Molecular double core-hole electron spectroscopy for chemical analysis

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We explore the potential of double core hole electron spectroscopy for chemical analysis in terms of x-ray two-photon photoelectron spectroscopy (XTTPS). The creation of deep single and double core vacancies induces significant reorganization of valence electrons. The corresponding relaxation energies and the interatomic relaxation energies are evaluated by CASSCF calculations. We propose a method how to experimentally extract these quantities by the measurement of single and double core-hole ionization potentials (IPs and DIPs). The influence of the chemical environment on these DIPs is also discussed for states with two holes at the same atomic site and states with two holes at two different atomic sites. Electron density difference between the ground and double core-hole states clearly shows the relaxations accompanying the double core-hole ionization. The effect is also compared with the sensitivity of single core hole ionization potentials (IPs) arising in single core hole electron spectroscopy. We have demonstrated the method for a representative set of small molecules LiF, BeO, BF, CO, N₂, C₂H₂, C₂H₄, C₂H₆, CO₂ and N₂O. The scalar relativistic effect on IPs and on DIPs are briefly addressed.

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I. INTRODUCTION

The effect of the chemical environment manifests itself in energy differences of molecular core levels with respect to the atomic ones referred to as ”chemical shifts”. These can be measured by core level spectroscopies, e.g., by x-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA) and by x-ray-induced Auger electron spectroscopy (XAES). Both spectroscopies have shown to be exceedingly successful tools to reveal the quantitative elemental composition of molecules and solids.

More than two decades ago, Cederbaum et al.2,3 discovered that the creation of double core vacancies in molecular systems probes the chemical environment more sensitively than the creation of single core vacancies. Two-atomic site double ionization potentials, or briefly two-site DIPs (or two-site double ionization energies, DIEs) are particularly sensitive to the chemical environment as the examples of the C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$\textsuperscript{2} and C$_6$H$_6$\textsuperscript{3} molecules demonstrate. The chemical shifts of one-atomic site DIPs, or briefly one-site DIPs, were found to be similar to the chemical shifts of the single core level ionization potentials (IPs), or ionization energies (IEs). This finding has given impetus to a number of theoretical studies aimed at elucidating properties of molecular double core hole states4–7.

So far experimental explorations of double core hole states with conventional XPS were restricted to those having two vacancies on the same atomic site only8,9 since the probability to produce a two-site double core hole state with one-photon absorption is practically zero at third-generation synchrotrons due to low x-ray intensities. This prevented further progress of the subject. The situation has changed with development of x-ray free-electron lasers (x-ray FELs)\textsuperscript{10}. At FEL facilities in operations, such as FLASH in Hamburg\textsuperscript{11} and SPring-8 Compact SASE Source (SCSS) test accelerator\textsuperscript{12}, multi-photon absorption processes resulting in multiply ionized states of various systems have been extensively studied\textsuperscript{13–17}. In the x-ray FEL facility LCLS at SLAC National Accelerator Laboratory, which has just started operations\textsuperscript{18}, ultrashort pulses of a duration about 1-fs containing $2.4 \times 10^{11}$ photons with energies of 1 keV are expected to be generated\textsuperscript{19,20} thus opening up the possibility to study molecular two-site double core hole states. Inspired by the advent of the x-ray FEL at LCLS, Santra et al.\textsuperscript{21} have demonstrated theoretically by the proof-of-principle simulations on the organic para-aminophenol molecule that two-site double core hole states can indeed be probed by means of x-ray two-photon photoelectron spectroscopy (XTPPS).
The operating principle of XTPPS is depicted schematically in Fig. 1. The initial step in XTPPS corresponds conventional XPS, i.e., a neutral molecule with an energy $E_0$ is irradiated by an x-ray photon with an energy $\omega_X$ and a photoelectron with the kinetic energy $\mathbf{k}_{p1}/2$ is ejected. This photoelectron carries information about a singly core ionized state $E^+$ of the molecule. If a second x-ray photon is absorbed before the intermediate core hole state decays, the second photoelectron expelled from the cation with the kinetic energy $\mathbf{k}_{p2}/2$ carries information about a double ionization potential. It is important to have an intense x-ray pulse with a duration that is significantly shorter than the core-hole lifetimes (typical lifetimes of core ionized states of F, O, N and C atoms are 3 to 7 femtoseconds). If the pulse duration is longer than these lifetime, then Auger decay is likely to occur prior to absorbing the second photon and thus the double core hole states may not be probed. A dicationic state $E^{++}$ of the system prepared by two-photon absorption decays electronically. Two primary Auger decays take place which overlap in time. An Auger decay happens preferably at that atomic site where the core hole has the shorter lifetime and an Auger electron with kinetic energy $\mathbf{k}_{A1}/2$ is ejected. This process proceeds in the presence of the second core hole which also decays via the Auger mechanism emitting an electron with kinetic energy $\mathbf{k}_{A2}/2$. The electrons ejected via such a cascade of Auger decays can in principle be measured by a novel Auger spectroscopy which we call x-ray two-photon-induced Auger electron spectroscopy (XTPAES).

It is worthwhile to note that double core ionization can be accompanied by various shake-up processes similar to single core ionization. These many-body effects should manifest themselves in XTPPS spectra as satellites which are of interest as well. Both x-ray two-photon-induced Auger spectra and satellites structures will be addressed elsewhere.

The subject of the present paper is the main double core hole states. In order to provide a guideline for XTPPS experiments, we have performed \textit{ab initio} calculations of core level single and double ionization potentials of LiF, BeO, BF, CO, N$_2$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, CO$_2$, and N$_2$O molecules. In addition we have explored the sensitivity of the DIPs to the chemical environment of the core ionized atoms. We decompose the DIPs in three physical contributions such as the orbital energies, the electrostatic repulsion energy between two core holes and the generalized relaxation energy and describe how the latter can be extracted from the experimental XTPPS spectra.
II. COMPUTATIONAL METHODS

*Ab initio* calculations of the vertical ionization potentials of the single and double core vacancy states of LiF, BeO, BF, CO, N₂, C₂H₂, C₂H₄, C₂H₆, CO₂, and N₂O were performed using the \(\Delta\text{SCF}\) and CASSCF methods. The molecular geometries used in these calculations were optimized at the Møller-Plesset level of theory (MP2) employing the correlation-consistent polarized valence triple zeta (cc-pVTZ) basis sets of Dunning. Depending on whether singly or doubly ionized states were considered, the configurations in the CASSCF method were restricted to those having one or two holes in the K-shell orbitals, respectively. We used the active spaces comprising all the occupied molecular orbitals (except for the 1s orbitals of the atoms other than H) and all the valence unoccupied \(\pi^*\) and \(\sigma^*\) ones which contain large contributions from different atomic \(p\) orbitals. Thus, the active space of the CASSCF calculations consists of \(2s, \sigma, \pi, \pi^*\) and \(\sigma^*\) orbitals with core occupancy being fixed. The cc-pVTZ basis sets were employed in all the CASSCF and \(\Delta\text{SCF}\) calculations. For CO and C₂H₂, the cc-pVDZ, cc-pCVTZ and cc-pVQZ basis sets were also used in order to examine the basis set dependence of our results. All the single and double core-hole states were solved by independent CASSCF calculations using different configuration space and, therefore, the calculated states are not strictly orthogonal to each other. However, the one and two-site double core-hole states are well separated in energy and their interaction are expected to be negligible.

