

Excited state X-ray absorption spectroscopy: Probing both electronic and structural dynamics

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We investigate the sensitivity of X-ray absorption spectra, simulated using a general method, to properties of molecular excited states. Recently, Averbukh and co-workers [M. Ruberti *et al.*, J. Chem. Phys. **140**, 184107 (2014)] introduced an efficient and accurate \mathcal{L}^2 method for the calculation of excited state valence photoionization cross-sections based on the application of Stieltjes imaging to the Lanczos pseudo-spectrum of the algebraic diagrammatic construction (ADC) representation of the electronic Hamiltonian. In this paper, we report an extension of this method to the calculation of excited state core photoionization cross-sections. We demonstrate that, at the ADC(2)x level of theory, ground state X-ray absorption spectra may be accurately reproduced, validating the method. Significantly, the calculated X-ray absorption spectra of the excited states are found to be sensitive to both geometric distortions (structural dynamics) and the electronic character (electronic dynamics) of the initial state, suggesting that core excitation spectroscopies will be useful probes of excited state non-adiabatic dynamics. We anticipate that the method presented here can be combined with *ab initio* molecular dynamics calculations to simulate the time-resolved X-ray spectroscopy of excited state molecular wavepacket dynamics. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4964369]

I. INTRODUCTION

Ultrafast pump-probe techniques such as time-resolved photoelectron spectroscopy¹ offer powerful probes of excited state molecular dynamics. Until recently, the probe wavelengths most commonly employed have spanned the UV/visible range, partially due to the constraints of available ultrafast light sources. However, ongoing technological advancements are now resulting in femtosecond light sources with wavelengths in the X-ray regime. An X-ray probe pulse has a number of properties that make it appealing from the viewpoint of the probing of ultrafast dynamics.²⁻⁹ A high degree of atom specificity is endowed by the localisation of the core orbitals, resulting in a sensitivity to changes in bonding around specific atomic cores. Additionally, a high photon energy ensures that large amplitude motion, which may result in large energetic relaxation, may be followed on multiple electronic states. The question we ask here is to what extent may X-ray (core excitation) spectroscopies be good probes of excited state molecular dynamics?

Following electronic excitation, the Born-Oppenheimer approximation can be expected to break down as a result of strong vibronic coupling between energetically proximate electronic states. The resulting evolution of the electronic character of the excited state wavefunction dictates that any

useful probe scheme must be sensitive to the electronic state of the system. Additionally, large amplitude nuclear motion typically accompanies electronic excitation and, therefore, a good probe scheme must also be sensitive to the nuclear geometry. In other words, in excited molecular states, there will be electronic dynamics, structural dynamics, and the coupling between these two. To assess the extent to which X-ray absorption spectroscopy (XAS) is sensitive to these dynamics, we first develop a procedure to accurately calculate excited state XAS based on the second-order algebraic diagrammatic construction (ADC(2)) method. By invoking the so-called core-valence separation (CVS) approximation, the ADC(2) method may be extended to the accurate simulation of the bound part of the XAS.¹⁰⁻¹² We here extend this approach by applying the techniques of Stieltjes-Chebyschev moment theory to the CVS-ADC(2) Lanczos pseudospectrum, demonstrating that the continuum part of the XAS may also be accurately calculated. The potential usefulness of X-ray absorption in the probing of excited-state non-adiabatic dynamics is then explored by the simulation of excited state XAS for a number of prototypical molecules of photochemical interest. The simulated excited state XASs are found to be sensitive to both the electronic character of the initial state and the nuclear geometry. We conclude that core-excitation X-ray spectroscopy will be a useful probe of excited-state non-adiabatic molecular dynamics.

II. THE ADC METHOD

Originally, the ADC scheme was conceived as a perturbative approximation to the polarization propagator using the Møller-Plesset partitioning of the electronic Hamiltonian.¹³ Later, Schirmer and Trofimov reformulated the ADC scheme as a wavefunction-based method via the intermediate state representation (ISR) approach.^{14,15} At the centre of the ISR ADC approach is the expansion of the exact excited state wavefunction $|\Psi_n\rangle$ in terms of a complete set of the so-called intermediate states (ISs) $|\tilde{\Psi}_J\rangle$,

$$\left|\Psi_{n}\right\rangle = \sum_{J} X_{Jn} \left|\tilde{\Psi}_{J}\right\rangle. \tag{1}$$

The ISs $|\tilde{\Psi}_J\rangle$ are in turn constructed from the set of correlated excited states (CESs) $|\Psi_J^0\rangle$ defined by the operation of the physical excitation operators \hat{C}_J^{\dagger} on the (in principle) exact ground state wavefunction $|\Psi_0\rangle$,

$$\left|\Psi_{J}^{0}\right\rangle = \hat{C}_{J}^{\dagger} \left|\Psi_{0}\right\rangle,\tag{2}$$

$$\hat{C}_{J}^{\dagger} \in \left\{ \hat{c}_{a}^{\dagger} \hat{c}_{i}; \hat{c}_{a}^{\dagger} \hat{c}_{b}^{\dagger} \hat{c}_{i} \hat{c}_{j} (a < b, i < j); \ldots \right\}.$$
(3)

Here, \hat{c}_p^{\dagger} and \hat{c}_p denote, respectively, the elementary creation and annihilation operators corresponding to the canonical Hartree-Fock orbitals φ_p . We follow the convention that the indices i, j, \ldots index occupied orbitals, the indices a, b, \ldots index unoccupied orbitals, whilst the indices p, q, \ldots are used to index general orbitals. The construction of the orthogonal ISs $|\tilde{\Psi}_J\rangle$ from the non-orthogonal CESs $|\Psi_J^0\rangle$ is achieved via the Gram-Schmidt orthogonalization of each excitation class (1h1p, 2h2p, etc.) against all lower excitation classes followed by symmetric orthogonalization within the individual excitation classes.

