are good models for the adsorbed ones, in fact in a previous study⁶ it has been shown that the Bader charges on the individual Pt atoms of the clusters remain quite small, reaching at most 0.2–0.3 electrons. Moreover these values are distributed for both positive and negative values, and the centroid is quite close to zero. This finding means that there are modest charge transfer but inside the cluster, not with respect to graphene. Therefore the present models should be adequate to describe such charge transfer effects.

The Pt₁₂ cluster models are reported in Fig. 1, while the structural parameters are reported in Tables S1–S4 of the SI.

The A and B cluster structures are very similar, exhibiting a symmetry close to C_{2v} symmetry whereas the C and D clusters display a more compact layered structure. In Fig. 1, the Pt atoms of each cluster are color-coded according to their atomic coordination number (CN): green Pt atoms correspond to the lowest CN (CN = 3); red Pt atoms to intermediate CN value (CN = 4), and blue Pt atoms to the highest CN values (ranging from CN = 5 and 6 up to CN = 7 in the Pt₁₂-D cluster). It is worth noting that the number of Pt atoms with CN > 5 increases in the C and D clusters compared with the A and B clusters. The CN value reflects the local atomic arrangement surrounding each Pt atom within the cluster and can therefore be used to

analyze the Pt N₅-edge absorption spectrum in terms of the distinct contributions of individual Pt atomic sites.

Fig. 2 compares the experimental Pt N₅-edge NEXAFS spectrum of the Pt₁₂ clusters with the theoretical spectrum obtained by averaging the spectra of the four cluster models (upper panel), as well as with the individual spectra of each cluster model (lower panel).

Three spectral features can be distinguished in the experimental data below the Pt 4d_{5/2} ionization threshold (at 315.86 eV): a lower energy feature α , located around 303 eV, followed by two broader and more intense peaks, labelled β and γ , extending over the energy ranges 306–310 eV and 310–313 eV, respectively.

The theoretical averaged spectrum accurately reproduces the three experimental features below edge region, both in terms of the energy positions and intensity distribution. The results indicate the reliability of the TDDFT approach in describing the metal N-edge, in particular the importance of including the configuration mixing to treat core excitations involving degenerate core hole, like the 4d core electrons, as well as degenerate final atomic np states. The above edge energy region shows some discrepancies with the experiment since the LCAO-MO approach in a finite basis set is not suitable to properly treat the continuum absorption above the edge, due to different boundary conditions: while bound states must decay far away from the cluster, the unbound continuum states display an oscillating behavior which cannot properly be described by finite basis set. If one attempts to describe the above ionization threshold region with finite basis set, a “discretization” of the continuum is observed and therefore the description is formally incorrect and only a qualitative match with experiment can be obtained. For this reason, we will not examine in detail the high energy region of the spectrum and will instead consider the attribution of the calculated spectral feature in the pre-edge region.

In the following, we consider the spectral contributions of the cluster models to the averaged theoretical spectrum and their comparison with the experimental spectrum, as reported in the lower panel of Fig. 2. We observe that the spectral profiles exhibit a clear dependence on the cluster morphology, with the most pronounced differences occurring in the energy region associated with feature α (below 305 eV). In particular, the spectra of the A and B clusters are remarkably similar, reflecting the structural similarity between these two configurations. Both exhibit a well defined low energy feature around 303 eV, which is only weakly observed in the spectra of clusters C and D. All clusters provide similar contributions to features β and γ , although feature β is shifted to higher energies (by about 1 eV) in the spectra of the C and D clusters compared with those of the A and B clusters. Based on these observations and on the comparison with the experimental spectrum, we selected the Pt₁₂-A cluster as the most suitable model for a more detailed investigation of the nature of the Pt 4d_{5/2} pre-edge NEXAFS features. To this end, the calculated Pt₁₂-A spectrum has been investigated with the help of the calculated spin polarized partial density of unoccupied states (PDOS), as shown in Fig. 3. The reported PDOS corresponds to the sum of all the