For molecules with equivalent atoms, N₂, C₂H₂, C₂H₄, C₂H₆ and CO₂, we calculated double ionization potentials using both localized and delocalized molecular orbital pictures following the recipe given by Cederbaum et al. and discuss differences between them. Note that only core orbitals were localized which was performed with the Boys method. In the localized representation we obtained the ionization potentials of the one-site double core hole states \(S_1^{-2}\) and \(S_2^{-2}\) as well as of the two-site double core hole states \(S_1^{-1}S_2^{-1}\). Carrying out calculations with wave functions described by the linear combinations \(S_1^{-2} \pm S_2^{-2}\) gives rise to double ionization potentials in the delocalized picture. Differences between single ionization potentials arising due to applying localized and delocalized representations are not studied in the present paper because they have been discussed in detail before.

In this work, we ignore the geometry relaxation of ionized state. In core ionization the change of geometry can be significant, depending on the case under investigation.
single core ionization one can explain the measurements well by employing the concept of vertical transitions. As in single ionization, also in XTPPS where the two X-ray photons must be absorbed within a time shorter than the Auger decay times, the concept of vertical transitions can be expected to be very useful.

In order to assess the impact of scalar relativistic effects on the core level single and double ionization potentials we made relativistic CASSCF calculations for the CO and BF molecules using the eighth order Douglas-Kroll-Hess Hamiltonian (DKH8)\textsuperscript{29–33}. To get insight into the dynamic correlations, we also performed CI calculations with the CAS space plus single excitations from the CAS for both single and double core-hole states.

All calculations were done with the Molpro2008 quantum chemistry package\textsuperscript{34}.

III. RESULTS AND DISCUSSIONS

A. Single core hole states

Let us first discuss single core hole IPs. The ionization potential for the formation of a vacancy $S^{-1}$ can be represented as

$$IP(S^{-1}) = -\varepsilon_S - RC(S^{-1}),$$

where $\varepsilon_S$ is the corresponding orbital energy and $RC(S^{-1})$ is a contribution to the ionization potential due to relaxation $R(S^{-1})$ and correlation $C(S^{-1})$ effects:

$$RC(S^{-1}) = R(S^{-1}) + C(S^{-1})$$

The relaxation and electron correlations intermix with each other and cannot be strictly separated. The separation of these quantities was discussed in details in a perturbative way\textsuperscript{35} and in a nonperturbative way using MRCC\textsuperscript{36}. The correlation contribution can be further decomposed into two parts C1 and C2 (see Refs. 37 and 28) where C1 describes a part of the ground state pair correlation energy disappearing upon removal of an electron from the spin orbital $S$, and C2 accounts for changes in the remaining pair correlation energy due to relaxation. Except for C1 which is a very small contribution, all contributions to $RC$ are thus associated with relaxation of molecular orbitals. Therefore, for brevity of discussion, we may call $RC$ the generalized relaxation energy.
A straightforward way to obtain the relaxation energy is to perform ∆SCF calculations. \( R(S^{-1}) \) is then derived as the difference between the respective orbital energy (with opposite sign) and the calculated IP. In order to get a correlation contribution to IP, post-Hartree-Fock calculations are generally needed. CASSCF is one of these methods. Noteworthy, in systems with core holes delocalized due to symmetry requirements, C2 can be accounted by performing ∆SCF calculations using localized orbitals instead of delocalized ones as shown by Cederbaum and Domcke\(^\text{28}\).

In Table I we list IPs calculated with the CASSCF and ∆SCF methods together with available experimental values\(^\text{38–44}\). Table I also contains the constituting parts of IPs, namely the orbital energies, the relaxation energies obtained from ∆SCF calculations, as well as the generalized relaxation and pure correlation contributions, both obtained from CASSCF calculations. The correlation contributions were calculated by subtracting the CASSCF IPs from the ∆SCF ones. Note that, since ∆SCF calculations for molecules with equivalent atoms were performed using the localized representation, the calculated IPs correspond to the localized 1s orbitals rather than to the delocalized 1\(\sigma_g\) and 1\(\sigma_u\).

In general, the agreement between the CASSCF and experimental results is reasonable. This concerns both the absolute values of IPs and the g-u energy splittings for molecules with equivalent atoms. Except for basis set effects which always are an issue in \textit{ab initio} calculations, and relativistic effects, deviations from the experiment are attributed to the lack of dynamic correlations in the ground and single core hole states, and to the core-valence separation approximation employed in the calculations. We notice that influences of the above-mentioned effects and approximations partially compensate for each other. Indeed, performing calculations without core-valence separability lowers IPs\(^\text{45}\). A lowering of IPs can also be achieved by improving basis sets. On the other hand, taking into account relativistic effects increases IPs. In Appendices A and B we explore the basis sets and relativistic effects in more detail.

It is interesting to compare the different contributions to IPs in Eq. (1). After the orbital energy, the relaxation energy represents the largest constituent part of a core level IP. It increases nearly proportional to the atomic number \(Z\). For some molecules, however, remarkable deviations from this trend occur under influence of the chemical environment. A crucial role for the relaxation energy plays the change of the electron density distribution of valence electrons, \(\Delta \rho\), in an atom due to a formation of chemical bonds with neighbors,
and the interaction of $\Delta \rho$ with the core hole. Ionic bonds give rise to the strongest changes of the electron density distribution. As a consequence, the relaxation energies associated with core ionization of electron acceptors in ionic molecules (e.g. O and F in BeO and LiF, respectively) are noticeably larger than the relaxation energies of the same atoms bound by covalent bonds with their neighbors (O and F in CO and BF, respectively). For other factors influencing the relaxation energies see Ref. 2.

In comparison to relaxation effects, correlation effects induced by core ionization are rather small. According to our calculations, the magnitude of the static correlation effects does not exceed 3 eV for the molecules studied and accounting for missing dynamic correlation can hardly modify this situation dramatically. Interestingly, the largest correlation effects manifest themselves in atoms whose neighbors are the strong electron acceptors O and F.