Within the ISR, the problem of calculating the excited state wavefunctions $|\Psi_n\rangle$ and excitation energies E_n is reduced to that of determining the eigenvectors and eigenvalues of the shifted Hamiltonian operator $\hat{H} - E_0$ represented in the basis of ISs

$$M_{IJ} = \left\langle \tilde{\Psi}_I \left| \hat{H} - E_0 \left| \tilde{\Psi}_J \right. \right\rangle \right\rangle. \tag{4}$$

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The excitation energies E_n and expansion coefficient vectors X_n are obtained as the eigenvalues and eigenvectors of the secular matrix M. Furthermore, transition dipole moments between the ground and excited states as well as between excited states may be obtained as

$$D_{0n} = \left\langle \Psi_0 \left| \hat{D} \right| \Psi_n \right\rangle = \sum_{I} \left\langle \Psi_0 \left| \hat{D} \right| \tilde{\Psi}_I \right\rangle X_{Jn}$$
(5)

and

$$D_{mn} = \left\langle \Psi_m \left| \hat{D} \right| \Psi_n \right\rangle = \sum_{IJ} X_{Im}^* \left\langle \tilde{\Psi}_I \left| \hat{D} \right| \tilde{\Psi}_J \right\rangle X_{Jn}, \quad (6)$$

respectively, where \hat{D} is the molecular dipole operator.

To proceed, Møller-Plesset perturbation theory is used to provide a representation of the ground state wavefunction and energy

$$\left|\Psi_{0}\right\rangle = \left|\Psi_{0}^{HF}\right\rangle + \left|\Psi_{0}^{[1]}\right\rangle + \left|\Psi_{0}^{[2]}\right\rangle + \cdots, \tag{7}$$

$$E_0 = E_0^{HF} + E_0^{[1]} + E_0^{[2]} + \cdots,$$
(8)

where $|\Psi_0^{HF}\rangle$ denotes the Hartree-Fock ground state wavefunction and $|\Psi_0^{[i]}\rangle$ the *i*th-order correction to the Hartree-Fock wavefunction. The quantities entering into Equation (8) are defined analogously. A hierarchy of approximations is obtained via the truncation of the excitation classes used in the construction of the IS basis as well as the perturbative expansions for the included classes in a way that is consistent with the original ADC representation of the polarization propagator. In the ADC(2) model, the IS basis is truncated to one-hole-one-particle (1h1p) and two-hole-two-particle (2h2p) excitation classes, and the perturbative expansion of the shifted Hamiltonian matrix elements extends through the second, first, and zeroth order in the 1h1p block, the 1h1p-2h2p block, and the diagonal 2h2p block, respectively. The extended, ADC(2) or ADC(2)x, model is an ad hoc extension of the ADC(2) model that is the same as the latter except that the (now non-diagonal) 2h2p block is expanded to first-order of perturbation theory. For the calculation of valence-excited states that are dominated by single excitations, the strict ADC(2) method is known to provide more accurate results. In contrast, due to a fortuitous cancellation of errors, the ADC(2)x method is known to provide a more accurate description of core-excited states.¹⁶ As such, we use the ADC(2) and ADC(2)x methods to calculate valence and core-excited states, respectively.

III. THE CORE-VALENCE SEPARATION APPROXIMATION

The core-excited states lie in the high-energy X-ray part of the electronic spectrum, well above the valence-excited states. This, combined with the use of iterative diagonalisation techniques that furnish extremal eigenstates, means that a prohibitive number of excited states would have to be calculated in order to gain access to the core-excited states of interest. This bottleneck may, however, be avoided via the application of the CVS approximation,¹⁷ which is based on the observation that the following families of Coulomb integrals are extremely small and hence can reasonably be set to zero:

$$\langle Ip|qr \rangle = \langle pI|qr \rangle = \langle pq|Ir \rangle = \langle pq|rI \rangle = 0,$$

$$\langle IJ'|pq \rangle = \langle pq|IJ' \rangle = 0,$$

$$\langle IJ|Kp \rangle = \langle IJ|pK \rangle = \langle Ip|JK \rangle = \langle pI|JK \rangle = 0.$$

(9)

Here, uppercase letters are used to denote core orbitals and lowercase indices to denote valence orbitals. Additionally, the unprimed-primed pair of core-level indices IJ' indicates that I and J index different core levels. The justification of the neglect of these integrals arises from the small coupling between the singly core-excited states and their orthogonal complement, and the strong spatial localization of the core orbitals and their large energetic separation from the valence orbitals. Setting the integrals in Equation (9) to zero, the singly core-excited states are decoupled from the valence-excited and doubly core-excited states. The ADC secular matrix M may then be constructed in the space spanned by 1h1p and 2h2p configurations corresponding to the excitation out of one, and only one, core orbital. That is, only the matrix elements $M_{Ia,Kb}$ (1h1p-1h1p block), $M_{Ijab,Kc}$ (2h2p-1h1p block), $M_{Ia,Klbc}$ (1h1p-2h2p block), and $M_{Ijab,Klcd}$ (2h2p-2h2p block) need to be considered. Diagonalization of the resulting matrix (the CVS-ADC(2) secular matrix) then directly yields the singly core-excited states of interest.

IV. CALCULATION OF X-RAY ABSORPTION SPECTRA

We adopt the following partitioning of the total XAS $\sigma(E)$:

$$\sigma(E) = \sigma^{(b)}(E) + \sigma^{(c)}(E),$$

where $\sigma^{(b)}(E)$ is the part of the spectrum arising from excitation into bound states and $\sigma^{(c)}(E)$ the part arising from excitation into continuum states, that is, from ionization. Owing to the different normalizations of the final states contributing to $\sigma^{(b)}(E)$ and $\sigma^{(c)}(E)$, different methodologies have to be used in their calculation. These are discussed in Sections IV A and IV B.