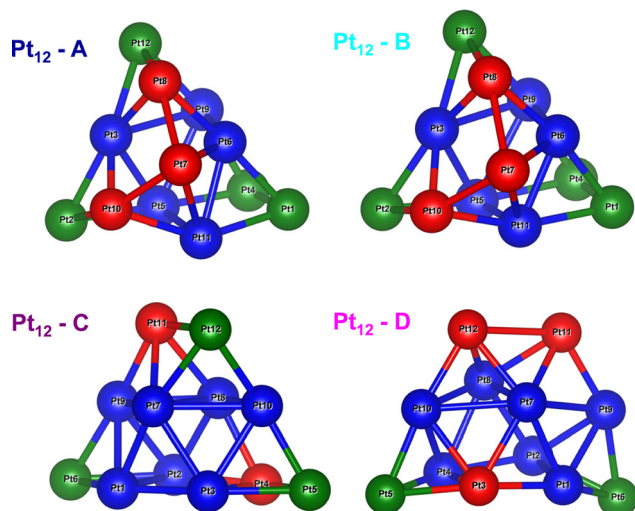


Fig. 1 Structures of the Pt₁₂ cluster models. The color-code of the Pt atoms in each cluster are based on the Pt coordination number (CN): green color for CN = 3; red for CN = 4; blue for CN ≥ 5. The colour of the name of the clusters is the same as the calculated profiles of the individual clusters reported in the lower panel of Fig. 2.

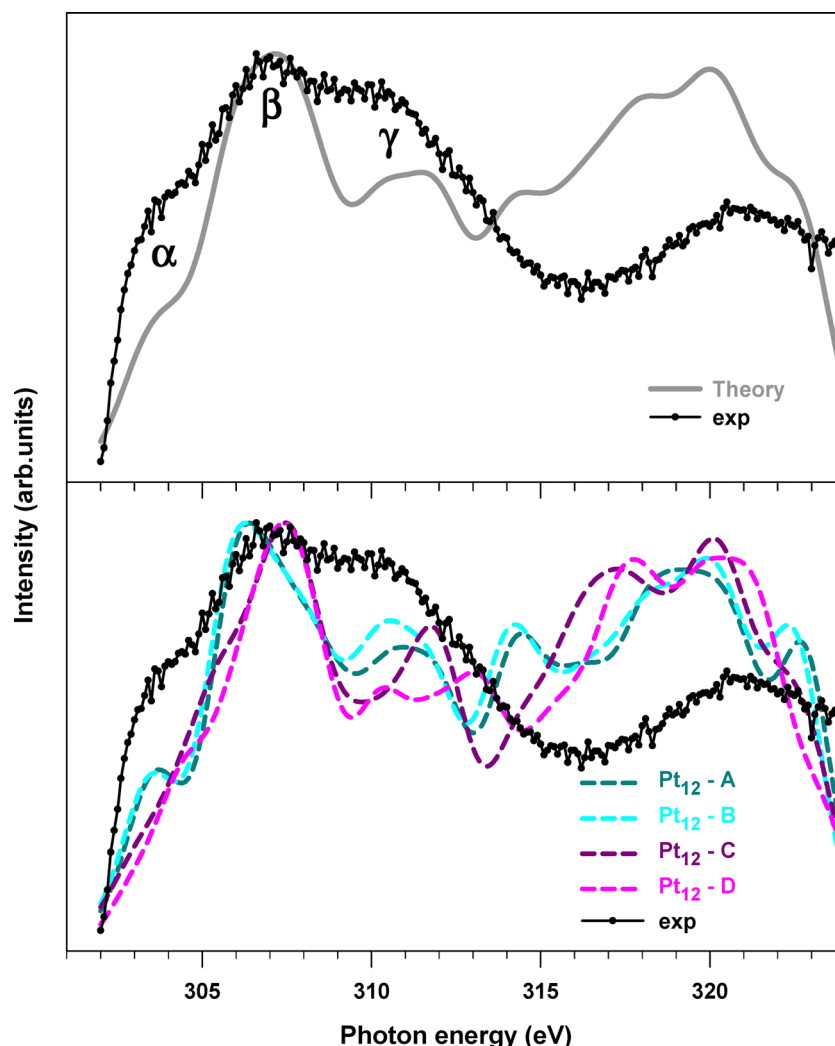


Fig. 2 N_5 -edge NEXAFS spectrum of the Pt_{12} cluster. Upper panel: comparison between the theoretical averaged Pt_{12} spectrum and the experimental spectrum. Lower panel: comparison between the experimental spectrum and the calculated spectra of the Pt_{12} cluster models. Pt $4d_{5/2}$ ionization threshold: 315.86 eV.

