Published in final edited form as:

J Chem Theory Comput. 2017 July 11; 13(7): 3120–3135. doi:10.1021/acs.jctc.6b00958.

Assessment of electron propagator methods for the simulation of vibrationally-resolved valence and core photoionization spectra

A. Baiardi^{*,†}, L. Paoloni[†], V. Barone[†], V.G. Zakrzewski[‡], and J.V. Ortiz[‡]

[†]Scuola Normale Superiore, piazza dei Cavalieri 7, I-56126 Pisa, Italy

[‡]Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849-5312

Abstract

The analysis of photoelectron spectra is usually facilitated by quantum mechanical simulations. Due to the recent improvement of experimental techniques, the resolution of experimental spectra is rapidly increasing, and the inclusion of vibrational effects is usually mandatory to obtain a reliable reproduction of the spectra. With the aim of defining a robust computational protocol, a general time-independent formulation to compute different kinds of vibrationally-resolved electronic spectra has been generalized to support also photoelectron spectroscopy. The electronic structure data underlying the simulation are computed using different electron propagator approaches. In addition to the more standard approaches, a new and robust implementation of the second-order self-energy approximation of the electron propagator based on a transition operator reference (TOEP2) is presented.

To validate our implementation, a series of molecules has been used as test cases. The result of the simulations shows that, for ultraviolet photoionization spectra, the more accurate non-diagonal approaches are needed to obtain a reliable reproduction of vertical ionization energies, but diagonal approaches are sufficient for energy gradients and pole strengths. For X-ray photoelectron spectroscopy, the TOEP2 approach, besides being more efficient, is also the most accurate in the reproduction of both vertical ionization energies and vibrationally-resolved bandshapes.

1 Introduction

Ionization energies (IEs) are fundamental quantities in chemistry, since they determine the energy needed to remove an electron from a molecule, which, in turn, plays a key role in tuning chemical reactivity. From an experimental point of view, several techniques are available to determine IEs, such as zero-electron kinetic energy spectroscopy,¹ photoelectron-photoion coincidence spectroscopy^{2,3} and photoelectron spectroscopy.^{4,5} Among them, photoelectron spectroscopy has received in recent years particular attention since, due to the availability of synchrotron sources and analysers,^{6,7} the resolution of the experimental spectra is increasing rapidly, and therefore a large amount of information is contained in an

* a.baiardi@sns.it.

experimental spectrum. However, in order to fully characterize the recorded spectrum and to extract all the available information, theoretical simulations are usually needed. For example, those spectra are usually characterized by asymmetric bandshapes, which are determined by the effects of molecular vibrations on the photoelectron processes.^{8–11} Due to the presence of those effects, it is not straightforward to extract a reliable value of the IE from the experimental spectrum. If the IE is taken as the energy corresponding to the maximum of intensity, the so-called vertical ionization energy (VIE) is considered, whereas when the lowest energy tail of the spectrum is selected, the adiabatic ionization energy (AIE) is obtained.^{12,13} Due to the presence of vibrational effects, those two quantities are in general different. Therefore, in order to reproduce the whole photoelectron spectrum, electronic structure calculations giving a single value of the IE are not sufficient, and the inclusion of vibrational effects is mandatory.

Several approaches to include vibrational effects in the simulation of photoelectron spectra have been proposed in the literature,^{8,14–16} most of which are based on quantum dynamics simulations. Within the present work, an alternative approach, based on a sum-over-states (also known as time-independent, TI) formulation will be proposed and integrated in a general framework developed by some of us for the simulation of several kinds of spectra.^{17,18}

The underlying electronic structure data have been obtained from density functional theory (DFT) for the neutral ground states, and from electron propagator theory (EPT) for the cationic states. As is well known, in EPT the properties of cationic states (such as their IEs) are computed from the one-particle Green function.¹⁹ Since only the Hartree-Fock (HF) canonical orbitals of the ground state are needed to build the Green function, the wavefunction for the cationic states are not explicitly constructed. The exact one-particle Green function is not known, thus a perturbation expansion in powers of the correlation potential is usually employed. The zeroth-order approximation corresponds to IEs computed at the Koopmans theorem level, but correlation effects can be included through higher-order approximation of the one-particle Green function. More in detail, the IEs are obtained as eigenvalues of a one-particle operator, where correlation effects are included in the so-called self-energy matrix, and the eigenfunctions are known as Dyson orbitals. Many approximate electron propagators have been proposed, which can be mainly divided in two classes. In the so-called diagonal approaches,^{20–22} the Dyson orbitals are proportional to the HF canonical orbitals. This approximation is usually well-suited for valence ionizations, but it becomes quite poor when dealing with core ionizations that involve large relaxation effects. In those cases, the more complete non-diagonal approaches are usually needed to obtain reliable results.^{20,23} However, the computational cost of non-diagonal approaches is much higher than that of the diagonal models, and this limits their applicability to medium-size systems. In order to tackle also larger-size systems, more efficient approaches must be devised.^{24,25} Among the propagator-based methods, the second-order approximation of the one-particle Green function with a transition operator reference (TOEP2) is particularly appealing in this respect. The transition operator method is a special case of the grand-canonical Hartree-Fock theory, where spin-orbitals may have fractional occupation numbers. Use of a grand-canonical reference incorporates relaxation effect in the definition of the orbitals, and therefore more accurate results are obtained using low-order approximations of the one-

particle Green function.^{26,27} Core IEs obtained at the TOEP2 level are usually more accurate than those obtained using standard EPT, both diagonal and non-diagonal.^{28,29} Here, we introduce a new implementation of the TOEP2 theory coupled with the maximum overlap method (MOM)^{30,31} to increase its reliability.

From another point of view, the performance of various EPT methods have been evaluated until now only by comparing computed VIEs to the experimental data which is, as discussed above, not sufficient for high-resolution spectra. A comparison of those approaches in the reproduction of vibrational signatures in photoelectron spectra is still scarce. Therefore, in this work we will simulate the whole photoelectron spectra of different, medium-size organic molecules taking vibronic effects into proper account. Together with geometries and vibrational frequencies of the neutral, ground state, we will compute IEs, pole strengths and energy gradients of cationic states using different EPT methods to assess the level of theory needed to reproduce accurately each quantity. In particular, the performance of the TOEP2 approach in the simulation of X-ray photoelectron spectra (XPS) will be tested, in order to check its reliability in the reproduction of core ionization processes. Through a direct comparison of theoretical and experimental photoionization spectra, hybrid schemes can also be defined, where different quantities required to compute the spectra (ionization energies, nuclear gradients of cationic states, pole strengths) are computed at different level of theory to obtain the best compromise between computational effort and accuracy. Regarding the computation of vibrational effects, the vertical gradient (VG) model will be employed, since the use of more refined models (such as adiabatic models¹⁷ both in cartesian and in internal coordinates^{32,33}) would require the calculation of harmonic frequencies of ionized states using propagator approaches, which is beyond the goal of this work. Anyway, even if more refined models have been proposed in the literature for the simulation of photoionization spectra,^{15,34,35} the reliability of vertical models in treating both semi-rigid and flexible systems with limited mode-mixing effects has been already reported in the literature both for absorption^{33,36} and for photoionization^{8,37} spectroscopies. As already reported in the literature,^{33,36} an internal-coordinates (possibly anharmonic)³⁸ treatment is required to tackle also flexible systems with the same level of accuracy.^{39,40}

The work is organized as follows. In the second section, the EPT approaches used in the work will be outlined, with particular attention to the description of the implementation of the TOEP2 approach. Furthermore, the extension of the framework developed for the simulation of vibrationally-resolved absorption and emission spectroscopies to photoelectron spectroscopy will be described. After a sketch of the computational details in the third section, the fourth section will present the application of the theory to the simulation of photoelectron spectra of several medium-size, biological systems. Furane and uracil will be used as test cases to assess the reliability of the EPT approaches in the simulation of valence photoelectron spectra, whereas ethanol and chloroethane will be used as a reference for core ionization spectra, due to the availability of recently recorded, high-resolution XPS spectra.^{39,41}

2 Theory

2.1 Electron propagator methods

To simulate vibrationally-resolved photoelectron spectra, Green-function techniques will be employed. Within those approaches, the ionization energies are determined as the poles of the electron propagator $G(E)$. Let us express $G(E)$ in a basis of one-particle functions ϕ . The matrix elements $G(E)_{pq}$ between functions ϕ_p and ϕ_q can be expressed as follows:⁴²

$$G_{pq}(E) = \lim_{\eta \rightarrow 0} \left[\sum_r \frac{\langle \Phi_0^N | a_p^\dagger | \Phi_r^{N-1} \rangle \langle \Phi_r^{N-1} | a_q | \Phi_0^N \rangle}{E - E_0^N + E_r^{N-1} - i\eta} + \sum_s \frac{\langle \Phi_0^N | a_q | \Phi_s^{N+1} \rangle \langle \Phi_s^{N+1} | a_p^\dagger | \Phi_0^N \rangle}{E + E_0^N - E_s^{N+1} + i\eta} \right] \quad (1)$$

where Φ_r^{N-1} and Φ_s^{N+1} are $N-1$ and $N+1$ -electron states with energy E_r^{N-1} and E_s^{N+1} , respectively. Furthermore, $|\Phi_0^N\rangle$ is the exact electronic ground-state wavefunction, and η is a positive, infinitesimal quantity, which is used to avoid singularities in the definition of $G(E)$. Equation 1 shows that $G(E)$ has poles for $E = E_0^N - E_r^{N-1} + i\eta$ and $E = E_r^{N+1} - E_0^N + i\eta$, when E approaches the energy of an ionization or of an electron attachment. To compute in practice those poles, it is useful to express the one-particle Green function in the vector space composed by all the combinations of second-quantization operators changing the number of electrons by ± 1 . A consistent definition of the scalar product between two elements $\mathbf{a}$ and $\mathbf{a}'$ of this vector space, and of the action of the Hamiltonian superoperator $\mathcal{H}$ on $\mathbf{a}$ is obtained using the following rules:⁴³

$$(\mathbf{a} | \mathbf{a}') = \langle \Phi_0^N | [\mathbf{a}^\dagger, \mathbf{a}']_+ | \Phi_0^N \rangle$$

$$\mathcal{H} \mathbf{a} = [\mathbf{a}, H] \quad (2)$$

where the square brackets represent the commutator, whereas the square brackets with the + subscript represent the anticommutator. Using equation 2, it is possible to express the inverse of the electron-propagator matrix as follows:⁴²

$$\mathbf{G}^{-1}(E) = E\mathbf{I} - \mathbf{F} - \mathbf{\Sigma}(E) \quad (3)$$

where $\mathbf{F}$ is the matrix associated to the Fock operator, and $\mathbf{\Sigma}(E)$ is the so-called self-energy matrix, which contains the corrections to $\mathbf{G}(E)$ due to correlation effects. When E approaches the energy of a pole, $\det(\mathbf{G}^{-1}(E)) = 0$. As a consequence, the poles are found as eigenvalues of the following generalized one-electron equations:

$$[\mathbf{F} + \mathbf{\Sigma}(E)]\mathbf{C} = E\mathbf{C} \quad (4)$$

The eigenvector matrix $\mathbf{C}$ defines the transformation between the molecular orbitals and the so-called Dyson orbitals ψ_p^{Dyson} . The Dyson orbitals are, in general, not normalized, and their norm π_p is defined as pole strength and is related, as will be shown in the following, to peak intensities in photoelectron spectra. The relation between π_p and $\mathbf{C}$ is the following:¹³

$$\pi_p^{-1} = 1 - \left(\mathbf{C}^\dagger \frac{d\mathbf{\Sigma}}{dE} \mathbf{C} \right)_{pp} \quad (5)$$