The effect of the chemical environment on core level ionization potentials of various systems including the molecules explored here is rather well established and we therefore refrain from long discussions on this subject. We only mention that the chemical environment is able to introduce large changes in the ionization potentials as, for example, can be realized by comparing molecules with ionic and covalent bonds. On the other hand, in the sequence of the C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$ molecules characterized by the triple, double and single carbon-carbon bond, respectively, the impact of the chemical environment is rather moderate. In contrast to single core hole ionization potentials, double core hole ionization potentials reveal much more pronounced sensitivity to the chemical environment as it was first demonstrated in Refs. 2 and 3.

B. Double core hole states

1. General equations and results

In analogy to Eq. (1), we represent the double ionization potential of a state with two core vacancies $S_i^{-1}$ and $S_j^{-1}$ as

$$DIP(S_i^{-1}, S_j^{-1}) = -\varepsilon_S - RC(S_i^{-1}, S_j^{-1}) + E_{RE},$$

where $E_{RE}$ is the repulsion-exchange energy of the two core holes. For an one-site double core hole state, it is described by the two-electron integral $V_{S_iS_iS_jS_j}$, or $(S_iS_i|S_jS_j)$, and,
for a two-site double core hole state, by a linear combination of the integrals $V_{S_iS_iS_j}$ and $V_{S_iS_jS_j}$, where the exchange term is negligibly small when the core holes are well localized

The generalized relaxation $RC(S_i^{-1}, S_j^{-1})$ can be decomposed into three parts

$$RC(S_i^{-1}, S_j^{-1}) = RC(S_i^{-1}) + RC(S_j^{-1}) + NRC(S_i^{-1}, S_j^{-1}),$$

where $RC(S_i^{-1})$ given by Eq. (2) describes relaxation and correlation effects induced by creation of the core vacancy $S_i^{-1}$ as there were no core vacancy $S_j^{-1}$. The relaxation and correlation energies are expected to be non-additive upon creation of multiple vacancies. A possible deviation from additivity is thus described in Eq. (4) by the non-additivity term $NRC(S_i^{-1}, S_j^{-1})$.

Depending on whether two core holes were created on the same atomic site or on different atomic sites, $NRC(S_i^{-1}, S_j^{-1})$ may be called the excess generalized relaxation energy, $ERC(S_i^{-1}, S_i^{-1})$, or the interatomic generalized relaxation energy, $IRC(S_i^{-1}, S_j^{-1})$. Note that, while the $RC(S_i^{-1})$ and $ERC(S_i^{-1}, S_i^{-1})$ measure local properties of a core ionized atom, $IRC(S_i^{-1}, S_j^{-1})$ measures the impact of the environment “between” the atoms involved.

In Table II we list the calculated double ionization potentials. We also show the correlation contributions to DIPs. As one can see these contributions are remarkably larger than those to the single IPs and may constitute 5.6 eV. In the special cases, however, when we performed calculations with delocalized core orbitals, differences between $\Delta$SCF and CASSCF values rise to 27-35 eV resulting from the failure of the $\Delta$SCF method in the delocalized picture to account for all relaxation contributions as described by Cederbaum et al.

One can notice by comparing Table I and II that the impact of the chemical environment is different for double and single ionization potentials. Of particular interest is to compare two-site DIPs with single IPs since their sensitivities to the chemical environment reveal major differences. A prominent example already discussed in detail in Ref. 2 is the hydrocarbons $C_2H_2$, $C_2H_4$ and $C_2H_6$. Here, the chemical shifts in the two-site DIPs are much more pronounced than in the single IPs being also attributed to different carbon-carbon bondlengths resulted from a different number of hydrogen atoms in these molecules. In XPS one can hardly distinguish between these three compounds while in XTPPS this should be possible in principle. The situation is somewhat different for the individual molecule $N_2O$. In this molecule the sensitivity of two-site DIPs to the chemical environment is lower
compared to that of single IPs. Indeed, the core ionization potentials of the terminal and central nitrogen atoms differ by 4 eV whereas the difference between the N\textsubscript{t}1s\textsuperscript{−1}O1s\textsuperscript{−1} and N\textsubscript{c}1s\textsuperscript{−1}O1s\textsuperscript{−1} double ionization potentials constitutes 2.3-2.8 eV. The latter energy difference is much lower than 11 eV which one would expect taking into account only the differences between the N\textsubscript{c}O and N\textsubscript{t}O bondlengths and between the single core hole ionization potentials. As we show below, the reason for such a dramatic reduction of the chemical shift has to do with distinct relaxation processes induced by the creation of different pairs of core holes.

Taking into account Eqs. (1) and (4), we can represent $DIP(S_{i}^{-1}, S_{j}^{-1})$ as

$$DIP(S_{i}^{-1}, S_{j}^{-1}) = IP(S_{i}^{-1}) + IP(S_{j}^{-1}) - NRC(S_{i}^{-1}, S_{j}^{-1}) + E_{RE},$$

and define the ionization potential of the core vacancy $S_{i}^{-1}$ in the presence of the core vacancy $S_{j}^{-1}$ as

$$IP(S_{j}^{-1}; S_{i}^{-1}) = IP(S_{i}^{-1}) - NRC(S_{i}^{-1}, S_{j}^{-1}) + E_{RE},$$

whereas

$$IP(S_{i}^{-1}; S_{j}^{-1}) = IP(S_{j}^{-1}) - NRC(S_{i}^{-1}, S_{j}^{-1}) + E_{RE}$$

is defined as the ionization potential of the core vacancy $S_{j}^{-1}$ in the presence of the core vacancy $S_{i}^{-1}$.

Both the ionization potentials $IP(S_{i}^{-1})$ of a neutral system and the ionization potentials $IP(S_{i}^{-1}; S_{j}^{-1})$ of a core-ionized one can be obtained experimentally, e.g., by means of XTPPS. In XTPPS, the kinetic energy $KE(S_{i}^{-1})$ of the first photoelectron ejected from the orbital $S_{i}$ defines $IP(S_{i}^{-1})$, whereas the kinetic energy $KE(S_{i}^{-1}; S_{j}^{-1})$ of the second photoelectron ejected from the orbital $S_{j}$ defines $IP(S_{i}^{-1}; S_{j}^{-1})$. Obviously, the sum $IP(S_{i}^{-1}) + IP(S_{i}^{-1}; S_{j}^{-1})$ gives $DIP(S_{i}^{-1}, S_{j}^{-1})$. As shown below, important properties of the system under study can be extracted also from the measurable energy difference

$$\Delta E = KE(S_{i}^{-1}) - KE(S_{j}^{-1}; S_{i}^{-1}) = IP(S_{i}^{-1}; S_{j}^{-1}) - IP(S_{i}^{-1})$$
$$= DIP(S_{j}^{-1}, S_{i}^{-1}) - IP(S_{i}^{-1}) - IP(S_{j}^{-1}).$$