A. Calculation of the bound part of the spectrum

The bound part of the spectrum, $\sigma^{(b)}(E)$, may be calculated simply from the CVS-ADC oscillator strengths f_{ij} corresponding to excitation from an initial state $|\Psi_i\rangle$ to final state $|\Psi_j\rangle$ whose energy E_j lies below the threshold for core-ionization, E_T ,

$$\sigma^{(b)}(E) = \left(\left[\sum_{j} f_{ij} \delta(E - E_j) \right] \otimes g(E; \eta) \right) \Theta(E_T - E).$$
(10)

Here, \otimes denotes the convolution operation, $g(E;\eta)$ corresponds to a Gaussian function with full width at half-maximum of η , and $\Theta(E_T - E)$ is the reverse Heaviside step function centred at the core-ionization threshold energy E_T . The free parameter η is chosen phenomenologically to simulate a typical experimental spectral resolution.

B. Calculation of the continuum part of the spectrum

Owing to the \mathcal{L}^2 Gaussian-type basis used in the ADC calculations, the cross-sections above the ionization threshold cannot be determined directly from the oscillator strengths for transition to the ADC states that lie within this domain. This arises from the different normalizations of the ADC states $|\Psi_n\rangle$ and the "true" continuum states $|\phi(E)\rangle$: the former are normalized to a Kronecker- δ , $\langle \Psi_m | \Psi_n \rangle = \delta_{mn}$, whilst the latter are normalized to a Dirac δ -function, $\langle \phi(E) | \phi(E') \rangle = \delta(E - E')$. As such, a direct use of the ADC states in the calculation of oscillator strengths for excitation to states above the ionization threshold would lead to both incorrect values and incorrect dimensionalities. However, it is possible to indirectly extract oscillator strengths corresponding to photo-ionization using an \mathcal{L}^2 basis via

a procedure pioneered by Langhoff.^{18–28} The basis of this procedure is the observation that the spectral moments S(k) defined with respect to a given electronic state $|\Psi\rangle$,

$$S(k) = \left\langle \Psi \left| \hat{D}^{\dagger} \hat{H}^{k} \hat{D} \right| \Psi \right\rangle, \tag{11}$$

can be accurately calculated via the insertion of the resolution of the identity expressed in terms of a basis $\{\Phi_{\alpha}\}$ of \mathcal{L}^2 basis functions

$$S(k) = \sum_{\alpha} \langle \Psi | \hat{D}^{\dagger} \hat{H}^{k} | \Phi_{\alpha} \rangle \langle \Phi_{\alpha} | \hat{D} | \Psi \rangle$$
$$= \sum_{\alpha} E_{\alpha}^{k} | \langle \Psi | \hat{D} | \Phi_{\alpha} \rangle |^{2}.$$
(12)

Equivalently, the resolution of the identity may be expressed in terms of the true bound and continuum states, $\{\psi_i\}$ and $\{\phi(E)\}$, respectively, giving

$$S(k) = \sum_{i} E_{i}^{k} |\langle \Psi | \hat{D} | \psi_{i} \rangle|^{2} + \int_{E_{T}}^{\infty} E^{k} |\langle \Psi | \hat{D} | \phi(E) \rangle|^{2} dE$$
$$= \sum_{i} E_{i}^{k} |\langle \Psi | \hat{D} | \psi_{i} \rangle|^{2} + \frac{3}{2} \int_{E_{T}}^{\infty} E^{k-1} f(E) dE.$$
(13)

With this equivalence established, the methods of Stieltjes-Chebyshev moment theory may then be used to extract the continuum oscillator strengths f(E) from a series of spectral moments S(k) evaluated using an \mathcal{L}^2 basis. This procedure is commonly referred to as Stieltjes imaging. In the context of the present work, the \mathcal{L}^2 basis used in the evaluation of the spectral moments would be the CVS-ADC(2)x eigenstates. The problem with this approach is that it requires that the entire spectrum of the ADC Hamiltonian be known, which is possible for only the smallest of systems. It has, however, recently been demonstrated that the spectral moments may be accurately and tractably approximated using the Lanczos pseudo-spectrum of the ADC Hamiltonian,²⁹⁻³¹ and it is this approach which is used in this work. In particular, we use the block variant of the Lanczos method^{32,33} to generate the spectral moments S(k) used in the Stieltjes imaging procedure.

C. Calculation of the threshold for core-ionization

In order to construct the bound and continuum parts, $\sigma^{(b)}(E)$ and $\sigma^{(c)}(E)$, of the total XAS using the prescription given in Sections IV A and IV B, we require an estimate of where the threshold energy for core-ionization, E_T , occurs in the CVS-ADC(2)x spectrum. To do so, we make use of an idea, used for many years now in equation-of-motion coupled cluster theory, whereby ionization to form an (N - 1)-electron state is described in an N-electron framework by including an *extremely* diffuse orbital φ_{α} in the one-electron basis and restricting the N-electron basis to span the subspace for which this "continuum" orbital is occupied.³⁴ Accordingly, we calculate the energies of the singly core-ionized states within the N-electron CVS-ADC(2)x framework by including a single uncontracted s-type orbital in the one-electron basis with an exponent of 10^{-30} and constructing the ADC secular matrix in the space spanned by configurations that correspond to excitation of one, and only one, core electron and for which only a single electron is excited into the "continuum" orbital

 φ_{α} . That is, only the matrix elements $M_{I\alpha,K\alpha}$ (1h1p-1h1p block), $M_{Ij\alpha a,K\alpha}$, (2h2p-1h1p block), $M_{I\alpha,Kl\alpha a}$ (1h1p-2h2p block), and $M_{Ij\alpha a,Kl\alpha b}$ (2h2p-2h2p block) are considered, where α indexes the "continuum" orbital. This method is denoted as CVS-IP-ADC(2)x.

We note that within the IP-ADC(2) framework, the 1h1p and 2h2p excitation operators mimic the effect of the 1h and 2h1p operators of non-Dyson ADC(2) theory,³⁵ and that the two methods should give essentially the same results. The reason for our adoption of the IP-ADC(2)x method is purely pragmatic. Namely, it allows for the calculation of ionization potentials with only a small change to an existing ADC(2) code. Additionally, as is discussed in Section IV D, this method allows for the calculation of approximate Dyson orbitals for excited-state ionization using the pre-existing machinery of ADC(2) theory.