Equation 4 must be solved iteratively, since E appears both on both sides of the equation. Different expressions for $\mathbf{\Sigma}(E)$ are obtained, depending on the perturbation order which is used to approximate the ground-state wavefunction. The methods used to compute $\mathbf{\Sigma}(E)$ can be divided in two main classes, diagonal and non-diagonal. Within the diagonal approaches, off-diagonal elements of $\mathbf{\Sigma}(E)$ are neglected. This approximation simplifies the solution of equation 4, since the $[\mathbf{F} + \mathbf{\Sigma}(E)]$ matrix is already diagonal in the canonical molecular orbitals basis, meaning that the Dyson orbitals are proportional to the canonical ones. Within diagonal approaches, the lowest-order non-zero contribution to $\mathbf{\Sigma}$ is obtained at the second order (usually referred to as second-order electron propagator, EP2), and can be expressed as follows:

$$\omega_k = \epsilon_k + \sum_a \sum_{i < j} \frac{|\langle ka || ij \rangle|^2}{\omega_k + \epsilon_a - \epsilon_i - \epsilon_j} + \sum_i \sum_{a < b} \frac{|\langle ki || ab \rangle|^2}{\omega_k + \epsilon_i - \epsilon_a - \epsilon_b} \quad (6)$$

where ω_k is the energy of the pole, ϵ_k are the orbital energies and $\langle ij || kl \rangle$ are bielectronic integrals. Furthermore, i, j, k label occupied orbitals, whereas a, b label virtual ones. The third term is usually referred to as the two particle-one hole (2p-1h) term and the second one as two hole-one particle (2h-1p) term. The arithmetic scaling of Equation 6 is determined by the evaluation of the second term, which scales as OV^2 , where O is the number of occupied orbitals and V is the number of the virtual ones. Despite its efficiency, the EP2 approach usually underestimates experimental ionization energies. Third-order terms can be included within the so-called third-order electron propagator (EP3) approach, but in this case the experimental results are overestimated.¹³ More accurate results are obtained within the so-called outer valence Green function (OVGF) approach,^{20,44} where higher-order terms are included in an approximate way. Even if the diagonal approximation is retained, the main limitation of the OVGF approach is the arithmetic scaling as OV^4 . More efficient approaches, such as the partial third order approximation (P3)²¹ and the renormalized partial third-order approximation (P3+)²² have been devised, and will be used in the following.

Diagonal approaches are usually well-suited if orbital relaxation effects are not relevant, but their accuracy decreases when significant differences are present between canonical and Dyson orbitals. To obtain more accurate results, the full self-energy matrix $\mathbf{\Sigma}$ is needed to compute the poles through equation 4, within the so-called non-diagonal approaches. Among the non-diagonal approaches which have been proposed in the literature, here the

non-diagonal, renormalized second-order approach (NR2)²³ and the third-order algebraic diagrammatic construction (ADC(3))²⁰ will be employed. It is noteworthy that, besides the generation of the full self-energy matrix (which scales as $\mathcal{O}^2 V^3$ for NR2 and as $\mathcal{O} V^4$ for ADC(3)), the computational cost of non-diagonal approaches increases also due to the diagonalization step.

The range of applicability of non-diagonal approaches is strongly limited by their computational costs, and therefore, to tackle also larger-size systems, more efficient approaches must be developed. The main limitation of the standard propagator approaches described above in describing ionizations accompanied by significant relaxation effects is the large difference between the canonical Hartree-Fock and the Dyson orbitals. For this reason high-order approximations of the propagator must be used to obtain reliable results.⁴⁵ To get results of the same quality using lower-order approximations of the one-body Green function, a different set of reference orbitals must be used.

In this respect, molecular orbitals obtained by solving grand-canonical Hartree-Fock equations,^{46,47} where fractional occupation numbers are used, are particularly appealing for the simulation of ionization processes. In grand-canonical Hartree-Fock theory, the one-particle density operator ρ is defined as follows:⁴⁸

$$\rho = \prod_i [1 - \langle \mathbf{n}_i \rangle + \mathbf{n}_i (2 \langle \mathbf{n}_i \rangle - 1)] \quad (7)$$

where $\mathbf{n}_i$ is the occupation number operator for the i -th orbital. Even if the occupation numbers are usually determined under equilibrium conditions by statistical thermodynamics, Equation 7 is valid also for general ensembles, that do not correspond to any equilibrium distribution. Therefore, the population of the orbitals can be tuned to obtain grand-canonical orbitals, which are closer to those of the ionic state and which are therefore a better reference for a perturbative expansion of the propagator. Once the distribution n_i is set, the Fock operator $\mathcal{F}$ and the density matrix $\mathcal{P}$ in the atomic basis are given by:^{29,49}

$$P_{\mu\nu} = \sum_{i=1}^{N_{occ}} n_i C_{\mu i} C_{\nu i} \quad (8)$$

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{i=1}^{N_{occ}} \langle \mu i | | \nu i \rangle n_i \quad (9)$$

where μ and ν label two atomic basis functions, while the sum over N_{occ} includes the spin-orbitals with non-null occupation numbers. Furthermore, $\mathbf{C}$ is the matrix with the coefficients of the molecular orbitals in terms of the basis set and $\mathbf{n}$ is the vector of the occupation numbers. In the following, the transition operator (TO) approach, where the occupation number is fractional only for one spin-orbital, whereas it is either null or 1 for

the other orbitals will be used to compute ionization energies. In this way, by lowering the occupation number of the orbital involved in the transition, the resulting orbitals are well-suited to perform propagator calculations.²⁸

The orbital energies obtained from a TO computation provide a significantly more reliable estimate of the ionization energies than the canonical orbital energies.⁵⁰ However, the accuracy of those results is comparable to that of standard, non-diagonal approaches, which is still not satisfactory (with errors above 1 eV) for core ionizations.²⁸ To further improve the accuracy of the results, perturbative corrections to the one-particle Green function must be computed. Such corrections may be based on the spin-orbitals of the TO SCF. By replacing the pure reference state, $|\Psi_0^N\rangle$, of equation 1 with a reference ensemble defined by $|0\rangle = (|\Psi_0^N\rangle + |\Psi_f^{N-1}\rangle)/\sqrt{2}$, where $|\Psi_f^{N-1}\rangle$ is a core-ionized state, one may generate low-order, self-energy improvements to TO orbital energies.^{26–28} The latter expressions employ grand-canonical density operators and generalize the usual self-energy formulae through the introduction of spin-orbital occupation numbers.^{51,52} In this manner, the electron propagator may be adapted to the consideration of a specific electron binding energy in which strong orbital relaxation must be described, but without the evaluation of otherwise necessary self-energy corrections of high order. As for standard, canonical orbitals, the first non-zero contribution for grand-canonical orbitals still arises from the second-order term. The expression for the pole energy ω_k using the diagonal, second-order correction for general occupation numbers n_k , is the following:^{26–28}

$$\omega_k = \epsilon_k + \sum_{q,s,t} \frac{|\langle kq | st \rangle|^2}{\omega_k + \epsilon_q - \epsilon_s - \epsilon_t} \cdot [n_q(1 - n_s - n_t) + n_s n_t] \quad (10)$$

where ϵ_n are the grand-canonical orbital energies. The sum over q, s, t includes both the (possibly fractionally) occupied and the virtual orbitals. When standard HF orbitals are employed, and therefore the occupation number is 1 for the occupied orbitals and 0 for the virtual ones, the only non-null terms correspond to $n_q = 0, n_s = n_t = 1$ and $n_q = 1, n_s = n_t = 0$, and the standard second-order, diagonal approximation of the propagator given in equation 6 is obtained. On the other hand, if the TO method is used, and therefore, besides the occupied and virtual orbitals, an orbital k has a fractional occupation number n_k , equation 6 can be expressed as follows:²⁸

$$\omega_k = \epsilon_k + \sum_a \sum_{i < j} \frac{|\langle ka | ij \rangle|^2}{\omega_k + \epsilon_a - \epsilon_i - \epsilon_j} n_i n_j + \sum_i \sum_{a < b} \frac{|\langle ki | ab \rangle|^2}{\omega_k + \epsilon_i - \epsilon_a - \epsilon_b} \quad (11)$$

$$+ \sum_i \sum_a \frac{|\langle ki | ka \rangle|^2}{\omega_k + \epsilon_i - \epsilon_a - \epsilon_k} (1 - n_k) \quad (12)$$

In this case, the sum over i and j includes also the fractionally-occupied orbital k . The introduction of a fractionally occupied orbital modifies the standard expression of EP2 propagator given in equation 10 in two respects. First of all, the terms in the sum of the 2h-p term are scaled by the occupation numbers. Furthermore, a third, additional term is present, involving the bielectronic integrals $\langle ki||ka \rangle$, where i is an occupied orbital and a a virtual one. As for all the diagonal approaches, the pole ω_k appears on both sides of equation 12, which therefore must be solved iteratively by taking as a first guess for ω_k the orbital energy obtained from the TO calculation.