Pt atomic contributions provided by the employed basis set. Within the single-particle approximation, the core excitation spectrum can be related to the unoccupied PDOS of a selected atom, provided that the transition is allowed by the electric dipole selection rule. The Pt unoccupied PDOS profiles of the Pt_{12} -A cluster is therefore useful to identify the dominant contributions of the Pt atomic orbitals to the final molecular orbital (MO) involved in the NEXAFS transitions. As shown in Fig. 3, a pronounced tail of the valence 5d occupied orbitals extends just above the LUMO KS energy (-6.25 eV), while a high density of empty s states is found around 310 eV. At higher energies, the contribution from 6d states becomes dominant. The Pt 6p orbitals are empty in the Pt_{12} -A cluster, and their contribution to the virtual MOs is distributed over the entire energy range considered, although it is generally weaker than that of the s and d states, especially in the energy region below 305 eV. According to the electric-dipole selection rules, the intensity of the $4d_{5/2}$ core transitions reflects the p character of the virtual valence final states. Therefore, the Pt 6p density of

states of the Pt_{12} -A cluster provides qualitative insight into the nature of the Pt $4d_{5/2}$ core transitions. This is evident from the comparison between the p-DOS distribution and the Pt_{12} -A spectrum shown in Fig. 3, where a clear similarity between the two profiles is observed, confirming that the below-edge spectral features can be assigned to Pt $4d_{5/2} \rightarrow 6p$ transitions.

It should, however, be noted that TDDFT calculations introduce a mixing of configurations; consequently, the intensity distribution of the $4d_{5/2}$ transitions can only be qualitatively compared with the single-particle PDOS distribution. In this respect, the reduced intensity of peaks α and γ peaks relative to peak β can be partially attributed to the hybridization between the 6p and s components in the virtual MOs whereas in the energy region corresponding to peak β the density of p states responsible for the $4d_{5/2}$ core excitations is dominant. Moreover, above the $4d_{5/2}$ ionization threshold, the calculated spectral intensity still qualitatively reflects the distribution of the 6p orbitals, which are hybridized with the 6d components that become dominant at high energies.