D. Analysis of the continuum part of the spectrum

Although the Stieltjes imaging procedure is capable of furnishing accurate photoionization cross-sections, it is not straightforward to extract information about the underlying transitions. A previously used technique for doing so relies on the construction of so-called Stieltjes orbitals,³⁶ which provide a representation of the photoionization continuum at a discrete set of energies. This method, however, does not provide any information about the final cation states of the dominant underlying photoionization channels. As a first step towards a general method for extracting this information that is applicable to large molecules and complex electronic wavefunctions, we make use of an analysis based on approximate Dyson orbitals calculated at the ADC(2)/CVS-IP-ADC(2) level of theory. The Dyson orbital $\psi_{D,if}$ for ionization from an N-electron state $|\Psi_i\rangle$ to an (N – 1)-electron state $|\Psi_f\rangle$ is a one-electron quantity defined by

$$\psi_{D,if} = \sqrt{N} \int d\boldsymbol{r}_1 \cdots d\boldsymbol{r}_{N-1} \Psi_i^*(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N) \\ \times \Psi_f(\boldsymbol{r}_1, \dots, \boldsymbol{r}_{N-1}), \tag{14}$$

where r_n denotes the coordinates of the *n*th electron. In the weak field limit, the squared norm of the Dyson orbital $\psi_{D,if}$ is proportional to the total probability (integrated over all photoelectron kinetic energies) for ionization to occur from $|\Psi_i\rangle$ to $|\Psi_f\rangle$.³⁷ Hence, by calculating the Dyson orbitals $\psi_{D,if}$ for all core-ionized final states in the energy interval of interest, the dominant transitions underlying the continuum part of the calculated XAS may be identified.

In order to proceed, we note that Equation (14) may be re-written in the second quantization form

$$\psi_{D,if} = \sum_{p} \left\langle \left. \Psi_{f} \right| \hat{c}_{p} \right| \Psi_{i} \right\rangle \varphi_{p}, \tag{15}$$

where $\{\varphi_p\}$ denotes the set of canonical Hartree-Fock orbitals. We now replace the true (N - 1)-electron wavefunction $|\Psi_f\rangle$ in the expansion (15) by $\hat{c}_{\alpha} |\bar{\Psi}_f\rangle$, where $|\bar{\Psi}_f\rangle$ denotes the corresponding N-electron CVS-IP-ADC(2) state and α indexes the diffuse "continuum" orbital used in its construction (see Section IV C). The resulting approximate formula for the Dyson orbital $\psi_{D,if}$ reads

$$\psi_{D,if} \approx \sum_{p} \left\langle \bar{\Psi}_{f} \right| \hat{c}_{\alpha}^{\dagger} \hat{c}_{p} | \Psi_{i} \right\rangle \varphi_{p}$$
$$= \sum_{p} \rho_{\alpha p}^{(f,i)} \varphi_{p}, \tag{16}$$

where $\rho^{(f,i)}$ denotes the transition density matrix between the CVS-IP-ADC(2) state $|\bar{\Psi}_f\rangle$ and the ADC(2) state $|\Psi_i\rangle$. Equation (16) represents our working equation for the calculation of approximate Dyson orbitals for excited state core-ionization.

It remains to note that the CVS-IP-ADC(2) states corresponding to shake-up processes generally have significant contributions from large numbers of 2h2p ISs. Accordingly, it is generally a non-trivial task to assign characters to the CVS-IP-ADC(2) states. One possibility would be to calculate the associated natural ionization orbitals.³⁸ However, this treatment falls outside the scope of this work, and we do not attempt such a characterization here. Instead we simply use the associated approximate Dyson orbitals to help identify shape resonances in the calculated continuum XAS. To do so, we note that if there exists significant intensity in a given region of the continuum XAS, but there are no CVS-IP-ADC(2) states appearing before the onset of this region with non-zero squared Dyson orbital norms, then the spectral intensity may be assigned to a shape resonance.

V. COMPUTATIONAL DETAILS

The canonical Hartree-Fock orbitals required for the construction of the ADC Hamiltonian matrix were calculated using the GAMESS program.³⁹ For all molecules considered, the aug-cc-pVTZ basis set was used on all atoms. To describe the discretized continuum, these basis sets were augmented with uncontracted continuum-type diffuse functions of the Kaufmann-Baumeister-Jungen (KBJ) type⁴⁰ placed at the centre of mass. The convergence of the Stieltjes imaging photoionization cross-sections with respect to the number of diffuse functions is somewhat system-specific. Moreover, the cost of the ADC calculations scales steeply with respect to the basis size. Therefore, different sets of KBJ diffuse functions were used for each molecule, with the numbers being determined such that converged cross-sections were obtained.

A block Lanczos procedure was used to generate the Lanczos pseudospectra used in the calculation of the spectral moments. The number of Lanczos vectors required to converge the continuum part of the spectrum is sensitive to the choice of initial Lanczos vectors and, to accelerate convergence, the following strategy was used. The initial Lanczos vectors used correspond to a collection of 1h1p and 2h2p unit vectors with the greatest transition dipole moments with the initial state. A dynamically determined block size was used, determined by the number of 1h1p and 2h2p unit vectors with transition dipole moments with the initial state that are greater in magnitude than a preset threshold of $\epsilon = 10^{-4}$ a.u., with a maximum block size of 200 being used.

The Stieltjes imaging procedure requires the recursive calculation of a number of quantities, and, as such, is highly

susceptible to numerical roundoff errors. In order to ameliorate associated problems, all Stieltjes imaging calculations were performed in arbitrary precision using the MPFUN2015 package,⁴¹ using a precision level of 1000 digits. The positive spectral moments S(k) diverge for k > 2, and can only be used if appropriate regularization schemes are employed.²³ Therefore, the Stieltjes imaging procedure was performed using the negative spectral moments. The Stieltjes imaging calculation was performed using the procedure outlined in Sections 3.1-3.5 of Reference 22. Typical Stieltjes orders of 20-25 were used, and the resulting spectra were interpolated using monotonicity-constrained cubic splines⁴² to yield the final continuum part of the XAS.