In practice, SCF calculations with fractional occupation numbers raise additional issues with respect to the standard case. In fact, during the SCF procedure, the energy order of the orbitals may change, and when such change occurs, the components of the vector $\mathbf{n}$ must be permuted in a consistent way. A consistent permutation can be done using the maximum-overlap criterion (MOM).^{28,30,31} Let $\mathbf{C}^{(m)}$ and $\mathbf{C}^{(m+1)}$ be the matrix coefficient of the molecular orbitals in terms of the basis set for two successive SCF cycles (m -th and $m+1$ -th). An overlap matrix $\mathbf{O}$ can be built as follows:

$$\mathbf{O} = \mathbf{C}^{(m+1),T} \mathbf{S} \mathbf{C}^{(m)} \quad (13)$$

where $\mathbf{S}$ is the matrix with the overlap integrals between the basis functions. For each occupied orbital k of the m -th SCF cycle, the k -th row of the $\mathbf{O}$ matrix ($\mathbf{O}_k$) is considered and the squared elements of its components are computed. The maximum of those values determines the index h of molecular orbital of the $m+1$ -th cycle most similar to the k -th one of the m -th cycle. Thus, the occupation number vector at the $m+1$ -th cycle ($\mathbf{n}^{(m+1)}$) is built from the previous one ($\mathbf{n}^{(m)}$) setting $n_h^{(m+1)} = n_k^{(m)}$. Even if for valence ionization of small- and medium-size systems the order of the molecular orbitals remains usually unchanged during the SCF cycles, this is not the case for core ionizations. The energy difference between the core orbitals centered on atoms of the same type is usually small, and therefore changes in the orbital order are frequent.

2.2 Bandshape simulation

Before describing the inclusion of vibrational effects in the simulation of photoelectron spectra, it is useful to present briefly the framework developed by some of us to simulate vibrationally-resolved one-photon spectra.^{17,53} Within this framework, the Born-Oppenheimer approximation is used to neglect non-adiabatic couplings between the electronic states involved in the transition. Then, the harmonic approximation is used to compute the vibrational wavefunction for each electronic state. Using those approximations, the spectrum can be expressed using the following general sum-over-states formula:³⁸

$$I(\omega_0) = \alpha \omega_0^\beta \sum_{I,F} \rho_I \langle \mathbf{v}_I | \boldsymbol{\mu}^e | \mathbf{v}_F \rangle \langle \mathbf{v}_F | \boldsymbol{\mu}^e | \mathbf{v}_I \rangle \delta(\Delta E + |\varepsilon_F - \varepsilon_I| - \omega_0) \quad (14)$$

where $I(\omega_0)$ is a general observable, whose definition changes with the spectroscopy of interest. $|v_I\rangle$ and $|v_F\rangle$ are the initial and final vibrational levels of the transition, with energy ε_I and ε_F , respectively and ω_0 is the frequency of the incident light. μ^e is the electric transition moment, which is a function of the nuclear coordinates, and is usually approximated as a zero-th (Franck-Condon approximation, FC)⁵⁴ or first-order (Herzberg-Teller approximation, HT)⁵⁵ Taylor expansion in terms of the normal modes of one of the states. Using either the FC or the HT approximation, Equation 14 contains sums of Franck-Condon integrals ($\langle v_F | v_I \rangle$), which are computed, in the so-called time-independent (TI) approaches, using either analytical or recursive equations.^{56–58} Since the sum over the FC integrals is virtually unbound, in our implementation a class-based prescreening scheme is used to select *a-priori* the most relevant transitions, and the convergence of the spectrum is checked *a-posteriori* comparing the computed integrated intensity with analytical sum rules.

This framework can be extended to support also photoelectron spectroscopy. In this case, the electronic states involved in the transition are the ground electronic state of the neutral molecule, labelled as I , and the cationic state, labelled as F . The only quantity which must be changed in Equation 14 to simulate photoelectron spectra is the electronic coupling between the neutral and the cationic state. The electronic wavefunction of the cationic state can be approximated as $\Psi_F = \Psi_F^{N-1} \otimes \Psi_c$, where Ψ_F^{N-1} is the electronic wavefunction of the $N-1$ electrons of the cation, whereas Ψ_c is the unbound wavefunction of the electron, which has been ionized. As discussed in ref.,^{60,61} this factorization can be used to express the electronic coupling as follows:

$$k_i^e = K \cdot \langle \phi_i | \mu | \Psi_c \rangle \quad (15)$$

where the ionization of interest is labelled as i , and $|\phi_i\rangle$ is the Dyson orbital associated to this ionization. As already recalled above, $|\phi_i\rangle$ can be expressed as $P_i \cdot |\phi'_i\rangle$, where P_i^2 is the pole strength of the transition and $|\phi'_i\rangle$ is the normalized Dyson orbital. In principle, both the electric transition dipole moment $\langle \phi'_i | \mu | \Psi_c \rangle$ and the pole strength P_i change with the nuclear coordinates. The nuclear dependence of the first term is usually neglected and the electric transition dipole moment is assumed to be the same for all the transitions.⁴² Under these approximations, Equation 14 can be expressed as follows:

$$\sigma(\omega_0) = \alpha \omega_0 \sum_{I,F} \rho_I P_{eq}^2 |\langle v_I | v_F \rangle|^2 \delta(\Delta E + \varepsilon_F - \varepsilon_I - \omega_0) \quad (16)$$

where σ is the photoionization cross section, and α is a fixed proportionality constant. In the following, all the theoretical spectra will be reported using relative unities, and therefore α will be set to match the experimental results. It should be noted that considering the pole strength as a constant is equivalent to a zero-th order Taylor expansion with respect to the nuclear coordinates, which is equivalent to the FC approximation of the transition dipole

moment. In order to check the reliability of this approximation, also first order terms can be included in the treatment, following the same strategy used to support HT effects.⁶²

As already recalled above, the model used to compute vibrationally-resolved spectra relies on the harmonic approximation of both the neutral and the cationic state. However, different models can be developed, depending on the reference geometry used for the Taylor expansion of the cationic state PES. Two different families of models are usually employed, namely vertical approaches, where the PES of the cationic state is expanded about the equilibrium geometry of the neutral ground state, and the adiabatic ones, where the expansion is performed about the minimum of the cationic PES.^{17,63} In the following, vertical models will be employed, since the optimization of the cationic electronic state would increase significantly the computational costs and goes beyond the goal of this work. Among them, the Vertical Gradient (VG) model will be employed, where mode-mixing effects are neglected (meaning that the Duschinsky matrix $\mathbf{J}$ is equal to the identity matrix $\mathbf{I}$), and the shift vector is given by the following expressions:

$$\mathbf{K} = -\mathbf{\Omega}_I^{-2} \mathbf{L}_I^{-1} \mathbf{M}^{-1/2} \mathbf{g}_F \quad (17)$$

where $\mathbf{\Omega}_I$ is the diagonal matrix with the harmonic frequencies of the neutral state and $\mathbf{L}_I$ is the matrix with its normal modes. $\mathbf{M}$ is the diagonal matrix of the atomic masses, and $\mathbf{g}_F$ is the gradient of the cationic state PES computed at the equilibrium geometry of the neutral electronic state. The extension to the more refined Vertical Hessian (VH) model requires the calculation of second derivatives of the ionization energies with respect to nuclear displacements, which increases significantly the computational cost of the overall procedure.

3 Computational details

All the computations have been performed with a development version of the Gaussian suite of quantum chemical programs,⁶⁴ locally modified to support also TOEP2 calculations. Electronic structure calculations on neutral electronic states were carried out using density functional theory (DFT),⁶⁵ with the B3LYP exchange-correlation functional⁶⁶ and the SNSD basis set,⁶⁷ which is obtained by adding to the 6-31G(d,p) basis set a minimal number of corevalence (one s function on all non-hydrogen atoms) and diffuse (s,p,d on non-hydrogen atoms and p on hydrogen atoms) functions optimized specifically for global hybrid functionals.^{68,69} For uracil, the geometry optimization and harmonic frequencies calculation for the neutral state has been performed at the MP2 level, following the computational procedure described elsewhere.⁷⁰ Propagator calculations for valence ionizations have been performed in all cases using the cc-pVTZ and aug-cc-pVTZ basis sets. For the calculation of core ionizations, the EPRIII-d basis set also has been employed. The EPRIII-d basis set is derived from the EPR-III one,⁷¹ which is a triple- ζ basis set with diffuse and polarization functions and an improved description of the core region (the contractions are (6,2)/[4,2] for H and (11,7,2,1)/[7,4,2,1] for the atoms from B to F), by adding the diffuse polarization functions (p on hydrogen and d on atoms from B to F) taken from the aug-cc-pVTZ basis set.⁷² If not otherwise stated, a threshold of 10^{-6} has been used

to assess the convergence of the iterative search of the poles, both for diagonal and for non-diagonal approaches.

All the vibronic computations are based on a time-independent (TI) approach that uses a class-based prescreening scheme to select *a-priori* the most relevant Franck-Condon integrals.¹⁷ If not otherwise specified, the standard parameters of the prescreening scheme have been used, where:

$$C_1^{max}=20, \quad C_2^{max}=13, \quad N_I^{max}=10^8$$

where N_I^{max} is the maximum number of Franck-Condon integrals computed in a given class and C_1^{max} and C_2^{max} are the maximum quanta of excitations included in class 1 (corresponding to the overtones) and 2 (corresponding to the combination bands with 2 excited modes), respectively. A more detailed description of the prescreening scheme can be found elsewhere.^{59,73} Vibrational levels of the excited states with up to seven simultaneously excited modes have been taken into account (class 7) and, in all cases, a nearly complete convergence (> 99 %) of the TI computation has been reached.

Regarding the calculation of the nuclear gradients of ionization energies ($\mathbf{g}_{IP}$), the expression obtained for the i -th component using a numerical differentiation procedure is the following:

$$g_{IP,i} = \frac{E_{IP}(+\delta_i) - E_{IP}(-\delta_i)}{2\delta} \quad (18)$$

where δ is the value of the displacement used in the numerical differentiation procedure, and $E_{IP}(+\delta_i)$ and $E_{IP}(-\delta_i)$ are the ionization energies computed by changing the i -th cartesian coordinates by $+\delta$ and $-\delta$ with respect to its equilibrium value. If not otherwise stated, δ has been set to 0.001 Å, following the procedure used in previous works.^{74,75} An analogous procedure has been used to compute the nuclear gradients of the pole strengths in computations performed at the FCHT level.

It has been noted that the $\mathbf{g}_F$ which is used in equation 17, is the gradients of the total energy E_{tot} , which can be expressed as $E_0 + E_{IP}$, where E_0 is the electronic energy of the ground state and E_{IP} is the ionization energy.⁷⁶ By using this definition, the gradient $\mathbf{g}_F$ can be decomposed as follows:

$$g_{F,i} = \frac{\partial E_0}{\partial x_i} + \frac{\partial E_{IP}}{\partial x_i} = g_{0,i} + g_{IP,i} \quad (19)$$

However, the first term is zero, since the derivative is computed at an equilibrium geometry of the ground state, therefore $\mathbf{g}_F = \mathbf{g}_{IP}$, and can be computed using equation 18. In practice, the numerical differentiation has been performed using an external program interfaced to GAUSSIAN.