Similar to $DIP(S_{i}^{-1}, S_{j}^{-1})$, the kinetic energy $KE(S_{i}^{-1}; S_{j}^{-1})$ depends significantly on the mutual arrangement of the core vacancies $S_{j}^{-1}$ and $S_{i}^{-1}$ in a molecule. This is clearly
seen from Table III where we collect the kinetic energies of all the core electrons of the CO molecule which one would detect in an XTPPS experiment given that the molecule is irradiated by an x-ray pulse with photon energies of 1 keV. First of all, we notice that it is more difficult to remove an electron from the core ionized CO molecule than from the neutral one. The respective energy difference is about 70-90 eV when the first and the second core electrons are ejected from the same core orbital. This energy difference reduces drastically to about 15 eV when different core orbitals are affected. Apparently, the electrostatic interaction between the two core holes plays a crucial role here. \( NRC(S_{-1}^{-1}, S_{-1}^{-1}) \) exerts an influence on the above energy differences too, as can be deduced from Eqs. (6) and (7).

2. One-site double core hole states

If \( S_i = S_j = S \) then \( \Delta E \) takes the form

\[
\Delta E_1(S^{-2}) = -\text{ERC}(S^{-1}, S^{-1}) + V_{SSSS}.
\]

We calculated \( \Delta E_1(S^{-2}) \) for the molecules under study using the respective CASSCF single and double core hole ionization potentials and collect them in Table IV. The dependence of \( \Delta E_1(S^{-2}) \) on the atomic number \( Z \) is displayed in Fig. 2(a).

The excess generalized relaxation energy \( \text{ERC}(S^{-1}, S^{-1}) \) can be easily obtained by measuring the energy difference \( \Delta E_1(S^{-2}) \) provided that the integral \( V_{SSSS} \) is known. \( V_{SSSS} \) can be extracted from \textit{ab initio} Hartree-Fock calculations on the electronic ground state of neutral molecules. Alternatively, it can be calculated by using the approximate analytical expression suggested in Ref. 2:

\[
V_{SSSS} = (2^{5/2}/3\pi)(Z - 2^{-3/2}).
\]

The respective results for \( V_{SSSS} \) and a difference between them are discussed in Appendix C.

Using Eq. (11) we represent \( \text{ERC}(S^{-1}, S^{-1}) \) as

\[
\text{ERC}(S^{-1}, S^{-1}) = \text{RC}(S^{-1}, S^{-1}) - 2\text{RC}(S^{-1}).
\]

It has been shown in Ref. 2 that at the second order perturbation theory the following relationship between the relaxation energies is valid:

\[
R(S^{-1}, S^{-1}) = 4R(S^{-1}).
\]
Since the impact of correlation into ionization potentials is small compared to the impact of relaxation, we expect that a similar relationship exists between the generalized relaxation energies $RC(S^{-1}, S^{-1})$ and $RC(S^{-1})$. Let us therefore introduce that

$$RC(S^{-1}, S^{-1}) = n \times RC(S^{-1}),$$

and find the optimal $n$. After the substitution of Eqs. (11) and (13) into (9), we get

$$\Delta E_1(S^{-2}) = -(n - 2)RC(S^{-1}) + V_{SSSS}.$$  

Now we can easily calculate $n$ by using the ab initio results for $\Delta E_1$, $RC$ and $V_{SSSS}$. The respective values of $n$ as a function of the atomic number $Z$ are shown in Fig. 3. As one can see, deviations of the calculated $n$ from the expected value of 4 are rather small (15% in the worst case of Li) and therefore $n = 4$ can be considered as a plausible approximation for the molecules studied in the present work.

As a result, we obtain the following expression for the generalized relaxation energy:

$$RC(S^{-1}) = (V_{SSSS} - \Delta E_1(S^{-2}))/2.$$  

The values of $RC(S^{-1})$ calculated by means of Eq. (15) are given in Table IV and also plotted in Fig. (b) as a function of $Z$. It is worthwhile to note a reasonable agreement between them and the corresponding results from Table I.

### 3. Two-site double core hole states

If $S_i \neq S_j$ then $\Delta E$ takes the form

$$\Delta E_2(S_i^{-1}, S_j^{-1}) = -IRC(S_i^{-1}, S_j^{-1}) + 1/r,$$

where the repulsion-exchange energy $E_{RE}$ has been approximated by the inverse of the distance $r$ between the two atoms with the core vacancies $S_i^{-1}$ and $S_j^{-1}$. We calculated $\Delta E_2(S_i^{-1}, S_j^{-1})$ using the CASSCF double and single core hole ionization potentials and collected these results in Table IV.

By looking at Eq. (16), one expects a linear dependence between $\Delta E_2(S_i^{-1}, S_j^{-1})$ and $1/r$. This expectation is not realized however as seen from Fig. 4(a) where a variation of $\Delta E_2$ with $1/r$ is shown. To elucidate the complex behavior of $\Delta E_2$ we calculated the interatomic generalized relaxation energy $IRC(S_i^{-1}, S_j^{-1})$ from Eq. (16) and plotted these
results as a function of $r$ in Fig. 4(b). We found both positive and negative values of $IRC$ (see also Table IV) which indicate on an enhancement or suppression of relaxation effects, respectively.

In the case of diatomic molecules, $IRC$ is always negative and thus the relaxation is suppressed. This suppression may be interpreted by considering the change of the electron density. A core hole $S_i^{-1}$ attracts valence electrons and increases the electron density in its vicinity, yielding a deficiency of the electron density in the vicinity of the atom with a core orbital $S_j$. The relaxation energy corresponding to the creation of the core vacancy $S_j^{-1}$ in the presence of the core hole $S_i^{-1}$ is therefore reduced. The amplitudes of $IRC$ are smaller for LiF, BF, and $N_2$ than for BeO, and CO. This is because the electrons are strongly attracted to the F site in LiF and BF, or tightened in the triple bond in $N_2$ and thus the electron density flow due to core hole creation is suppressed by these chemical environments.

Values of $IRC(S_i^{-1}, S_j^{-1})$ for the polyatomic molecules $C_2H_2$, $C_2H_4$, and $C_2H_6$ are, in contrast, positive. The enhancement of the relaxation for these molecules occurs due to the electron density flowing from the C-H bonds to the two carbon core hole sites.