VI. RESULTS

A. Ground state X-ray absorption spectra

It is well known that the oscillator strengths and excitation energies furnished by the CVS-ADC(2)x method can provide an accurate description of the pre-edge part of the XAS.^{16,43}

Additionally, the application of Stieltjes imaging to the block Lanczos pseudospectrum of the ADC(2) Hamiltonian has previously been shown to be capable of yielding accurate valence photoionization cross-sections.^{29–31} However, the CVS-ADC(2)x method has not previously been used in the calculation of core ionization cross-sections. Therefore, before discussing the calculated excited state XAS, we present calculated ground state XAS, for which a comparison to experimental results can be readily made.

We consider the ground state XAS of a selection of small molecular systems that may be regarded as prototypical with regards to their excited state dynamics: water, ammonia, carbon dioxide, and ethylene. The calculated ground state XAS for these systems are shown in Figure 1 alongside their experimental counterparts. The details of these calculations are given in Table I. For all calculations, the bound parts of the XAS were computed using a broadening parameter $\eta = 1.0$ eV (see Equation (10)). It has long been recognised that the CVS-ADC(2)x method is capable of accurately reproducing preedge XAS, both in terms of transition energies and intensities, and this is found to be the case for the systems considered here.



FIG. 1. Calculated (black) and experimental (red) ground state X-ray absorption spectra for: (a) water, (b) carbon dioxide, (c) ammonia, and (d) ethylene. The dashed lines mark the threshold for K-shell ionization as calculated at the CVS-IP-ADC(2)x level of theory. The vertical blue lines correspond to the calculated squared Dyson orbital norms. The experimental spectra are adapted from Refs. 53 (ethylene and carbon dioxide), 54 (water), and 55 (ammonia).

TABLE I. Basis sets, Lanczos block sizes and number of Lanczos vectors used in the calculation of the XAS for ethylene, ammonia, water, and CO₂.

Molecule	Basis	Block size	No. Lanczos vectors
C ₂ H ₄	aug-cc-pVTZ + 3s6p4d	200	6000
NH ₃	aug-cc-pVTZ + 3s4p3d	200	6000
H ₂ O	aug-cc-pVTZ + 3s6p4d	200	6000
CO_2	aug-cc-pVTZ + 4s6p4d	200	6000

Additionally, we find that the CVS-ADC(2)x-Stieltjes imaging method is capable of accurately describing the continuum part of the XAS for all four systems. As such, we consider the CVS-ADC(2)x-Stielties imaging method to be suitable for the calculation of both the bound and continuum part of the XAS. Also shown in Figure 1 are the calculated thresholds for core ionization and the squared Dyson orbital norms corresponding to core ionization from the ground state, both calculated at the CVS-IP-ADC(2)x level. It is notable that the calculated ground state XAS all have continuum parts dominated by states corresponding to 1h ionization from the core-level orbitals, with the 2h1p ionized states contributing very little to the calculated photoionization cross-sections. Also worthy of note is the accuracy of the CVS-IP-ADC(2)x method used to estimate the core ionization energies required in the partitioning of the total XAS into bound and continuum parts. The CVS-IP-ADC(2)x K-shell ionization energies for water, ammonia, carbon dioxide, and ethylene are given in Table II together with the experimentally determined values. Overall, the CVS-IP-ADC(2)x method is found to furnish rather accurate core ionization energies, with the calculated energies being on average within 0.19% of the experimental values.

With the accuracy of the CVS-ADC(2)x and CVS-ADC(2)x-Stieltjes imaging methods established for ground state XAS, we now consider the XAS spectra of the low-lying singlet excited states of the same set of molecules. In this paper, we place particular emphasis on the potential of core-excitation to probe excited state non-adiabatic dynamics, requiring the XAS to be sensitive to both the electronic and nuclear degrees of freedom. That is, the XAS spectrum would be required to vary significantly as a function of both the nuclear coordinates (i.e., structural dynamics) and the initial electronic state (i.e., electronic dynamics) of the molecule.

TABLE II. Calculated (CVS-IP-ADC(2)x) and experimental core-ionization potentials for ethylene, ammonia, water, and CO_2 . The basis sets used are the same as those given in Table I.

Molecule	Core	Calculated	Experimental
C ₂ H ₄	C 1s	290.58	290.8ª
NH ₃	N 1s	404.89	405.6 ^b
H ₂ O	O 1s	538.66	539.7 ^b
CO_2	C 1s	298.73	297.7°
CO_2	O 1s	540.44	541.28 ^d

^aReference 49.

^bReference 50.

^cReference 51.

^dReference 52.

Whether or not these criteria are likely to be fulfilled is the subject of Secs. VI B and VI C.

B. Sensitivity of the XAS to electronic dynamics

How does XAS depend on the electronic character of the state being probed? In this section, we consider the calculated XAS of the low-lying electronically excited states of ethylene, ammonia water, and carbon dioxide at their Franck-Condon geometries. It is found that the calculated XAS for all systems are sensitive to the initial electronic state. In particular, it is predicted that, for singly excited states, the pre-edge part of the spectrum, $\sigma^{(b)}(E)$, may act as a fingerprint of the electronic character of the initial state.

1. Ethylene

We here consider vertical core-excitation from the $B_{3u}(\pi 3s)$ and $B_{1u}(\pi \pi^*)$ states of ethylene. The calculated XAS for these states are shown in Figure 2. To aid analysis, the calculated carbon 1s ionization potentials for each state are marked by dashed lines. Additionally, the squared Dyson orbital norms for core ionization from each state are also shown.