4 Applications

4.1 Valence photoionization of furane

Furane is the first system used to test the reliability of the theoretical framework. Due to its small size, both the ionization energies and gradients of the cationic state PES can be computed with a limited computational costs, and therefore the performances of all the methods described in the theoretical section can be tested. Furthermore, experimental high-resolution photoelectron spectra of furane are reported in the literature,^{77–79} where single vibronic bands are detectable, and therefore the reliability of the approaches can be checked by comparing experimental and theoretical results. In this work, the experimental data will be taken from ref.⁷⁹ which is, to the best of our knowledge, the most recent and highest resolution spectrum available in the literature. The photoelectron spectrum of furane has been already studied using both propagator-based^{80,81} and other electronic structure methods, such as symmetry-adapted cluster configuration interaction (SAC-CI)⁸² and complete active space SCF (CAS-SCF).⁸³ However, vibrational signatures on the photoelectron spectrum have been usually neglected in theoretical calculations, with the exception of a limited number of studies, also using more refined models than the ones presented here.^{15,84,85} In particular, in ref.¹⁵ the photoelectron spectra of furane, pyrrole and thiophene were simulated using a diabatic picture and including couplings between the two lowest ionic states, that are neglected in the study presented here. However, the results reported in ref.¹⁵ prove that, even if non-adiabatic effects are relevant for pyrrole and thiophene, they are negligible for furane, and models neglecting the coupling between the cationic PESs can be used to reproduce the vibronic bandshape. Therefore, furane can be chosen as a test case to simulate the photoelectron spectrum at the VG level with different combinations of Green function-based approaches in order to find the best compromise between computational cost and accuracy.

Two separate bands are present in the experimental spectrum of furane, which are associated to ionizations of the HOMO and HOMO-1 orbitals, leading to cationic states of 2A_2 and 2B_1 types, respectively. The theoretical energies for those ionizations computed using different combinations of propagator methods and basis sets are reported in table 1. As expected, the largest error is obtained using the EP2 and EP3 approaches, where the difference between computed and theoretical ionization potentials is above 0.2 eV. This inaccuracy is recovered using the other approaches, OVGF, P3 and P3+. Among them, the best reproduction of both the absolute and relative values of the ionization energies is obtained with the OVGF approach, where the difference between theoretical and experimental data is below 0.1 eV for both electronic states. This result is compatible with a recent benchmark,¹³ where it is shown that, among the diagonal methods, the most accurate results are obtained at the OVGF level employing a medium-size basis set.

The use of the non-diagonal approaches NR2 and ADC(3) does not lead to any significant improvement in the reproduction of ionization energies, which are comparable to those obtained with the diagonal approaches, since the relative ionization energy is underestimated at the NR2 level and overestimated at the ADC(3) level with respect to the OVGF results.

Among the non-diagonal approaches, the NR2 results are more reliable with respect to the ADC(3) ones, and this trend also is coherent with the reported benchmark.¹³

A similar comparison of the reliability of the different Green function approaches has been performed also for the computation of the energy gradient of the cationic state. In all cases, the gradients have been computed at the equilibrium geometry of the neutral state, obtained at the B3LYP/SNSD level and, instead of considering the numerical values of the gradient, the comparison has been performed directly on the vibrationally-resolved spectra, which are reported in figure S1. In order to facilitate the comparison of the band-shapes, all the spectra have been shifted to match the energy of the 0-0 transition with the value computed at the EP2 level (for the upper figure) and at the ADC(3) level (for the lower figure). Those results show that the effect of the propagator method used in the simulation does not affect significantly the computed value of the gradient, since the bandshape is nearly superimposable for all the propagator methods which have been used. Therefore, high-order approximations of the one-particle propagator are needed to recover accurate vertical ionization energies, whereas lower-order approaches are sufficient for the computation of the gradients. Based on those results, the full valence photoelectron spectrum has been computed at the OVGF/cc-pVTZ level and compared to the experimental spectrum, taken from ref.,⁷⁹ in figure 2. The major discrepancy between the experimental and the theoretical spectrum is an overall shift of the latter of about 2000 cm^{-1} toward lower energies, whereas the relative value of the IEs, as well as the overall bandshape, is reproduced accurately. A more detailed analysis of the active vibronic progressions for the photoionization spectrum of furane is reported in tables S1 and S2 of the Supporting Information, where the most intense vibrational bands, based on the OVGF/cc-pVTZ intensities, are reported. As expected, for both the cationic states, the most intense transitions involve excitations of totalsymmetric modes (6, 9, 11, 12, 15 and 16), that are the only ones giving, at the VG|FC level, non-null overlap with the ground state vibrational wavefunction (that is totalsymmetric as well and is the unique initial state when temperature effects are neglected, as in the present case). In both cases, the 0-0 transition, involving the vibrational ground levels, are the most intense ones. This suggests that the geometrical shift is limited, and therefore the VG model can be employed. Furthermore, vibrational progressions are more extended, on average, for the ionization to the 2A_2 state than for the 2B_1 one. This is coherent with the analysis reported in the reference theoretical paper,¹⁵ and is further confirmed by the fact that the components of $\mathbf{K}$ are larger, on average, for the 2A_2 state, as shown in the graphical representation reported in figure S2 of the Supporting Informations. For the 2A_2 state, the most intense vibronic bands are fundamentals of modes 11, 15 and 16, in agreement with the analysis reported in ref.¹⁵ However, it should be noted that our analysis differs from the reference one for the assignment of a band at about 1500 cm^{-1} , corresponding to the fundamentals of mode 16 in our calculation, that was assigned to an overtones of mode 10 in ref.¹⁵ For the second electronic state (2B_1 symmetry), vibrational transitions involving modes above 1000 cm^{-1} are less intense than for the 2A_2 state, and the most intense vibrational transition is the fundamental of mode 6, in agreement with ref.¹⁵

The VG|FC spectra for the ionization to the 2A_2 cationic state of furane computed at the OVGF/cc-pVTZ has been used also as test case to check the stability of the computation of

the gradient by numerical differentiation with respect to the step size and with respect to the threshold used to assess the convergence of the propagator calculation. The upper panel of figure S3 shows that the spectra computed using a threshold of 10^{-4} , 10^{-6} and 10^{-8} in the Green function computation are superimposable, so the standard values can be safely used to obtain reliable results. The same consideration holds also for the spectra computed using different step-sizes (0.05, 0.1 and 0.2 Å) in the numerical differentiation, as shown in the lower panel of figure S3. Therefore, the parameters reported in the computational details have been used for all the simulations.

As a conclusion, the theoretical photoionization spectrum of furane to the 2A_2 state has been computed at the FCHT level, therefore including also the first-order derivatives of the pole strength in the simulation. The comparison with the spectrum obtained at the VG|FC level reported in figure S4 shows that the effects of the HT terms is in this case negligible, and the two spectra are nearly superimposed.

4.2 Uracil

To check the reliability of the computational methods here proposed, another useful case study is uracil, which is one of the four nucleobases of the RNA. The VIEs have been computed using both diagonal and non-diagonal approaches, whereas the gradients have been computed in all cases at the OVGf level since, as shown above for furane, the choice of the propagator method used in the simulation has a minor impact in the reproduction of the gradients, which can therefore be computed using cheaper methods. The reliability of the various propagator approaches has been checked comparing the theoretical results with the experimental photoelectron spectrum taken from ref.86 that is, up to our knowledge, the most accurate spectrum available in the literature, displaying an higher resolution with other spectra available in the literature.^{87,88} The theoretical results have been also compared with previous computational studies performed by some of us on the IEs of uracil⁷⁰ and more recent simulations of the vibronic photoelectron spectrum of this system.⁸⁹ Unlike the other computations reported in this section, and following the procedure reported elsewhere,⁷⁰ the geometries have been optimized at the MP2 level in conjunction with the aug-cc-pVTZ basis set. In fact, the equilibrium structures computed at this level are in good agreement with the experimentally determined geometry.^{90,91}

The computed IEs for the first 4 valence orbitals computed using different propagator approaches and using the cc-pVTZ and aug-cc-pVTZ basis sets are summarized in tables 2 and 3, respectively. As already noticed for furane, the results obtained using Koopmans' theorem (zeroth-order approximation for the propagator) and lower-order electron propagator methods, such as EP2, do not provide a satisfactory agreement with the experimental results, not even at the qualitative level since, for both the approaches, the energy order of the orbitals is incorrectly reproduced. For example, the Koopmans' theorem results predict the energy of the π_2 ionization being lower than that of the σ_{O-} one, in disagreement with the experimental energy order. Similarly, also at the EP2 level, the relative position of the ionization energies of the π_1 and σ_{O-} orbitals is incorrect. The use of higher-order diagonal methods, such as OVGf and P3, furnish, as expected, better results and the energy order of the IEs is reproduced correctly. However, the relative ionization

energies are still inaccurate. For example, the energy separation between the ionizations of the σ_{O_-} and the π_2 orbitals is underestimated at the OVGF level. A significant improvement in the agreement with the experimental results is obtained at the P3 level. It should be also noted that, using the larger aug-cc-pVTZ basis set, the reproduction of the absolute IEs worsens for both the OVGF and the P3 approaches, whereas the energy differences are nearly constant. This is in agreement with the results reported previously,⁷⁰ where the best agreement was obtained at the P3 level, using the relatively small 6-311G** basis set. A further improvement in the reproduction of the experimental data is obtained using non-diagonal approaches, as shown in the last two columns of tables 2 and 3. In fact, the difference between the ionization energies obtained at the NR2/cc-pVTZ level and the experimental data are within 0.1 eV, except for the σ_{O_+} orbital, where the difference is about 0.2 eV. However, the accuracy is recovered using the larger aug-cc-pVTZ basis set, which is best-suited to describe the diffuse σ_{O_+} orbital, which has mostly a non-bonding character. Therefore, to conclude, the best results for vertical IEs are obtained at the NR2 level in conjunction with aug-cc-pVTZ basis set.