The interatomic generalized relaxation energy exhibits a very interesting behavior with $r$ in triatomic molecules as seen from Fig. 4(b). $IRC(S_i^{-1}, S_j^{-1})$ is positive for CO$_2$ and $N_2$O when $S_i^{-1}$ and $S_j^{-1}$ are in adjacent atoms, namely in C and O in CO$_2$ and in $N_t$ and $N_c$ or in $N_c$ and O in $N_t$O$_c$. In these cases, the third atom plays the role of an electron donor and enhances the relaxation of the double core hole in the other two sites. The values of $IRC$ are, on the other hand, negative for CO$_2$ and $N_2$O with two holes in the terminal atoms, namely with holes in the two O sites of CO$_2$ and with holes in the $N_t$ and O sites of $N_2$O. In these cases, the creation of the core hole on one site already withdraws the electron density from the central atom and thus reduces the possibility of relaxation due to the creation of the second hole in the other terminal site.

In order to analyze the reorganization caused by double core hole ionization, we calculated the electron density difference between the ground and double core hole ionized states. These electron density differences without the 1s contribution are plotted in Fig. 5 to better visualize the reorganization of the valence electrons. In the blue or green region, the electron density increases, while the density decreases in the red region. In the $C_11s^{-2}$ state of $C_2H_4$, the electron density of the $C_1$-$C_2$, $C_1$-H bond and H atoms connected to $C_1$ atom reduces and flows to the region around $C_1$ atom as shown in Fig. 5(a). In the $C_11s^{-1}C_21s^{-1}$
state of \( \text{C}_2\text{H}_4 \), on the other hand, the electron density in the region of C-H bonds and H atoms flows to the region of both C atoms as in Fig. 5(b). This explains the positive value of IRC in the \( \text{C}_11s^{-1}\text{C}_21s^{-1} \) state as noted above. In the case of the \( \text{O}1s^{-2} \) state of CO, the electron density of the CO bond is used for the reorganization around the O atom (Fig. 5(c)).

IV. CONCLUSIONS

We have computed the ionization potentials of single and double core hole states of the small molecules LiF, BeO, BF, CO, \( \text{N}_2 \), \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{H}_6 \), CO\(_2\), and \( \text{N}_2\text{O} \) by means of the \( \Delta \text{SCF} \) and CASSCF methods in order to explore the impact of the chemical environment on the respective ionization processes and provide a guidance for x-ray two-photon photoelectron spectroscopy (XTTPS) experiments.

Our calculations have demonstrated that except for \( \text{N}_2\text{O} \), the double ionization potentials, especially the two-site ones of all these molecules are more sensitive to the chemical environment than the single ionization potentials. The sensitivity to the chemical environment of the two-site DIPs of \( \text{N}_2\text{O} \) is mainly governed by the interatomic relaxation energies which, in turn, strongly depend on the electron density distribution between the core-ionized atoms.

The quantities extracted from XTPPS are differences between the kinetic energies of core electrons ejected via the first and second ionization steps, i.e., of core electrons ejected from neutral and core-ionized systems, respectively. These kinetic energy differences are defined by a localization of the two core vacancies created and by relaxation processes induced by double core ionization. We have shown how one can extract the generalized relaxation energy associated with single core ionization as well as the excess and interatomic generalized relaxation energies associated with one-site and two-site double core ionizations, respectively, from experimental data by knowing the repulsion energy between the two core holes. The corresponding XTPPS experiments are now in preparation in the x-ray free electron laser facility LCLS at SLAC National Accelerator Laboratory.
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Appendix A: Scalar relativistic effects

It is essential in view of their large impact to take into account relativistic effects when considering systems with heavy atoms. For light atoms, relativistic effects are of less importance but still should be accounted when highly accurate results are needed. In the present work we assess the impact of scalar relativistic effects on IPs and DIPs by carrying out calculations with the relativistic DKH8 Hamiltonian for the CO and BF molecules. The results of these calculations are shown in Table [A]. As one can see the magnitude of the scalar relativistic effects on the single ionization potentials grows with the increasing atomic mass constituting 0.03, 0.09, 0.35, and 0.59 eV in the case of the B, C, O and F atoms, respectively. One of us has shown that a similar tendency is observed also for the third-row Si, P, S, Cl atoms. A growth of scalar relativistic effects with the atomic mass exhibits also in the case of double core hole ionization. We note that the relativistic effects on the one-site DIPs are about 2.3-3 times larger than those on the respective single IPs. Interestingly that in the case of two-site doubly ionized states the relativistic effects are perfectly described by the sum of the relativistic effects associated with the constituting single core vacancies.

Appendix B: Basis set effects

In this section we explore the basis set dependence of the single and double core hole ionization potentials by examples of the C_2H_2 and CO molecules. We have examined four
basis sets: the Dunning’s correlation-consistent basis sets cc-pVXZ (X=D,T,Q) and the cc-pCVTZ one. The latter contains tight basis functions which are added for a better description of properties of core-level states. The results are collected in Table VI. By looking at the sequence of the cc-pVXZ results we find significant differences between the cc-pVDZ and cc-pVQZ values, especially in the case of the one-site DIPs where differences of nearly 10 eV are present. The major changes occur upon improving the basis set from a double- to triple-zeta quality. Choosing the cc-pVQZ basis sets lowers ionization potentials by only 0.2-1.2 eV relative to the cc-pVTZ values. The cc-pCVTZ results are lower in energy than the cc-pVTZ ones whereby they nearly coincide with the cc-pVQZ results in the case of the CO molecule. We used the cc-pVTZ basis throughout as a compromise between the accuracy of the results and the computational costs. For the double core-hole states, the relaxation of valence orbitals is important, in particular for the one-site states where all 1s electrons on one atom are missing.

Appendix C: Evaluation of the $V_{SSSS}$ integral

The approximate analytical expression (10) was proposed in Ref. 2 for the two electron integral $V_{SSSS}$. By comparing the analytical results with the explicit ab initio ones (dotted curve and filled circles in Fig. 6, respectively) we found a progressively growing deviation between them with increasing $Z$ (1.5 eV for lithium, 4.5 eV for fluorine). This deviation can be removed by substituting $1.037 \cdot Z$ instead of $Z$ in Eq. (10), where the coefficient 1.037 has been extracted from a linear fit (dashed curve in Fig. 6) of the ab initio results.

Appendix D: Effect of dynamic correlations

We performed the CI calculations with the space of the singly excited configurations from the CASSCF configurations and examined the semi-internal correlation. The results for the single and double core-hole states of C$_2$H$_2$ and CO were summarized in Table VII. The difference between the results of CI and CASSCF provides the effect of the semi-internal correlation. The semi-internal correlation has small effect on IPs of the single hole states, less than +0.03 eV for C1s$^{-1}$ and +0.25 eV for O1s$^{-1}$. The effect for the one-site double core-hole states is significant as +0.24 $\sim$ +0.54 eV, while it is small for the two-site double
core-hole states as $+0.08 \sim +0.12\;\text{eV}$.