The calculated XAS for the $B_{3u}(\pi 3s)$ and $B_{1u}(\pi \pi^*)$ states are found to be qualitatively different to the ground state spectrum, in terms of both the bound and continuum parts of the spectrum. The continuum parts of the $B_{3\mu}(\pi 3s)$ and $B_{1u}(\pi\pi^*)$ state XAS are characterised by broad, relatively intense peaks centred around 305 eV. This is in contrast to the ground state XAS, for which the continuum part of the spectrum is flatter and somewhat less intense. For the $B_{3u}(\pi 3s)$ XAS, the broad peak appearing above the coreionization threshold is most probably attributable to excitation into one or more quasi-bound states: that is, we attribute it to a shape resonance. Evidence for this interpretation is provided by the calculated $\|\psi_{D,if}\|^2$ values for core-ionization from the $B_{3u}(\pi 3s)$ state. These are found to have vanishingly small values below 308 eV, implying that the intensity in the calculated XAS below this energy must arise from bound-bound transitions. Unfortunately, owing to the very large number of CVS-ADC(2)x states underlying this energy interval, we are not able to identify the underlying transitions. It is, however, relevant to note that previous computational studies have implicated the role of $1s \rightarrow C-C \sigma^*$ type transitions in giving rise to the majority of the intensity associated with shape resonances in the ground state XAS of ethylene.44

Perhaps more interesting are the spectral features present below the ionization threshold. For the ground state, the bound part of the spectrum is found to contain significant contributions from numerous electronic transitions. The intense peak centred at 284.9 is found to arise from a single transition to a $1s\pi^*$ state. The peak at 287.8 eV is dominated by a single transition, corresponding to excitation to a 1s3pstate. Finally, the peak at 289.3 eV is found to contain large contributions from excitation to three states: one 1s3p state and two 1s3d states. In contrast, the pre-edge parts of the $B_{3u}(\pi 3s)$ and $B_{1u}(\pi\pi^*)$ state XAS are significantly less congested, with



FIG. 2. Calculated XAS for ethylene at the CVS-ADC(2)x level of theory corresponding to the initial states: (a) $B_{3u}(\pi 3s)$ and (b) $B_{1u}(\pi \pi^*)$. The dashed lines mark the threshold for C 1s ionization as calculated at the CVS-IP-ADC(2)x level of theory. The vertical blue lines correspond to the calculated squared Dyson orbital norms.

each being dominated by a single intense peak. A single transition is found to underlie the intense pre-edge peak in the $B_{3u}(\pi 3s)$ state spectrum, with the final-state wavefunction being dominated by the 1h1p excitations $1s \rightarrow 4s$, $1s \rightarrow 3s$, and $1s \rightarrow 5s$. Now, the ADC(2) wavefunction for the $B_{3u}(\pi 3s)$ state is found to be dominated by configurations corresponding to the 1h1p excitations $\pi \to 4s, \pi \to 3s$, and $\pi \to 5s$. As such, the dominant pre-edge transition for the $B_{3u}(\pi 3s)$ state could be seen to correspond, in the single-configuration limit, to excitation of an electron from the doubly occupied 1s core orbital to the singly occupied π valence orbital. A similar propensity is found for core excitation from the $B_{1\mu}(\pi\pi^*)$ state. The pre-edge spectrum for this is dominated by a single transition corresponding to excitation from the 1s orbital to two π^* orbitals. The dominant configurations entering into the $B_{1u}(\pi\pi^*)$ state wavefunction correspond to excitation from the HOMO (π) orbital to the same two π^* orbitals. Hence, as with the $B_{3u}(\pi 3s)$ state, core excitation from the $B_{1u}(\pi \pi^*)$ state

may be seen to be dominated by excitation from the doubly occupied 1s core orbital to the singly occupied π valence orbital. This predicted propensity for core-excitation to occur to a single state whose wavefunction is strongly correlated with that of the initial state is an interesting feature of the pre-edge part of the calculated XAS. An important conclusion is that core excitation below the ionization threshold may hold potential as a sensitive probe of the electronic character of the initial state of a molecular system. This idea is expounded in Secs. VI B 2–VI B 5.

2. Ammonia

The calculated XAS for the $A_2''(n3s)$ and $E''(n3p_e)$ Rydberg states of ammonia are shown in Figure 3. At the ADC(2) level, the $A_2''(n3s)$ wavefunction possesses dominant configurations corresponding to the excitations $n \rightarrow 3s$, $n \rightarrow 4s$, and $n \rightarrow 5s$. The dominant configurations



FIG. 3. Calculated XAS for ammonia at the CVS-ADC(2)x level of theory corresponding to the initial states: (a) $A_2''(n3s)$ and (b) $E''(n3p_e)$. The dashed lines mark the threshold for C 1s ionization as calculated at the CVS-IP-ADC(2)x level of theory. The vertical blue lines correspond to the calculated squared Dyson orbital norms.

entering into the $E''(n3p_e)$ wavefunction correspond to the excitations $n \to 3p_e$, $n \to 4p_e$, and $n \to 5p_e$. Similar to the case of ethylene, the pre-edge part of the calculated excited state XAS is dominated by single, intense peaks. Again, the identity of the underlying final states is found to correlate with that of the initial state. For the $A_2''(n3s)$ state, the dominant pre-edge peak corresponds to excitation to a coreexcited state whose wavefunction is dominated configurations corresponding to the single excitations $1s \rightarrow 3s$, $1s \rightarrow 4s$, and $1s \rightarrow 5s$. For the $E''(n3p_e)$ state, the dominant pre-edge peak corresponds to excitation to a state whose wavefunction possesses configurations corresponding to the excitations $1s \rightarrow 3p_e, 1s \rightarrow 4p_e, \text{ and } 1s \rightarrow 5p_e$. Hence, in the limit of a single configuration model, the dominant pre-edge transitions for both states may be seen to correspond predominantly to excitation from the N 1s orbital to the singly occupied norbital of the initial state.

For both the $A_2''(n3s)$ and $E''(n3p_e)$ states, the calculated XAS contain broad peaks above the calculated threshold for core-ionization, but below the onset of continuum states for which the calculated $||\psi_{D,if}||^2$ values are non-negligible. This is indicative of the existence of shape resonances. Through an analysis of the CVS-ADC(2)x wavefunctions for the bound states underlying this region, we find that the shape resonances in both cases correspond predominantly to N $1s \rightarrow 4p_{x/y}$ and N $1s \rightarrow 5p_{x/y}$ excitations out of the initial $A_2''(n3s)$ and $E''(n3p_e)$ states.