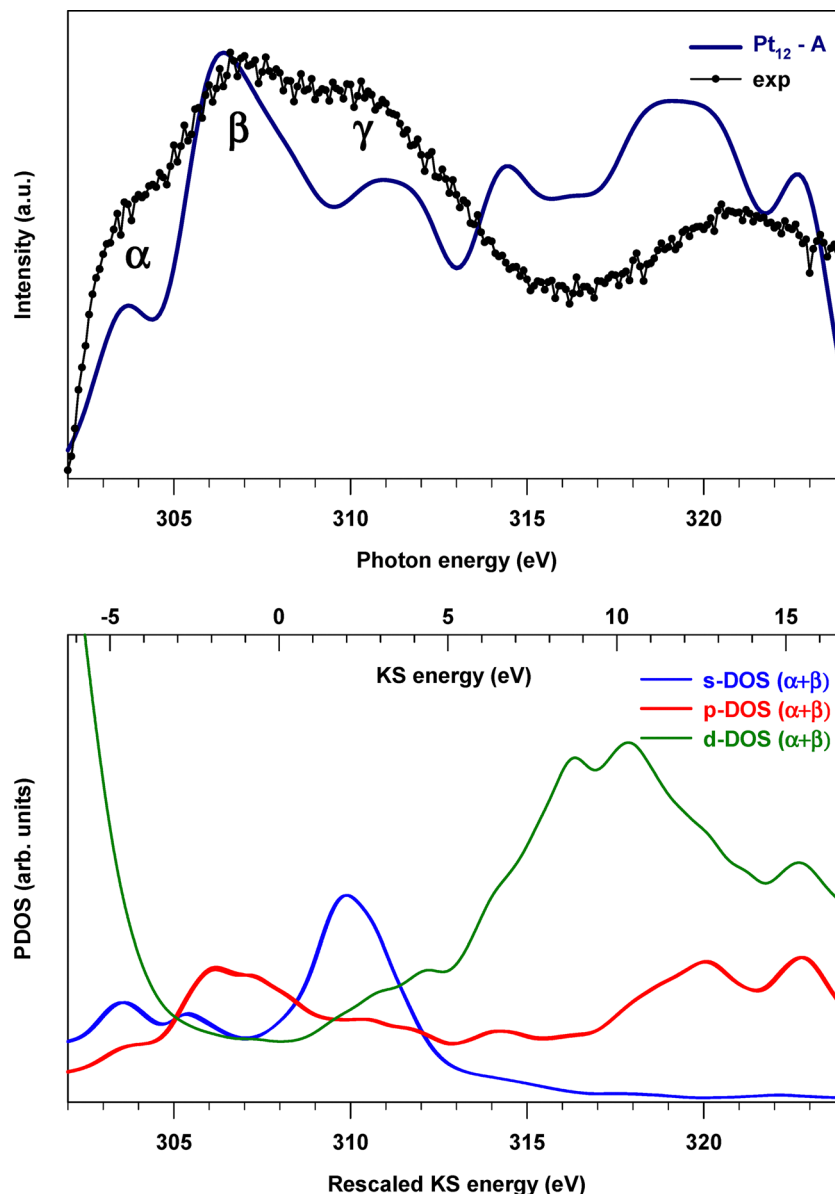


Fig. 3 Upper panel: N₅-edge NEXAFS spectrum of the Pt₁₂-A cluster compared with the experimental spectrum acquired in ultra-high vacuum at $T = 80$ K. Lower panel: spin-polarized unoccupied PDOS profiles (s, p and d) of the Pt₁₂-A cluster. The bottom x-axis reports the Kohn–Sham (KS) eigenvalues rescaled by the calculated IP 4d_{5/2} (307.25 eV) to facilitate the comparison with the NEXAFS spectra. PDOS profiles are convoluted with Lorentzian broadening (FWHM = 1.5 eV).

To investigate the relationship between the morphology of the Pt₁₂-A cluster and the calculated N₅-edge spectral features, we analysed the contributions of the individual Pt atoms to the Pt₁₂-A spectrum shown in Fig. 4, which reports only the below edge region of the spectrum.

As previously discussed, the coordination number (CN) of each Pt atom was identified as the most suitable parameter for relating the core excited spectrum and the local electronic environment of the Pt atom. Grouping the Pt atoms of the cluster according to their CN helps to highlight the main differences among their spectra, as illustrated in Fig. 4. In particular, a clear trend is observed below 305 eV, in the energy region associated with structure α : the intensity of α decreases

as the CN of the Pt atoms increases. Since the 4d_{5/2} transitions primarily probe the 6p character of the unoccupied molecular orbitals, this trend indicates a corresponding reduction of the 6p contribution to the empty MOs just above the LUMO KS energy. This decrease may be attributed to a participation of the 6p orbitals of Pt atoms with higher CN in bonding through hybridization with 5d/6s orbitals below the Fermi level. Furthermore, this interpretation may also explain the significant reduction of the feature α in the spectra of the C and D clusters, which contain a large number of Pt atoms with CN > 5 compared with the A and B clusters.