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TABLE I. Single core hole ionization potentials and their constituent parts (in eV) as calculated with the ∆SCF and CASSCF methods. Experimental values of the ionization potentials, where available, taken from Refs. 38-44 are also shown. The cc-pVTZ basis sets were employed.

| Molecule | Core level, $S$ | $\varepsilon_S$ | ∆SCF | CASSCF | Expt. |
|----------|----------------|-----------------|-------|--------|-------|
|          |                | $\varepsilon_S$ | IP ($S^{-1}$) | IP ($RC(S^{-1})$) | $C(S^{-1})$ |
| LiF      | Li1s           | 66.407          | 65.460 | 0.947  | 65.334 | 1.073  | 0.126  |
|          | F1s            | 710.484         | 688.187 | 22.297 | 688.044 | 22.440 | 0.143  |
| BeO      | Be1s           | 128.383         | 124.406 | 3.977  | 123.399 | 4.984  | 1.007  |
|          | O1s            | 556.694         | 535.181 | 21.513 | 535.075 | 21.619 | 0.106  |
| BF       | B1s            | 209.735         | 202.539 | 7.196  | 201.724 | 8.011  | 0.815  |
|          | F1s            | 717.810         | 695.873 | 21.937 | 695.915 | 21.895 -0.042 |
| CO       | C1s            | 309.111         | 298.256 | 10.855 | 296.358 | 12.753 | 1.898  | 296.069 |
|          | O1s            | 562.348         | 542.801 | 19.547 | 542.820 | 19.528 | -0.019 | 542.543 |
| N$_2$O   | N$_1$1s        | 427.159         | 409.615 | 17.544 | 408.614 | 18.545 | 1.001  | 408.5  |
|          | N$_c$1s        | 432.005         | 415.373 | 16.632 | 412.524 | 19.481 | 2.849  | 412.5  |
|          | O1s            | 563.760         | 543.046 | 20.714 | 542.537 | 21.223 | 0.509  | 542.0  |
| CO$_2$   | C1s            | 311.930         | 300.607 | 11.323 | 297.647 | 14.283 | 2.960  | 296.78 |
|          | O1g            | 561.956         | 541.979 | 19.977 | 542.870 | 19.086 | -0.891 | 540.6  |
|          | O1u            | 561.954         | 19.975  | 542.868 | 19.086 | -0.889 |
| C$_2$H$_2$| C1g            | 305.897         | 292.535 | 13.362 | 292.202 | 14.062 | 0.700  | 291.14, 291.20 |
|          | C1u            | 305.794         | 13.259  | 292.111 | 14.054 | 0.795  |
| C$_2$H$_4$| C1g            | 305.557         | 291.801 | 13.756 | 291.344 | 14.213 | 0.457  | 290.70, 290.88 |
|          | C1u            | 305.508         | 13.707  | 291.297 | 14.211 | 0.504  |
| C$_2$H$_6$| C1g            | 305.040         | 291.774 | 13.266 | 291.147 | 13.893 | 0.627  | 290.76, 290.74 |
|          | C1u            | 305.023         | 13.249  | 291.125 | 13.898 | 0.649  |
| N$_2$    | N1g            | 426.686         | 411.242 | 15.444 | 411.027 | 15.659 | 0.215  | 409.93  |
|          | N1u            | 426.588         | 15.346  | 410.932 | 15.656 | 0.310  | 409.82  |
TABLE II. Calculated double core hole ionization potentials and the static correlation energies C (in eV). T and S refer to triplet and singlet couplings of two core holes created on different atomic sites, respectively. The cc-pVTZ basis sets were employed.

| Molecule | Core level          | ∆SCF DIP     | CASSCF DIP | C    |
|----------|---------------------|--------------|------------|------|
| LiF      | Li1s$^{-2}$         | 173.125      | 172.595    | 0.530|
|          | F1s$^{-2}$          | 1480.418     | 1481.495   | -1.077|
|          | Li1s$^{-1}$F1s$^{-1}$, S | 763.447      | 763.211    | 0.236|
|          | Li1s$^{-1}$F1s$^{-1}$, T | 763.443      | 763.277    | 0.166|
| BeO      | Be1s$^{-2}$         | 300.585      | 298.032    | 2.553|
|          | O1s$^{-2}$          | 1158.135     | 1159.351   | -1.216|
|          | Be1s$^{-1}$O1s$^{-1}$, S | 672.823      | 671.801    | 1.022|
|          | Be1s$^{-1}$O1s$^{-1}$, T | 672.823      | 672.128    | 0.695|
| BF       | B1s$^{-2}$          | 468.243      | 465.323    | 2.920|
|          | F1s$^{-2}$          | 1494.930     | 1495.809   | -0.879|
|          | B1s$^{-1}$F1s$^{-1}$, S | 910.946      | 910.568    | 0.378|
|          | B1s$^{-1}$F1s$^{-1}$, T | 910.946      | 910.678    | 0.268|
| CO       | C1s$^{-2}$          | 667.902      | 664.418    | 3.484|
|          | O1s$^{-2}$          | 1175.376     | 1176.561   | -1.185|
|          | C1s$^{-1}$O1s$^{-1}$, S | 857.072      | 854.743    | 2.329|
|          | C1s$^{-1}$O1s$^{-1}$, T | 857.072      | 855.200    | 1.872|
| N$_2$O   | N$_t$1s$^{-2}$      | 894.485      | 893.926    | 0.559|
|          | N$_c$1s$^{-2}$      | 906.773      | 902.312    | 4.461|
|          | O1s$^{-2}$          | 1173.683     | 1173.249   | 0.434|
|          | N$_t$1s$^{-1}$N$_c$1s$^{-1}$, S | 838.282      | 832.962    | 5.320|
|          | N$_t$1s$^{-1}$N$_c$1s$^{-1}$, T | 838.279      | 833.215    | 5.064|
|          | N$_t$1s$^{-1}$O1s$^{-1}$, S | 965.806      | 963.041    | 2.765|
|          | N$_t$1s$^{-1}$O1s$^{-1}$, T | 965.806      | 963.266    | 2.540|
|          | N$_c$1s$^{-1}$O1s$^{-1}$, S | 968.082      | 965.793    | 2.289|
|          | N$_c$1s$^{-1}$O1s$^{-1}$, T | 968.082      | 965.623    | 2.459|
| Compound | 1s -2 | 1s -1 | 2s -2 | 2s -1 | 3s -2 | 3s -1 |
|----------|-------|-------|-------|-------|-------|-------|
| CO₂      | 670.280 664.629 5.651 | 1172.821 1171.909 0.912 | 854.682 851.059 3.623 | 854.682 851.199 3.483 | 1094.795 1094.090 0.705 | 1094.795 1094.167 0.628 |
| C₂H₂     | 651.265 650.228 1.037 | 598.281 594.590 3.691 | 598.281 595.197 3.084 | 681.646 651.334 30.312 | 681.646 651.334 30.312 |
| C₂H₄     | 648.964 648.556 0.408 | 594.850 591.514 3.336 | 594.850 591.956 2.894 | 679.386 649.703 29.683 | 679.386 649.703 29.683 |
| C₂H₆     | 649.714 648.827 0.887 | 591.447 589.007 2.440 | 591.447 589.192 2.255 | 677.339 649.898 27.441 | 677.339 649.898 27.441 |
| N₂       | 901.704 901.155 0.549 | 901.704 901.155 0.549 | 839.912 835.784 4.128 | 839.912 836.437 3.475 | 938.943 903.727 35.216 | 938.943 903.727 35.216 |
TABLE III. Kinetic energies of photoelectrons one would detect in an XTPPS experiment by irradiating the CO molecule with an x-ray pulse with photon energies of 1 keV. The sequence of the core vacancies in the records reflects the sequence of ionization steps. T and S refer to triplet and singlet couplings of two core holes created on different atomic sites, respectively.