3. Water

The calculated XAS for the $B_1(n3s)$ and $A_2(n3p)$ states of water are shown in Figure 4. Again, for both excited states the pre-edge parts of the calculated XAS are found to be dominated by single, intense peaks that map onto the wavefunction of the initial state. The dominant peak in the $B_1(n3s)$ state spectrum corresponds to excitation to a state whose wavefunction is dominated by the configurations corresponding to the single excitations $1s \rightarrow 3s$, $1s \rightarrow 4s$, and $1s \rightarrow 5s$. The wavefunction for the $B_1(n3s)$ state is dominated by configurations corresponding to the excitations $n \rightarrow 3s$, $n \rightarrow 4s$, and $n \rightarrow 5s$. For the $A_2(n3p)$ state, the pre-edge part of the calculated spectrum is dominated by a single peak corresponding to excitation to a state with a wavefunction with dominant configurations corresponding to the single excitations $1s \rightarrow 3p_y$, $1s \rightarrow 4p_y$, $1s \rightarrow 5p_y$, and $1s \rightarrow 6p_y$. The $A_2(n3p)$ state wavefunction is dominated by configurations corresponding to the excitations $n \rightarrow 3p_y$, $n \rightarrow 4p_y$, $n \rightarrow 5p_y$, and $n \rightarrow 6p_y$. Thus, we determine that the calculated pre-edge XAS for the $B_1(n3s)$ and $A_2(n3p)$ states can be seen in the single configuration limit to be dominated by excitation from the doubly occupied O 1s orbital to the singly occupied n orbital.

Similar to the cases of ethylene and water, from a consideration of the calculated squared Dyson orbital norms for core-ionization from the $B_1(n3s)$ and $A_2(n3p)$ states, we determine that the XAS for both states contain significant intensity arising from shape resonances occurring around 560 eV. For the $B_1(n3s)$, we determine the dominant underlying transition to correspond to the O $1s \rightarrow 3p_x$ excitation. For the $B_1(n3s)$ state, the high density of CVS-ADC(2)x states underlying this region and the often large number of 2h2p ISs contributing significantly to their wavefunctions precludes an identification of the dominant transitions.

4. Carbon dioxide

Shown in Figure 5 are the calculated C 1s XAS for the $\Pi_g(\pi 3s)$ and $\Sigma_u^-(\pi \pi^*)$ states of CO₂. Unlike for the other molecules considered in this work, the pre-edge parts of the $\Pi_g(\pi 3s)$ and $\Sigma_u^-(\pi \pi^*)$ state spectra have essentially zero intensity. For the other systems considered here (ethylene, ammonia, and water), we observe a strong propensity for core-excitation from a singly excited initial state to occur to a final state that may be accessed via the excitation of a core-level electron into the lowest-lying singly occupied



FIG. 4. Calculated XAS for water at the CVS-ADC(2)x level of theory corresponding to the initial states: (a) $B_1(n3s)$ and (b) $A_2(n3p)$. The dashed lines mark the threshold for O 1s ionization as calculated at the CVS-IP-ADC(2)x level of theory. The vertical blue lines correspond to the calculated squared Dyson orbital norms.



FIG. 5. Calculated XAS for carbon dioxide at the CVS-ADC(2)x level of theory corresponding to the initial states: (a) $\Pi_g(\pi 3s)$ and (b) $\Sigma_u^-(\pi \pi^*)$. The dashed lines mark the threshold for C 1s ionization as calculated at the CVS-IP-ADC(2)x level of theory. The vertical blue lines correspond to the calculated squared Dyson orbital norms.

orbital of the initial state. In the case of the $\Pi_g(\pi 3s)$ state of CO₂, this would correspond to transition to a core-excited state dominated by a configuration corresponding to the single excitation C 1s \rightarrow 3s, which would have Σ_{g}^{+} symmetry. The z and (x,y) components of the dipole operator generate the Σ_u^+ and Π_u irreducible representations, respectively. Hence, the single-photon transition from the $\Pi_g(\pi 3s)$ state to such a low-lying core-excited state is dipole-forbidden, resulting in the $\Pi_{g}(\pi 3s)$ XAS being essentially zero below the ionization threshold. Analogous symmetry arguments hold for the $\Sigma_{\mu}^{-}(\pi\pi^{*})$ state. Instead, the calculated XAS for the $\Pi_{\rho}(\pi 3s)$ is dominated by an intense peak centred at 298 eV. Noting that this peak occurs well below the onset of continuum states for which the calculated $\|\psi_{D,if}\|^2$ value is non-zero, we conclude that this feature corresponds to one or more shape resonances. Analysis of the bound CVS-ADC(2)x states lying above the core-ionization threshold reveals that the dominant transitions giving rise to this peak are of C $1s \rightarrow \pi^*$ character. The calculated $\Sigma_{\mu}^{-}(\pi\pi^{*})$ XAS is found to exhibit a very similar structure, with a shape resonance centred at 291 eV corresponding predominantly to the excitations C $1s \rightarrow \pi^*$ and C 1s \rightarrow 3d.

5. General trends

All of the initial valence-excited states considered here have wavefunctions that are dominated by 1h1p excitations from a closed-shell ground state. In the single determinant limit, and acknowledging that the dipole operator \hat{D} is a one-electron operator, a singly excited N-electron initial state $|\Psi_i\rangle$ will have a non-zero transition dipole matrix element only with the subset of final states $|\Psi_f\rangle$ possessing orbital occupancies that differ from those of $|\Psi_i\rangle$ for one, and only one, pair of orbitals. Hence, for the case of core-excitation from a singly valence-excited initial state $|\Psi_i\rangle$, the set of final states $|\Psi_f\rangle$ for which $\langle \Psi_i | \hat{D} | \Psi_f \rangle \neq 0$ would correspond to the set of doubly excited states

$$|\Psi_{abJk}\rangle = \hat{c}_a^{\dagger}\hat{c}_b^{\dagger}\hat{c}_J\hat{c}_k |\Psi_0\rangle, \qquad (17)$$

for which k and b index the singly occupied orbitals in the initial state $|\Psi_i\rangle$, J indexes a core orbital, and a an unoccupied orbital in $|\Psi_i\rangle$. In the multi-configurational case, this requirement will be relaxed. However, we may still expect that this single-determinant selection rule may map onto propensities for the magnitude of the excited state transition dipole matrix elements in the multi-configurational case.