The theoretical photoelectron spectrum computed at the VG|FC level is reported in figure 3. As already mentioned above, with the aim of limiting the computational cost, the gradient of the cationic PESs have been computed at the OVGF/cc-pVTZ level, whereas the IEs have been computed at the NR2/aug-cc-pVTZ level. Those results show that the inclusion of vibrational effects has a significant impact on the overall band-shape, since the extent of vibronic broadening is different for different ionizations. In fact, the most significant progressions are associated to the lowest-energy ionization (ionization of an electron from the π_1 orbital), leading to a less intense and more broadened bandshape. As shown in figure 4, the overall bandshape of the experimental spectrum is qualitatively reproduced correctly. For example, the band associated to the lowest-energy ionization is more broadened with respect to the other ones, and no progressions are detectable. Furthermore, the band-shape also for the other ionizations is reproduced satisfactorily and, for example, the maximum of the spectrum is obtained for the ionization of the π_2 orbital. However, the agreement is less satisfactory for the second band, associated to the ionization of the σ_{O_-} orbital, and one of the peaks present in the experimental spectrum is not reproduced in the simulations. Results obtained from quantum dynamics calculations, using the multi-configurational time-dependent Hartree (MCTDH) approach,⁸⁹ have shown that the further inclusion of anharmonicity effects withing a diabatic picture provide a better reproduction of the overall bandshape. The inclusion of such effects within our model would require the calculation of second derivatives of cationic state PES, and this would require either the implementation of analytical gradients for Green function-based approaches (following, for example, the strategy presented in ref.⁷⁶) or the calculation of the force constants by double numerical differentiation. In both cases, the computational costs of the electronic structure calculations underlying the simulations of vibrational effects would increase significantly, and therefore a similar analysis goes beyond the goal of the present work.

The results presented here shows that a qualitative reproduction of vibrational signatures in photoelectron spectra can be recovered in a cost-effective way using the VG|FC model, and by computing energy gradients a lower-accuracy (OVGF) level, using an higher accuracy approach (NR2) for the calculation of the vertical IEs. To further confirm this conclusion, in

figure 5 the vibrationally-resolved spectrum obtained computing both the IEs and the gradients at the OVGF/cc-pVTZ level is reported. The agreement with the experimental spectrum⁸⁶ is in this case poorer. The relative ionization energies of the σ_{O+} and π_2 orbitals is underestimated with respect to the experimental data at the OVGF level, and as a consequence the spectra associated to those two ionizations are superimposed, giving a single, intense band.

To further highlight the computational saving achieved using the hybrid scheme presented above, a comparison of the computational time of each calculation required to obtain the final spectrum is reported in the left panel of figure S5. The two most expensive computational steps are the calculation of the vertical IEs and of the gradients, and the cost of the vibronic simulation is negligible with respect to the other steps. Furthermore, as shown in the right panel the figure, by computing both IEs and gradients at the NR2/aug-cc-pVTZ, the relative weights of the calculation of the gradient would increase significantly, by increasing also the overall computational time.

4.3 XPS spectrum of ethanol and chloroethane

Up to this point, propagator methods have been applied to compute ionization potentials for the valence orbitals. Here, the analysis will be extended to the simulation of XPS spectra, involving the ionization of core orbitals. In fact, as already remarked above, due to the increasing power of synchrotron light source, the accuracy of XPS spectra is increasing as well, and the inclusion of vibrational effects is usually mandatory to reproduce correctly the experimental data. Here, we will focus on the simulation of the XPS spectrum of ethanol in the energy range between 290 and 295 eV, which is characterized by the presence of two main bands, associated to the ionization of the electrons of the two C 1s orbitals.^{39,41} Ethanol is a suitable test-case to check the reliability of the approaches described above in the simulation of XPS spectra since, thanks to its limited size, both diagonal and non-diagonal approaches can be employed to compute both IEs and gradients with a limited computational effort. Furthermore, the high-resolution spectrum of ethanol is available in the literature,^{39,41} and therefore the reliability of the different propagator methods in reproducing the bandshape with the inclusion of vibrational signatures can be tested by comparing the results with those experimental data.

In table 4, the ionization potentials for the C 1s core orbitals of ethanol, computed using different combinations of propagator approaches and basis sets, are reported. Two non-equivalent equilibrium structures (referred to as *a* and *b* in the following) are present in the ground state, whose structures are reported in figure 6. The main difference between the two structures is the position of the H atom bonded to the O atom, which is closer to the methyl group in the (b) conformers than in the (a) one. Whereas the energy separation between the two minima is comparable to the vibrational energies,⁴¹ the IEs have been computed for each conformer.

As already mentioned in the theoretical section, when an electron is removed from an inner-core orbital, relaxation effects may be relevant. In those cases, the diagonal approximation of the one-electron Green function is usually insufficient, and non-diagonal approaches are needed to simulate reliably the IEs. In fact, as shown in table 4 in both the diagonal OVGF

and P3 methods the IEs of both the C 1s orbitals are overestimated by 1.5-2 eV on average, employing either the cc-pVTZ or the aug-cc-pVTZ basis set. The accuracy of the results increases significantly by employing the TOEP2 approach, as shown in the last three rows of table 4. In fact, in this case the difference between the theoretical results and the experimental data decreases, and is below 0.7 eV for both the C 1s orbitals. The relative value of the ionization potentials for the two C 1s orbitals, which was already satisfactory for OVGf and P3, remains accurate at the TOEP2 level. In order to further check the reliability of the TOEP2 results, the ionization potentials have been computed also by using the EPR-IIIId basis set, which is characterized by an accurate description of the core orbitals, and which has already been used to compute vibrationally-resolved NEXAFS spectra.⁷² By using the EPR-IIIId basis set, the difference between theoretical and computed ionization potentials further decreases by 0.1 eV, whereas the difference between the two ionization potentials is nearly unchanged. The ionization energies have been computed also with the non-diagonal approaches NR2 and ADC(3), and the results are reported in table 4. By employing the NR2 approach, the difference with the experimental data decreases with respect to the OVGf and P3 results, but the discrepancy is still above 1 eV, and therefore is larger than for TOEP2. By using the more refined ADC(3) approach, the agreement between the theoretical and the experimental data worsens, becoming even poorer than the one obtained using the diagonal approaches described above. This is probably due to an incomplete description of the orbital relaxation effects even if non-diagonal, third-order terms are included at the ADC(3) level, and higher order terms should be included to obtain more reliable results. Therefore, for this test case, the TOEP2 approach is the most reliable propagator method in the reproduction of both the absolute and the relative value of the ionization energies for the C 1s core orbitals.

In order to simulate the XPS spectrum of ethanol at the VG level, the different propagator methods have been employed to compute the gradient of the PES of the cationic state at the equilibrium geometry of the neutral one, using in all cases the cc-pVTZ basis set. As a first step, the XPS spectrum for the ionization of the C_α 1s orbital has been computed. For the sake of simplicity, all the computations have been performed for the (a) conformer, since, as will be discussed in the following, the results for the (b) conformer are equivalent. In all cases, the cc-pVTZ basis set has been employed. The results obtained using the diagonal approaches are reported in figure 7, whereas the ones obtained with the non-diagonal ones are given in figure 8. In order to help the comparison of the bandshapes, all the spectra have been shifted to match the 0-0 transition with the one computed at the TOEP2 level. The comparison of the theoretical spectra obtained with Gaussian broadening functions with a smaller HWHM (0.01 eV) shows that, even if the overall bandshape is reproduced coherently by the three diagonal approaches, slight differences are present in the intensity of the bands in the higher energy region of the spectrum. More in detail, the computed intensity of those bands is lower at the TOEP2 level than at the OVGf (or P3) one. This difference is still detectable if a larger HWHM (0.075 eV) is used. The comparison of the spectra with the experimental results shows that the bandshape is reproduced more accurately if the TOEP2 and OVGf approaches are used, whereas the accuracy decreases employing the P3 approach. The same spectrum has been simulated also using the non-diagonal approaches NR2 and ADC(3), and the results are reported in figure 8. The TOEP2 spectrum is reported

as well to help the comparison with the previous results. Also in this case, the spectra have been shifted to match the energy of the 0-0 transition to the one, computed at the TOEP2 level. It is noteworthy that the spectra obtained at the NR2 and ADC(3) levels are nearly superimposable. However, as already noticed for the P3 approach, at both NR2 and ADC(3) levels the intensity of the bands in the higher-energy region of the spectrum is overestimated with respect to the experimental data. Therefore, in this case the TOEP2 approach is the most reliable also in the reproduction of the bandshape of the XPS spectrum.

The TOEP2 approach has thus been employed to simulate the whole XPS spectrum. In order to get a reliable reproduction of the experimental data, the ionization of the 1s orbital has been computed for the C_α and C_β atoms in both the conformers (a) and (b). The electronic energy difference between the two conformers, computed at the B3LYP/SNSD level is 7.704 meV, which corresponds to a population of 57 % of (a) and 43 % of (b) at room temperature. Those values have been used to weight the spectra of the two conformers and to obtain the overall spectrum. The comparison between the theoretical spectrum, computed at the TOEP2/cc-pVTZ level within the VG|FC model, and the experimental results, which is reported in figure 9, shows that, even if the computed spectrum is shifted by approximately 0.5 eV with respect to the experimental one, the relative position of the bands, as well as their shape, is reproduced accurately. In order to highlight the relevance of vibrational effects, in figure 10 the VG spectrum is compared to the vertical energy (VE) spectrum, where vibrational effects are neglected. This comparison shows that the relative intensity of the bands associated to the ionization of the core orbitals of the C_α and C_β atoms is poorly reproduced at the VE level. This is due to the fact that the impact of molecular vibration is different for the two bands, the broadening being more significant for the C_β atom than for the C_α one. This effect can be detected also in figure 9, where the contribution of each C atom and of each conformer is reported. In fact, it is evident that, for both conformers, more extended progressions are detected for the ionization of the 1s orbital of the C_β than the one of the C_α orbital, and therefore the maximum of intensity decreases. It should also be noted that, for the ionization of the C_α 1s orbital, the spectra obtained for the (a) and (b) conformers are nearly superimposable. On the other hand, both the position and the shape of the bands associated to the ionization of the C_β 1s orbital are different. Those results are in agreement with the analysis given in ref.,³⁹ where the difference in the ionization energies of the C_β 1s orbitals is ascribed to a different interaction, in the cationic state, between the positive hole in the C_β atom and the hydroxyl group. To further highlight the different impact of vibrational effects in the two bands of the XPS spectrum, a graphical representation of the shift vector $\mathbf{K}$ for the ionization of the two C 1s core orbitals for the (a) conformer is reported in figure 11 (the results for the (b) conformer have not been included for the sake of simplicity, and are nearly equivalent to the ones obtained for the first conformer). For the ionization of the C_β core orbital, the largest component of $\mathbf{K}$ is the one associated to the torsion along the H-O- C_α - C_β dihedral angle (mode 3 in figure 11, $K_3 \approx 34 \text{ amu}^{1/2} \cdot \text{Bohr}$), and the other ones are at least three times smaller. On the other hand, for the ionization of the C_α 1s orbital, the magnitude of the shift vector decreases significantly for all the components, especially for the torsional mode, since in this case $K_3 \approx 5.5 \text{ amu}^{1/2} \cdot \text{Bohr}$. Since, within the VG|FC model, the intensity of the progressions increases with the magnitude of the shift vector,^{38,92} the broadening is larger for the C_α atom due to the larger

shift of the torsional motion. This result is coherent with the analysis reported elsewhere,⁴¹ where the difference between the two spectra is ascribed to the different contributions of the torsional mode. However, it should be noted that, in the previous study,³⁹ the AH|FC model was employed, and therefore harmonic frequencies of the core-ionized state at its equilibrium geometry were explicitly computed. However, the core-ionization of the C_α orbital causes a large-amplitude distortion along the H-O- C_α - C_β dihedral angle. As already discussed in other works,^{32,33,63} large-amplitude distortions are poorly described by adiabatic models in cartesian coordinates, and therefore a monodimensional, anharmonic model is used to improve the description of the torsional mode.³⁹ On the other hand, here the simpler VG|FC model has been employed, which is better-suited to treat large-amplitude motions since, as discussed previously,³² for vertical models cartesian and internal coordinates give equivalent results. Furthermore, the computational cost of a VG simulation is significantly smaller than that of an AH simulation, since the core-ionized state is not optimized, and the calculation of the frequencies of the cationic state is avoided.