| State               | KE (eV) |
|---------------------|---------|
| C1s\(^{-1}\)        | 703.642 |
| C1s\(^{-1}\)C1s\(^{-1}\) | 631.940 |
| O1s\(^{-1}\)C1s\(^{-1}\), S | 688.077 |
| O1s\(^{-1}\)C1s\(^{-1}\), T | 687.620 |
| O1s\(^{-1}\)        | 457.180 |
| O1s\(^{-1}\)O1s\(^{-1}\) | 366.259 |
| C1s\(^{-1}\)O1s\(^{-1}\), S | 441.615 |
| C1s\(^{-1}\)O1s\(^{-1}\), T | 441.518 |
TABLE IV. Calculated energy differences $\Delta E_1(S_i^{-2})$ and $\Delta E_2(S_i^{-1}, S_j^{-1})$ together with the intra- and interatomic generalized relaxation energies $RC(S_i^{-1})$ and $IRC(S_i^{-1}, S_j^{-1})$ (in eV).

| Molecule | Energy difference | Generalized relaxation energy |
|----------|------------------|-----------------------------|
| LiF      | $\Delta E_1(Li1s^{-2})$ | 41.927 $RC(Li1s^{-1})$ | 1.41 |
|          | $\Delta E_1(F1s^{-2})$ | 105.407 $RC(F1s^{-1})$ | 20.17 |
|          | $\Delta E_2(Li1s^{-1}, F1s^{-1})$ | 9.833 $IRC(Li1s^{-1}, F1s^{-1})$ | -0.74 |
| BeO      | $\Delta E_1(Be1s^{-2})$ | 51.234 $RC(Be1s^{-1})$ | 5.23 |
|          | $\Delta E_1(O1s^{-2})$ | 89.201 $RC(O1s^{-1})$ | 19.90 |
|          | $\Delta E_2(Be1s^{-1}, O1s^{-1})$ | 13.327 $IRC(Be1s^{-1}, O1s^{-1})$ | -2.69 |
| BF       | $\Delta E_1(B1s^{-2})$ | 61.875 $RC(B1s^{-1})$ | 8.38 |
|          | $\Delta E_1(F1s^{-2})$ | 103.979 $RC(F1s^{-1})$ | 20.88 |
|          | $\Delta E_2(B1s^{-1}, F1s^{-1})$ | 12.929 $IRC(B1s^{-1}, F1s^{-1})$ | -1.52 |
| CO       | $\Delta E_1(C1s^{-2})$ | 71.702 $RC(C1s^{-1})$ | 11.87 |
|          | $\Delta E_1(O1s^{-2})$ | 90.921 $RC(O1s^{-1})$ | 19.03 |
|          | $\Delta E_2(C1s^{-1}, O1s^{-1})$ | 15.565 $IRC(C1s^{-1}, O1s^{-1})$ | -2.80 |
| N₂       | $\Delta E_1(N1s^{-2})$ | 79.196 $RC(N1s^{-1})$ | 17.65 |
|          | $\Delta E_2(N1s^{-1}, N21s^{-1})$ | 13.825 $IRC(N1s^{-1}, N21s^{-1})$ | -0.65 |
| C₂H₂     | $\Delta E_1(C1s^{-2})$ | 66.653 $RC(C1s^{-1})$ | 15.06 |
|          | $\Delta E_2(C1s^{-1}, C21s^{-1})$ | 11.015 $IRC(C1s^{-1}, C21s^{-1})$ | 0.96 |
| C₂H₄     | $\Delta E_1(C1s^{-2})$ | 65.915 $RC(C1s^{-1})$ | 15.42 |
|          | $\Delta E_2(C1s^{-1}, C21s^{-1})$ | 8.873 $IRC(C1s^{-1}, C21s^{-1})$ | 1.94 |
| C₂H₆     | $\Delta E_1(C1s^{-2})$ | 66.555 $RC(C1s^{-1})$ | 15.06 |
|          | $\Delta E_2(C1s^{-1}, C21s^{-1})$ | 6.735 $IRC(C1s^{-1}, C21s^{-1})$ | 2.72 |
| CO₂      | $\Delta E_1(C1s^{-2})$ | 69.335 $RC(C1s^{-1})$ | 13.76 |
|          | $\Delta E_1(O1s^{-2})$ | 86.171 $RC(O1s^{-1})$ | 22.70 |
|          | $\Delta E_2(C1s^{-1}, O1s^{-1})$ | 10.572 $IRC(C1s^{-1}, O1s^{-1})$ | 1.79 |
|          | $\Delta E_2(O1s^{-1}, O1s^{-1})$ | 8.352 $IRC(O1s^{-1}, O1s^{-1})$ | -2.19 |
| N₂O      | $\Delta E_1(N1s^{-2})$ | 76.698 $RC(N1s^{-1})$ | 17.78 |
|          | $\Delta E_1(N1s^{-2})$ | 77.264 $RC(N1s^{-1})$ | 17.47 |
|          | $\Delta E_1(O1s^{-2})$ | 88.175 $RC(O1s^{-1})$ | 20.40 |
|          | $\Delta E_2(N1s^{-1}, N21s^{-1})$ | 11.827 $IRC(N1s^{-1}, N21s^{-1})$ | 1.11 |
|          | $\Delta E_2(N1s^{-1}, O1s^{-1})$ | 2.7032 $IRC(N1s^{-1}, O1s^{-1})$ | 0.07 |
|          | $\Delta E_2(N1s^{-1}, O1s^{-1})$ | 11.890 $IRC(N1s^{-1}, O1s^{-1})$ | -6.00 |
TABLE V. Single and double core hole ionization potentials of CO and BF calculated with the CASSCF method using the relativistic DKH8 Hamiltonian and the differences between them and the respective non-relativistic results given in Tables II and III. All energies are in eV. T and S refer to triplet and singlet couplings of two core holes created on different atomic sites, respectively.