On the other hand, no significant correlation is observed between the CN value of the Pt atoms and their spectral

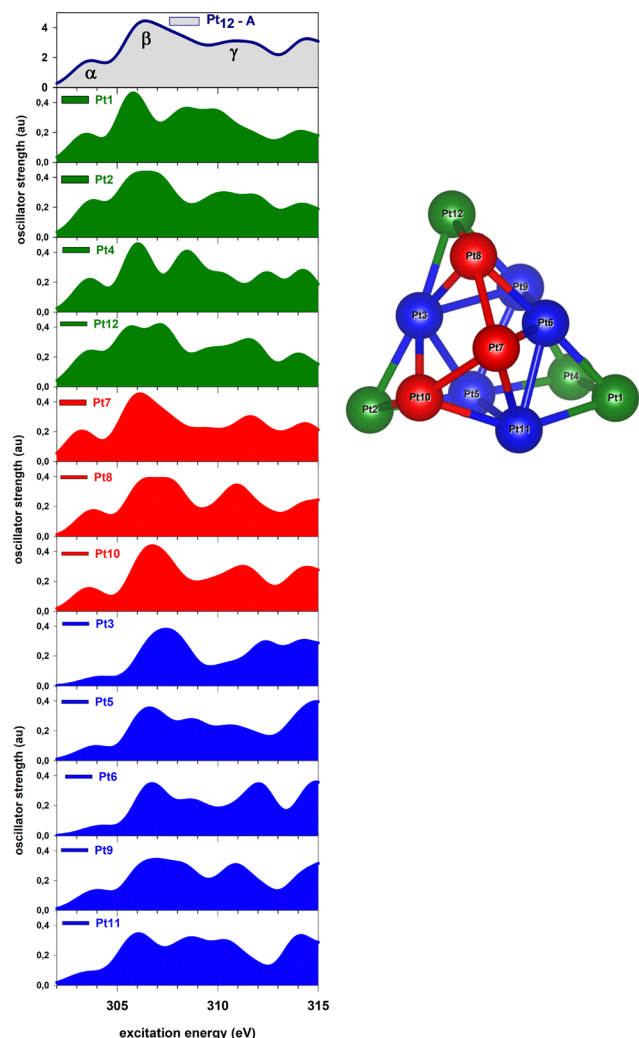


Fig. 4 Calculated N_5 -edge NEXAFS spectrum of the Pt_{12} -A cluster compared with the spectra of individual Pt atoms of the cluster. The color of the spectra is based on the CN color-code of the Pt atoms: green for CN = 3; red for CN = 4; blue for CN = 5,6. Only the energy region below $4d_{5/2}$ edge is reported. The structure of the Pt_{12} -A cluster is also shown.

contributions to peaks β and γ . The spectra of all Pt atoms exhibit a stronger contribution to the intensity of peak β compared to peak γ , in qualitative agreement with the distribution of 6p states density in the energy regions corresponding to these peaks (as reported in Fig. S2 of the SI). It can nevertheless be observed that the lower-energy side of peak β is mainly associated with Pt atoms with CN values of 3 and 4, whereas the contribution from atoms with higher CN is shifted toward to the higher-energy side of peak β . This trend may also account for the approximately 1 eV shift of peak β to higher energy in the spectra of the C and D clusters compared to the A and B clusters.

4. Conclusions

In this work, we have investigated atom-precise Pt_{12} clusters deposited on a graphene surface by means of Pt N_5 -edge

NEXAFS spectroscopy. To achieve an unambiguous interpretation of the experimental spectra, we performed first-principles calculations. The geometrical optimization of the Pt_{12} clusters performed at the DFT level revealed four energetically stable structures, for which the corresponding NEXAFS spectra were subsequently calculated within the TDDFT scalar-relativistic framework. The experimental profile was in remarkably fine agreement with the calculated one of one of the four optimized structures, namely Pt_{12} -A. Such spectrum has been analyzed in terms of individual contributions as well as DOS analysis. Such analysis showed that the feature at lower energy is strongly correlated with the number of Pt atoms with low coordination number, identifying a relationship between spectra features and geometrical structure. More generally, all experimentally observed spectral features are accurately reproduced by theory, enabling their assignment and rationalization in terms of both the electronic structure and the local coordination environment. These results demonstrate the capability of NEXAFS spectroscopy, combined with accurate first-principles calculations, to provide direct structural insights into atomically precise sub-nanometric clusters.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article (experimental data reported in Fig. 2, theoretical profiles of Fig. 2 and partial DOS analysis reported in Fig. 3) have been included as part of the supplementary information (SI). See DOI: <https://doi.org/10.1039/d6cp03276a>.

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