As a final check of the reliability of our computational tool, in figure 12 the comparison between the XPS spectrum of chloroethane computed at the TOEP2/cc-pVTZ level and the experimental one is reported. Also in this case, the overall bandshape is reproduced accurately, both for the band associated to the ionization of the C_α 1s orbital, with an intense peak at about 292 eV and a second shoulder at 292,4 eV, and for the C_β peak, which is less broadened. With respect to ethanol, in this case the shape of the bands is similar for the ionization of the two C 1s orbitals, and in both cases the broadening is less pronounced with respect to the one of the C_α ionization of ethanol. In fact, the torsional degree of freedom associated to the H-O- C_α - C_β dihedral angle, which was the main origin of the broadening in the previous case, is not present for chloroethane, and this reduces the overall broadening of the spectrum. To support this analysis, in figure 13 a graphical representation of the shift vector for the two ionizations is reported. In this case, at variance with ethanol, the order of magnitude of the components of $\mathbf{K}$ for the two ionizations is similar (let us recall that, for the VG model, the spectrum depends only on the squared values of the components of $\mathbf{K}$, and therefore their sign is not relevant). As a consequence, the bandshape is similar as well. Also in this case, the most significant inaccuracy in the reproduction of the experimental data lies in the computation of the VIEs, the IE for the C_α 1s orbital being overestimated by 0.5 eV and that of the C_β orbital by 0.9 eV. Contrary to ethanol, the difference between the theoretical and experimental ionization energy changes for the two core orbitals, and therefore, even if a constant shift is applied to the experimental spectrum, the theoretical and experimental spectra do not overlap. However, as shown in table 5, where the IEs obtained using higher-order propagator methods are reported, the accuracy of the theoretical results is not recovered using more accurate propagator approaches. Using the larger EPRIIId basis set introduced above, the difference between the computed and experimental splitting between the two C 1s ionization energy decreases, and is below 0.1 eV. Therefore, also in this case, TOEP2 is the approach providing the best theoretical estimate of the IEs among the one used in this work.

5 Conclusions

This work describes a computational protocol for the simulation of ultraviolet (UPS) and X-ray (XPS) photoelectron spectra with the inclusion of vibronic effects. The calculation of the vibronic bandshape has been performed by generalizing the implementation of the TI approach developed by some of us^{17,53} to photoelectron spectroscopy. Within this model, the position of the peaks is determined by the ionization energies, which are computed using electron propagator methods as poles of the one-particle Green function. Furthermore, the intensities are assumed to be proportional to the squared value of the pole strength. The vibronic bandshape is determined within the Vertical Gradient model, which requires as input data the frequencies and harmonic normal modes of the initial (neutral) state and the nuclear gradient of the final (cationic) state. The former are computed at the DFT level, whereas the latter are calculated by numerical differentiation of the ionization energies, using an approach already used for anharmonic calculations.^{74,93,94} The reliability of this protocol has been tested by comparing the theoretical UPS and XPS photoelectron spectra of several medium-sized organic molecules with their experimental counterparts. More in detail, different combinations of propagator methods have been tested in the computation of ionization energies and nuclear gradients, with the aim of determining the best compromise between computational cost and accuracy. In addition to the standard diagonal^{21,22} and non-diagonal^{20,23} propagator approaches, a new implementation of the second-order approximation of the one-particle Green Function using a transition operator reference (TOEP2) is presented.^{28,29}

The application of this computational tool to the simulation of vibronic photoelectron spectra of several medium-size molecules shows that, for UPS spectra, a quantitative description of the absolute value of the ionization energies can be reached using non-diagonal approaches and, among them, the most accurate results are obtained with the renormalized second order approach (NR2). This is in agreement with the results already reported in the literature.¹³ On the other hand, the choice of the propagator method is less relevant for the calculation of energy gradients, and reliable results are obtained already using the diagonal OVG and P3 approaches. Therefore, the best compromise between accuracy and computational costs can be achieved using an hybrid scheme, where the ionization energies are computed using non-diagonal approaches, whereas diagonal ones are used to compute gradients. These results pave also the route towards the definition of more advanced hybrid schemes, where the nuclear gradients are computed using more efficient, DFT-based approaches, whereas propagator calculations are used for VIEs and pole strengths. Such hybrid schemes would open the possibility of using adiabatic vibronic models, employing the optimized geometry and the harmonic frequencies computed at the DFT level,⁷² together with the ionization energies and the pole strengths computed using Green function-based approaches. The reliability of propagator approaches is significantly different for the simulation of XPS spectra. In fact, in this case, due to the presence of strong orbital relaxation effects, the difference between experimental and theoretical ionization energies obtained using diagonal approaches is higher than the one obtained for valence ionizations. An improvement is obtained using non-diagonal methods, but the discrepancy between theoretical and experimental results is still above 1.5 eV. The most accurate values

for core ionizations are obtained using the TOEP2 approach, both in the calculation of the ionization energies and of nuclear gradients, and theoretical ionization energies are reproduced correctly within less than 1 eV of error. Besides being more accurate than the other approaches, the TOEP2 method has the lowest computational cost, which is equivalent to that of a standard, second-order propagator calculation. Thus, those results might pave the way towards a systematic use of the TOEP2 approach in the simulation of XPS spectra also for larger-size systems.

The theoretical method presented in this work can be further improved in several respects. First of all, analytical formulae for the calculation of nuclear gradients of cationic states PESs have been proposed in the literature both for diagonal⁹⁵ and non-diagonal approaches.^{76,96} The implementation of those formulae in the computational tool presented here would facilitate the use of more refined vibronic models. For example, the harmonic force constants of cationic states might be computed by numerical differentiation of the analytical gradients, and those data might be used to extend the treatment at the so-called Vertical Hessian model,^{40,63} where mode-mixing effects are also considered. Furthermore, the implementation of analytical gradients would enable the geometry optimization of cationic states using propagator approaches and permit the use of adiabatic vibronic models, either in cartesian¹⁷ and internal coordinates,^{32,97} to tackle more flexible systems as well. Moreover, regarding the calculation of XPS spectra, the approach presented in this work supports only ionizations involving core orbitals localized on a single atom. This is not the case for symmetric molecules, where molecular orbitals are linear combinations of localized core orbitals which exhibit point-group symmetry. For symmetric molecules,^{98,99} a diabatic representation of the electronic PES would be better suited than the adiabatic one to describe vibronic effects. Therefore, full support of symmetric systems would require a further extension of the vibronic models used in this work.^{100,101}

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement n. [320951]. The high performance computer facilities of the SMART center (<http://smart.sns.it>) are acknowledged for providing computer resources. The National Science Foundation supported this research through grant CHE-1565760 to Auburn University.

References

- (1). Miller-Dethlefs K, Schlag EW. *Angew Chem Int Ed.* 1998; 37:1346–1374.
- (2). Eland J. *Int J Mass Spectrom Ion Phys.* 1972; 8:143–151.
- (3). Ng, CY. *Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and Clusters.* World Scientific Pub Co Inc.; 1991.
- (4). Berkowitz, J. *Photoabsorption, Photoionization, and Photoelectron Spectroscopy.* Academic Press; 1979.
- (5). Eland, J. *Photoelectron Spectroscopy: An Introduction to Ultraviolet Photoelectron Spectroscopy in the Gas Phase.* Butterworth-Heinemann; 1984.