| Molecule | State | Ionization Potential | Difference |
|----------|-------|-----------------------|------------|
| CO       | C1s\(^{-1}\) | 296.446 | 0.088 |
|          | O1s\(^{-1}\) | 543.166 | 0.346 |
|          | C1s\(^{-2}\) | 664.661 | 0.243 |
|          | O1s\(^{-2}\) | 1177.408 | 0.847 |
|          | C1s\(^{-1}\)O1s\(^{-1}\), S | 855.176 | 0.433 |
|          | C1s\(^{-1}\)O1s\(^{-1}\), T | 855.632 | 0.432 |
| BF       | B1s\(^{-1}\) | 201.758 | 0.034 |
|          | F1s\(^{-1}\) | 696.500 | 0.585 |
|          | B1s\(^{-2}\) | 465.425 | 0.102 |
|          | F1s\(^{-2}\) | 1497.177 | 1.368 |
|          | B1s\(^{-1}\)F1s\(^{-1}\), S | 911.187 | 0.619 |
|          | B1s\(^{-1}\)F1s\(^{-1}\), T | 911.297 | 0.619 |
TABLE VI. Basis set dependence of the CASSCF single and double core hole ionization potentials. All energies are in eV. T and S refer to triplet and singlet couplings of two core holes created on different atomic sites, respectively.

| Molecule | State               | cc-pVDZ  | cc-pVTZ  | cc-pCVTZ | cc-pVQZ  |
|----------|---------------------|----------|----------|----------|----------|
| C₂H₂     | C₁g⁻¹               | 293.262  | 292.202  | 292.111  | 291.728  |
|          | C₁u⁻¹               | 293.172  | 292.111  | 292.020  | 291.634  |
|          | C₁s⁻²               | 658.167  | 650.228  | 649.412  | 649.711  |
|          | C₁1s⁻¹C₂₁s⁻¹, S     | 598.350  | 594.590  | 594.337  | 593.908  |
|          | C₁1s⁻¹C₂₁s⁻¹, T     | 598.853  | 595.197  | 594.971  | 594.592  |
| C₁s⁻¹   | C₁1s⁻¹              | 298.062  | 296.358  | 296.239  | 296.229  |
|          | O₁s⁻¹               | 544.881  | 542.820  | 542.611  | 542.559  |
|          | C₁s⁻²               | 672.908  | 664.418  | 663.663  | 663.632  |
|          | O₁s⁻²               | 1184.846 | 1176.561 | 1175.469 | 1175.373 |
|          | C₁1s⁻¹O₁s⁻¹, S      | 859.146  | 854.743  | 854.452  | 854.425  |
|          | C₁1s⁻¹O₁s⁻¹, T      | 859.491  | 855.200  | 854.931  | 854.905  |
TABLE VII. Effect of dynamic correlations examined by the CI calculation. All energies are in eV.

| Molecule | State       | CASSCF | CI       |
|----------|-------------|--------|----------|
| C₂H₂      | C₁g⁻¹       | 292.202| 292.216  |
|          | C₁u⁻¹       | 292.111| 292.127  |
|          | C₁s⁻²       | 650.228| 650.586  |
| C₁s⁻¹C₂s⁻¹, S | 594.590  | 594.728|
| C₁s⁻¹C₂s⁻¹, T | 595.197  | 595.319|
| CO       | C₁s⁻¹       | 296.358| 296.386  |
|          | O₁s⁻¹       | 542.820| 543.070  |
|          | C₁s⁻²       | 664.418| 664.658  |
|          | O₁s⁻²       | 1176.561| 1177.096|
| C₁s⁻¹O₁s⁻¹, S | 854.743  | 854.833|
| C₁s⁻¹O₁s⁻¹, T | 855.200  | 855.276|
FIG. 1. (Color online). Schematic picture of x-ray two-photon photoelectron spectroscopy (XTPPS) and x-ray two-photon-induced Auger electron spectroscopy (XTPAES). See text for explanations. In this picture it is assumed that the second photon is absorbed before Auger decay takes place and that one core hole decays much faster than the other. In reality all processes overlap.

FIG. 2. (a) The energy difference \( \Delta E_1(S^{-2}) = DIP(S^{-1}, S^{-1}) - [IP(S^{-1}) + IP(S^{-1})] \) as a function of the atomic number \( Z \) of the atom with the core orbital \( S \); (b) The generalized relaxation energy \( RC(S^{-1}) \) calculated by means of Eq. (15) as a function of \( Z \).

FIG. 3. The ratio \( n = RC(S^{-1}, S^{-1})/RC(S^{-1}) \) as a function of the atomic number \( Z \) of the atom with the core orbital \( S \).

FIG. 4. (a) The energy difference \( \Delta E_2(S^{-1}, S^{-1}) = DIP(S^{-1}, S^{-1}) - [IP(S^{-1}) + IP(S^{-1})] \) as a function of the inverse distance \( r \) between the atoms with the core orbitals \( S_i \) and \( S_j \); (b) The interatomic generalized relaxation energy \( IRC(S^{-1}, S^{-1}) \) calculated by means of Eq. (16) as a function of \( r \).

FIG. 5. Differences between the valence electron density distributions of the ground and double core hole states: (a) \( C_11s^{-2} \) of \( C_2H_4 \); (b) \( C_11s^{-1}C_21s^{-1} \) (singlet) of \( C_2H_4 \); (c) \( O1s^{-2} \) of CO

FIG. 6. The two-electron integral \( V_{SSSS} \) as a function of the atomic number \( Z \) of the atom with the core orbital \( S \). The results extracted from the \textit{ab initio} calculations (filled circles) are compared with those calculated by means of Eq. (10) (dotted curve). A linear fit of the \textit{ab initio} results is also shown (dashed curve).

FIGURE CAPTIONS
(a) $C_1 1s^2$ of $C_2H_4$

(b) $C_1 1s^1 C_2 1s^1, ^3\Sigma^+$ of $C_2H_4$

(c) $O 1s^2$ of CO
$V_{SSSS}$ (eV)

Atomic number, $Z$

- **ab initio**
- $(\frac{2^{5/2}}{3\pi})(Z-2^{-3/2})$
- $(\frac{2^{5/2}}{3\pi})(1.037 \cdot Z-2^{-3/2})$