- (6). Kobayashi K, Yabashi M, Takata Y, Tokushima T, Shin S, Tamasaku K, Miwa D, Ishikawa T, Nohira H, Hattori T, Sugita Y, et al. *Appl Phys Lett*. 2003; 83:1005–1007.
- (7). Bawagan, ADO., Davidson, ER. *Advances in Chemical Physics*. John Wiley & Sons, Inc.; 2007. p. 215-266.
- (8). Hergenroth U. *J Phys B: At, Mol Opt Phys*. 2004; 37:R89.
- (9). Fronzoni G, Baseggio O, Stener M, Hua W, Tian G, Luo Y, Apicella B, Alf M, de Simone M, Kivimäki A, Coreno M. *J Chem Phys*. 2014; 141:044313. [PubMed: 25084916]
- (10). Palmer MH, Ridley T, Hoffmann SV, Jones NC, Coreno M, de Simone M, Grazioli C, Zhang T, Biczysko M, Baiardi A, Peterson K. *The Journal of Chemical Physics*. 2015; 143
- (11). Palmer MH, Ridley T, Hoffmann SV, Jones NC, Coreno M, de Simone M, Grazioli C, Biczysko M, Baiardi A, Limo-Vieira P. *The Journal of Chemical Physics*. 2015; 142
- (12). Myrseth V, Bozek J, Kukk E, Sthre L, Thomas T. *J Electron Spectrosc Relat Phenom*. 2002; 122:57–63.
- (13). Corzo HH, Galano A, Dolgounitcheva O, Zakrzewski VG, Ortiz JV. *J Phys Chem A*. 2015; 119:8813–8821. [PubMed: 26226061]
- (14). Köppel H, Domcke W, Cederbaum LS, Niessen Wv. *J Chem Phys*. 1978; 69:4252–4263.
- (15). Trofimov AB, Koppel H, Schirmer J. *J Chem Phys*. 1998; 109:1025–1040.
- (16). Assmann M, Köppel H, Matsika S. *J Phys Chem A*. 2015; 119:866–875. [PubMed: 25564985]
- (17). Bloino J, Biczysko M, Santoro F, Barone V. *J Chem Theory Comput*. 2010; 6:1256–1274.
- (18). Barone V. *Wiley Interdiscip Rev: Comput Mol Sci*. 2016; 6:86–110. [PubMed: 29075335]
- (19). Jan Linderberg, YO. *Propagators in quantum chemistry*. Wiley; 2004.
- (20). von Niessen W, Schirmer J, Cederbaum L. *Computer Physics Reports*. 1984; 1:57–125.
- (21). Ortiz JV, Zakrzewski VG. *J Chem Phys*. 1996; 105:2762–2769.
- (22). Ortiz JV. *Int J Quantum Chem*. 2005; 105:803–808.
- (23). Ortiz JV. *J Chem Phys*. 1998; 108:1008–1014.
- (24). Liang W, Fischer SA, Frisch MJ, Li X. *J Chem Theory Comput*. 2011; 7:3540–3547. [PubMed: 26598252]
- (25). Peng B, Lestrangé PJ, Goings JJ, Caricato M, Li X. *J Chem Theory Comput*. 2015; 11:4146–4153. [PubMed: 26575909]
- (26). Purvis GD, Öhrn Y. *J Chem Phys*. 1976; 65:917–922.
- (27). Ortiz J, Basu R, Öhrn Y. *Chem Phys Lett*. 1983; 103:29–34.
- (28). Flores-Moreno R, Zakrzewski VG, Ortiz JV. *J Chem Phys*. 2007; 127:134106. [PubMed: 17919010]
- (29). Flores-Moreno R, Melin J, Dolgounitcheva O, Zakrzewski VG, Ortiz JV. *Int J Quantum Chem*. 2010; 110:706–715.
- (30). Gilbert ATB, Besley NA, Gill PMW. *J Phys Chem A*. 2008; 112:13164–13171. [PubMed: 18729344]
- (31). Besley NA, Gilbert ATB, Gill PMW. *J Chem Phys*. 2009; 130:124308. [PubMed: 19334831]
- (32). Baiardi A, Bloino J, Barone V. *J Chem Theory Comput*. 2015; 11:3267–3280. [PubMed: 26575763]
- (33). Baiardi A, Bloino J, Barone V. *J Chem Phys*. 2016; 144:084114. [PubMed: 26931688]
- (34). Cederbaum LS, Köppel H, Domcke W. *Int J Quantum Chem*. 1981; 20:251–267.
- (35). Koppel H, Dscher M, Bidea I, Meyer H-D, Szalay PG. *J Chem Phys*. 2002; 117:2657–2671.
- (36). Cerezo J, Zuniga J, Requena A, Avila Ferrer FJ, Santoro F. *J Chem Theory Comput*. 2013; 9:4947–4958. [PubMed: 26583413]
- (37). Hazra A, Chang HH, Nooijen M. *J Chem Phys*. 2004; 121:2125–2136. [PubMed: 15260766]
- (38). Bloino J, Baiardi A, Biczysko M. *Int J Quantum Chem*. 2016; 115:1543–1574.
- (39). Abu-samha M, Børve KJ. *Phys Rev A*. 2006; 74:042508.
- (40). Hazra A, Nooijen M. *Phys Chem Chem Phys*. 2005; 7:1759–1771. [PubMed: 19787936]
- (41). Abu-samha M, Børve KJ, Sæthre LJ, Thomas TD. *Phys Rev Lett*. 2005; 95:103002. [PubMed: 16196926]

- (42). Ortiz JV. Wiley Interdiscip Rev: Comput Mol Sci. 2013; 3:123–142.
- (43). Goscinski O, Lukman B. Chem Phys Lett. 1970; 7:573–576.
- (44). Ortiz JV. Int J Quantum Chem. 2003; 95:593–599.
- (45). Thiel A, Schirmer J, Köppel H. J Chem Phys. 2003; 119:2088–2101.
- (46). Slater JC, Mann JB, Wilson TM, Wood JH. Phys Rev. 1969; 184:672–694.
- (47). Warren R, Dunlap B. Chem Phys Lett. 1996; 262:384–392.
- (48). Abdunur SF, Linderberg J, Öhrn U, Thulstrup PW. Phys Rev A. 1972; 6:889–898.
- (49). Slater, JC. Advances in Quantum Chemistry. Löwdin, P.-O., editor. Vol. 6. Academic Press; 1972. p. 1-92. Advances in Quantum chemistry
- (50). Goscinski O, Pickup B, Purvis G. Chem Phys Lett. 1973; 22:167–171.
- (51). Redmon LT, Purvis G, Öhrn Y. J Chem Phys. 1975; 63:5011–5017.
- (52). Corzo HH, Ortiz JV. Mol Phys. 2017; 115:545–551.
- (53). Barone V, Bloino J, Biczysko M, Santoro F. J Chem Theory Comput. 2009; 5:540–554. [PubMed: 26610221]
- (54). Franck J. Trans Faraday Soc. 1926; 21:536–542.
- (55). Herzberg G, Teller E. Z Phys Chem. 1933; 21:410.
- (56). Sharp TE, Rosenstock HM. J Chem Phys. 1964; 41:3453–3463.
- (57). Ruhoff PT. Chem Phys. 1994; 186:355–374.
- (58). Malmqvist, Pr, Forsberg, N. Chem Phys. 1998; 228:227–240.
- (59). Santoro F, Improta R, Lami A, Bloino J, Barone V. J Chem Phys. 2007; 126:084509. [PubMed: 17343460]
- (60). Langhoff P, Langhoff S, Rescigno T, Schirmer J, Cederbaum L, Domcke W, Niessen WV. Chem Phys. 1981; 58:71–91.
- (61). Ghanty TK, Davidson ER. J Phys Chem A. 1999; 103:8985–8993.
- (62). Santoro F, Lami A, Improta R, Bloino J, Barone V. J Chem Phys. 2008; 128:224311. [PubMed: 18554017]
- (63). Avila Ferrer FJ, Santoro F. Phys Chem Chem Phys. 2012; 14:13549–13563. [PubMed: 22847219]
- (64). Frisch, MJ., Trucks, GW., Schlegel, HB., Scuseria, GE., Robb, MA., Cheeseman, JR., Scalmani, G., Barone, V., Mennucci, B., Petersson, GA., Nakatsuji, H., et al. Gaussian Development Version, Revision I.03. Gaussian, Inc.; Wallingford CT: 2015.
- (65). Burke K. J Chem Phys. 2012; 136:150901. [PubMed: 22519306]
- (66). Becke AD. J Chem Phys. 1993; 98:5648–5652.
- (67). Double and triple- ζ basis sets of SNS family. are available for download <http://compchem.sns.it/downloads>.
- (68). Barone V, Cimino P. Chem Phys Lett. 2008; 454:139–143.
- (69). Barone V, Cimino P, Stendardo E. J Chem Theory Comput. 2008; 4:751–764. [PubMed: 26621090]
- (70). Dolgounitcheva O, Zakrzewski V, Ortiz J. J Phys Chem A. 2002; 106:8411–8416.
- (71). Barone, V. Structure, magnetic properties and reactivity of open-shell species from Density Functional and Self-Consistent hybrid methods. Vol. Chapter 8. World Scientific Publishing; 1995. p. 287
- (72). Baiardi A, Mendolicchio M, Barone V, Fronzoni G, Cardenas Jimenez GA, Stener M, Grazioli C, de Simone M, Coreno M. The Journal of Chemical Physics. 2015; 143:204102. [PubMed: 26627945]
- (73). Bloino J, Biczysko M, Crescenzi O, Barone V. J Chem Phys. 2008; 128:244105. [PubMed: 18601315]
- (74). Barone V. J Chem Phys. 2005; 122:14108. [PubMed: 15638643]
- (75). Barone V, Biczysko M, Bloino J. Phys Chem Chem Phys. 2014; 16:1759–1787. [PubMed: 24346191]
- (76). Ortiz JV. J Chem Phys. 2000; 112:56–68.

- (77). Derrick P, Asbrink L, Edqvist O, Lindholm E. *Spectrochimica Acta Part A: Molecular Spectroscopy*. 1971; 27:2525–2537.
- (78). Derrick P, Åsbrink L, Edqvist O, Jonsson B-O, Lindholm E. *Int J Mass Spectrom Ion Phys*. 1971; 6:161–175.
- (79). Rennie E, Cooper L, Johnson C, Parker J, Mackie R, Shpinkova L, Holland D, Shaw D, Hayes M. *Chem Phys*. 2001; 263:149–165.
- (80). Holland D, Karlsson L, von Niessen W. *J Electron Spectrosc Relat Phenom*. 2001; 113:221–239.
- (81). Trofimov AB, Zaitseva IL, Moskovskaya TE, Vitkovskaya NM. *Chem Heterocycl Compd*. 2008; 44:1101–1112.
- (82). Nakatsuji H, Kitao O, Yonezawa T. *J Chem Phys*. 1985; 83:723–734.
- (83). Nakano H, Tsuneda T, Hashimoto T, Hirao K. *J Chem Phys*. 1996; 104:2312–2320.
- (84). Köppel H, Gromov E, Trofimov A. *Towards Multidimensional Quantum Reaction Dynamics*. *Chem Phys*. 2004; 304:35–49.
- (85). Luis JM, Kirtman B, Christiansen O. *J Chem Phys*. 2006; 125:154114. [PubMed: 17059246]
- (86). Fulfer KD, Hardy D, Aguilar AA, Poliakoff ED. *J Chem Phys*. 2015; 142:224310. [PubMed: 26071713]
- (87). Padva A, O'Donnell T, Lebreton P. *Chem Phys Lett*. 1976; 41:278–282.
- (88). Dougherty D, Wittel K, Meeks J, McGlynn SP. *J Am Chem Soc*. 1976; 98:3815–3820. [PubMed: 932347]
- (89). Assmann M, Köppel H, Matsika S. *J Phys Chem A*. 2015; 119:866–875. [PubMed: 25564985]
- (90). Vaquero V, Sanz M, Lpez J, Alonso J. *J Phys Chem A*. 2007; 111:3443–3445. [PubMed: 17439111]
- (91). Puzzarini C, Barone V. *Phys Chem Chem Phys*. 2011; 13:7189–7197. [PubMed: 21409277]
- (92). Neese F, Petrenko T, Ganyushin D, Olbrich G. *Coord Chem Rev*. 2007; 251:288–327.
- (93). Barone V. *The Journal of Chemical Physics*. 2004; 120:3059–3065. [PubMed: 15268458]
- (94). Louant O, Champagne B, Liégeois V. *Chemical Physics Letters*. 2015; 634:249–254.
- (95). Cioslowski J, Ortiz JV. *J Chem Phys*. 1992; 96:8379–8389.
- (96). Ortiz JV. *J Chem Phys*. 1993; 99:6716–6726.
- (97). Baiardi A, Bloino J, Barone V. *J Chem Phys*. 2014; 141:114108. [PubMed: 25240346]
- (98). Kivimäki A, Kempgens B, Maier K, Köppe HM, Piancastelli MN, Neeb M, Bradshaw AM. *Phys Rev Lett*. 1997; 79:998–1001.
- (99). Dobrodey NV, Köppel H, Cederbaum LS. *Phys Rev A*. 1999; 60:1988–2001.
- (100). Picconi D, Lami A, Santoro F. *J Chem Phys*. 2012; 136:244104. [PubMed: 22755562]
- (101). Endicott JS, Joubert-Doriol L, Izmaylov AF. *J Chem Phys*. 2014; 141:034104. [PubMed: 25053298]

(a)

(b)

(c)

(d)

Figure 1.
Structure of the molecules studied in the work: furane (a), uracil (b), ethanol (c),
chloroethane (d).

Figure 2.

Comparison of the theoretical photoionization spectrum of furane, computed at the OVGF/cc-pVTZ level and using the VG|FC vibronic model, with the experimental spectrum, taken from ref.79 The experimental spectrum shifted by 2000 cm⁻¹ is also reported.

Figure 3.

Theoretical valence photoionization spectrum of uracil computed at the VG|FC level in the range 9-12 eV (solid, black line). The VIEs have been computed at the NR2/aug-cc-pVTZ level, whereas the OVGf/cc-pVTZ approach has been used for the computation of gradients. Gaussian functions with an HWHM of 0.075 eV have been used to simulate broadening effects. The individual contributions of the ionization of each orbital to the overall spectrum is also reported (green line for the π_1 orbital, purple line for the σ_{O-} orbital, red line for the π_2 orbital, blue line for the σ_{O+} orbital).

Figure 4.

Comparison between the experimental valence photoionization spectrum of uracil (dashed, black line)⁸⁷ with the vibronic spectrum computed at the VG|FC level (solid, red line). The vertical ionization energies have been computed at the NR2/aug-cc-pVTZ level, whereas the OVGF/cc-pVTZ approach has been used for the computation of gradients. The experimental spectrum has been shifted by 0.2 eV toward lower energy to facilitate the comparison with the theoretical results. Gaussian functions with an HWHM of 0.075 eV have been used to reproduce broadening effects. The vertical energy spectrum obtained from the VIEs computed at the NR2/aug-cc-pVTZ level is reported as well (solid, green line), where a single Gaussian broadening function with an HWHM of 0.15 eV has been used to reproduce broadening effects for each peak.

Figure 5.

Theoretical valence photoionization spectrum of uracil computed at the VG|FC level in the range 9-12 eV (solid, black line). Both the VIEs and the nuclear energy gradients have been computed at the OVGF/cc-pVTZ level. Gaussian functions with an HWHM of 0.075 eV have been used to simulate broadening effects. The individual contributions of the ionization of each orbital to the overall spectrum is also reported (green line for the π_1 orbital, purple line for the σ_{O-} orbital, red line for the π_2 orbital, blue line for the σ_{O+} orbital).

Figure 6. Graphical representation of the equilibrium geometry of ethanol for the two stable conformers in the S₀ state, computed at the B3LYP/SNSD level. The structure reported in the left panel will be labelled as (a), the one reported in the right one will be labelled as (b).

Figure 7.

XPS spectrum for the ionization of the C_{α} 1s electron of ethanol computed at the VG|FC level using different diagonal propagator methods (TOEP2 in red, OVGf in green, P3 in blue) using Gaussian functions with an HWHM of 0.01 eV (solid lines) and 0.075 eV (dashed lines) to simulate broadening effects.

Figure 8.

XPS spectrum for the ionization of the C_{α} 1s electron of ethanol computed at the VG|FC level using different non-diagonal propagator methods (NR2 in gray) and the TOEP2 approach (in red). Gaussian functions with an HWHM of 0.01 eV (solid lines) and 0.075 eV (dashed lines) have been used to simulate broadening effects.

Figure 9.

Comparison of the theoretical XPS spectrum for the ionization of the C 1s core electrons of ethanol, computed at the VG|FC level (solid, gray line) with the experimental results (solid, black line, taken from ref.41). The experimental spectrum has been shifted by 0.5 eV to facilitate the comparison with the theoretical spectra. Gaussian functions with an HWHM of 0.075 eV have been used to simulate broadening effects. The spectra for the individual contributions for the ionization of the (a) (solid red line for the C_{α} 1s orbital, solid light blue line for the C_{β} 1s orbital) and the (b) conformer (solid orange line for the C_{α} 1s orbital, solid dark blue line for the C_{β} 1s orbital) are reported.

Figure 10.

Comparison of the theoretical XPS spectrum for the ionization of the C 1s core electrons of ethanol, computed at the VG|FC (solid, red line) and VE (solid, blue line) with the experimental results (solid, black line, taken from ref.41). The experimental spectrum has been shifted by 0.5 eV to facilitate the comparison with the theoretical spectra. Gaussian functions with an HWHM of 0.075 eV for the VG spectrum, and with an HWHM of 0.25 eV for the VE spectrum, have been used to simulate broadening effects.

Figure 11.

Graphical representation of the shift vector $\mathbf{K}$ associated to the ionization of the C_α (left panel) and the C_β (right panel) 1s core orbitals of ethanol, computed at the VG|FC level. Positive values are represented with blue bars, negative values are represented with red bars. The components of $\mathbf{K}$ are reported in $\text{amu}^{1/2} \cdot \text{Bohr}$.

Figure 12.

Comparison of the theoretical XPS spectrum for the ionization of the C 1s core electrons of chloroethane, computed at the TOEP2 VG|FC level with the experimental results (solid, black line, taken from ref.41). Gaussian functions with an HWHM of 0.075 eV have been used to simulate broadening effects. The experimental spectrum has been shifted by 0.5 eV to facilitate the comparison with the computed spectra.

Figure 13.

Graphical representation of the shift vector $\mathbf{K}$ associated to the ionization of the C_α (left panel) and the C_β (right panel) 1s core orbitals of chloroethane, computed at the VG|FC level. Positive shifts are represented with blue bars, negative values are represented with red bars. The components of $\mathbf{K}$ are reported in $\text{amu}^{1/2} \cdot \text{Bohr}$.

Table 1

Ionization energies for the 2A_2 (first row) and 2B_1 (second row) electronic state of furane, computed using different diagonal (EP2, EP3, OVGF, P3, P3+) and non-diagonal (ADC(3) and NR2) electron propagator methods. The difference between the two ionization energies is also reported in the third row. All the energies are reported in eV.

		2A_2	2B_1	E
EP2	cc-pVTZ	8.71	9.87	1.16
	aug-ccp-VTZ	8.75	9.92	1.17
EP3	cc-pVTZ	8.91	10.54	1.63
	aug-ccp-VTZ	9.01	10.67	1.65
OVGF	cc-pVTZ	8.86	10.24	1.38
	aug-cc-pVTZ	8.95	10.35	1.40
P3	cc-pVTZ	9.02	10.44	1.42
	aug-cc-pVTZ	9.10	10.52	1.42
P3+	cc-pVTZ	8.97	10.34	1.37
	aug-cc-pVTZ	9.04	10.42	1.38
NR2	cc-pVTZ	8.92	10.26	1.34
	aug-cc-pVTZ	8.99	10.34	1.35
ADC(3)	cc-pVTZ	8.94	10.41	1.47
	aug-cc-pVTZ	9.02	10.50	1.48
Exp.15		8.88	10.31	1.43

Table 2

Theoretical ionization energies (in eV) for the valence orbitals of uracil computed using different electron propagator methods. In all cases, the cc-pVTZ basis set has been employed.

Orbital	Exp. ⁸⁷	Propagator method					
		Koop.	EP2	OVGf	P3	NR2	ADC(3)
π_1	9.5	10.00	9.29	9.31	9.78	9.58	9.52
σ_{O-}	10.1	12.17	9.09	10.56	10.40	10.02	10.65
π_2	10.6	11.83	10.02	10.59	10.78	10.54	10.69
σ_{O+}	11.2	13.11	10.11	11.50	11.34	10.99	11.55

Table 3

Theoretical ionization energies (in eV) for the valence orbitals of uracil computed using different electron propagator methods. In all cases, the aug-cc-pVTZ basis set has been employed.

Orbital	Exp.87	Propagator method					
		Koop.	EP2	OVGf	P3	NR2	ADC(3)
π_1	9.5	10.07	9.36	9.45	9.87	9.67	9.64
σ_{O-}	10.1	12.25	9.14	10.75	10.52	10.12	10.79
π_2	10.6	11.90	10.08	10.76	10.88	10.62	10.82
σ_{O+}	11.2	13.18	10.15	11.68	11.45	11.08	11.68

Table 4

Vertical ionization energies (in eV) for the C 1s orbitals of ethanol computed using different combinations of propagator methods and basis sets.

		C_{α}	C_{β}	$(C_{\alpha}-C_{\beta})$
OVGF	cc-pVTZ	294.67	293.04	1.63
	aug-cc-pVTZ	294.76	293.11	1.65
P3	cc-pVTZ	293.98	292.19	1.69
	aug-cc-pVTZ	294.08	292.38	1.70
NR2	cc-pVTZ	293.40	291.76	1.64
	aug-cc-pVTZ	293.42	291.79	1.66
ADC(3)	cc-pVTZ	294.71	293.16	1.55
	aug-cc-pVTZ	294.80	293.22	1.58
TOEP2	cc-pVTZ	292.68	291.03	1.65
	aug-cc-pVTZ	292.70	291.04	1.66
	EPR-III	292.61	290.06	1.65
Exp.41		292.01	290.04	1.70

Table 5

Vertical ionization energies (in eV) for the C 1s orbitals of chloroethane computed using different combinations of propagator methods and basis sets.

		C_α	C_β	$(C_\alpha - C_\beta)$
OVGF	cc-pVTZ	295.44	293.60	1.88
	aug-cc-pVTZ	295.10	293.64	1.46
P3	cc-pVTZ	294.48	292.80	1.54
	aug-cc-pVTZ	294.22	292.80	1.42
NR2	cc-pVTZ	293.81	292.37	1.44
	aug-cc-pVTZ	293.69	292.24	1.45
ADC(3)	cc-pVTZ	295.16	293.75	1.41
	aug-cc-pVTZ	296.07	292.95	3.12
TOEP2	cc-pVTZ	292.85	291.57	1.28
	aug-cc-pVTZ	292.83	291.56	1.29
	EPR-III	292.61	291.43	1.18
Exp.41		292.10	290.00	1.10