Such a propensity appears to be borne out in the calculated excited state XAS presented here. For all molecules considered here, with the exception of carbon dioxide, the pre-edge parts of the calculated excited-state XAS are dominated by single peaks corresponding to excitation from a core-level orbital into the SOMO of the occupied orbitals (for carbon dioxide, symmetry results in this transition being dipole-forbidden). We propose that there will exist a class of optically bright final states $|\Psi_f\rangle$ for each of the singly valence-excited initial states of each molecule, corresponding to a single excitation from a core orbital into one of the unoccupied or singly occupied orbitals of the initial state. However, the final state corresponding to excitation into the lowest-lying SOMO may be expected to be the lowest in energy of this class of states. As such, we may expect that this core-to-SOMO transition will appear as the first dominant bound-bound transition in the calculated XAS (symmetry permitting). The peaks corresponding to single excitation from the core orbitals into the singly-occupied and unoccupied virtual orbitals happen to lie above the ionization threshold in the cases considered here, therefore appearing as shape resonances in the calculated XAS.

C. Sensitivity of the XAS to structural dynamics

How does XAS depend on the geometrical structure of the state being probed? In this section, we consider the calculated excited state pre-edge XAS, $\sigma^{(b)}(E)$, of ethylene and CO₂ as a function of nuclear coordinates pertinent to the excited state dynamics of these molecules. For ethylene, the pre-edge XAS of the S₁ state is calculated along the torsional angle φ

that connects the planar D_{2h} Franck-Condon geometry to the anti-planar D_{2d} geometry which lies roughly 1.5 eV lower in energy. For CO₂, we consider the degenerate bending coordinate responsible for both strong Renner-Teller and pseudo-Jahn-Teller couplings in the molecule's first excited state. As we are only interested in the calculation of the pre-edge part of the spectrum, $\sigma^{(b)}(E)$, the use of large numbers of diffuse functions (required for the calculation of $\sigma^{(c)}(E)$) is not a necessity. To reproduce the pre-edge part of the XAS of both molecules, the 6-311++G^{**} basis set was found to be sufficient, and this basis was used in the following calculations.

1. Ethylene

Shown in Figure 6(a) is the calculated pre-edge XAS for the S₁ state of ethylene as a function of the dihedral angle φ defined between the C-H bonds of the terminal carbon atoms. For reference, the ADC(2) potential energy surfaces (PESs) for the S_0 , S_1 , and S_2 states along the dihedral angle φ are shown in Figure 6(b). At the Franck-Condon point, the S_1 and S_2 states are the $B_{3u}(\pi 3s)$ and $B_{1u}(\pi \pi^*)$ states, respectively. As discussed in Section VI B 1, the pre-edge part of the XAS at the Franck-Condon point is dominated by a single transition, which may be interpreted as the excitation of a C 1s electron into the hole in the singly occupied valence π orbital. For dihedral angles $0^{\circ} \ge |\varphi| < 30^{\circ}$ the pre-edge XAS remains dominated by the same single transition, the position of which evolves to higher energies. This is a consequence of the difference in the curvatures of the initial and final state potentials in this region. At $|\varphi| = 30^\circ$, a discontinuous shift of the dominant transition, by around 2 eV to the red, is observed. This is a result of the character of the S_1 state wavefunction changing from Rydberg 3s to valence $\pi\pi^*$ at the crossing of the S_1 and S_2 states. As detailed in Section VI B 1, core-excitation

from these states is predicted to result in transition to different final states and, at the point of crossing of the $S_1(\pi 3s)$ and $S_2(\pi \pi^*)$ states, the two final states are separated by ~2 eV. Between $|\varphi| = 30^\circ$ and $|\varphi| = 90^\circ$ the character of the S_1 state remains the same, resulting in a single peak which evolves to higher energies as the energy of the initial state is lowered.

2. CO₂

Shown in Figure 7(a) is the calculated pre-edge XAS for the S_1 state of CO₂ as a function of the bending angle θ . At the linear Franck-Condon geometry, the doubly degenerate S_1 state has Π_{ρ} symmetry, the degeneracy of which is lifted along the bending coordinate by both Renner-Teller and pseudo-Jahn-Teller couplings.^{45,46} As discussed previously, at the Franck-Condon point, the calculated pre-edge XAS has essentially zero intensity. However, as the bending coordinate is displaced, the calculated pre-edge spectrum rapidly begins to develop intensity, starting at an angle around 165°. This may be rationalised as arising due to the change in the character of the S_1 state wavefunction due to strong vibronic coupling to one or more higher-lying states. This interpretation is supported both by an analysis of the ADC(2) S_1 state wavefunction along the bending coordinate and the strong negative curvature of the S_1 PES with respect to this coordinate (which must arise due to strong first-order vibronic coupling to higher-lying states⁴⁵). Between $\theta = 165^{\circ}$ and $\theta = 135^{\circ}$, the main peak in the pre-edge XAS exhibits a "chirp" towards lower energies, a result of the lowering of the energy of the S_1 state. At an angle of $\theta \sim 130^\circ$ there exists a crossing of the S_1 and S_2 states. This is found to manifest itself in a discontinuous increase in the energy of the main peak in the calculated spectrum by around 1 eV. This is consistent with the discontinuous change in the character of the S_1 state wavefunction at this point. Thereafter, both peaks evolve to



FIG. 6. (a) Pre-edge XAS for the S_1 state of ethylene along the dihedral angle φ . (b) Potential energy surfaces of the S_0 , S_1 , and S_2 states of ethylene along the dihedral angle φ calculated at the ADC(2) level of theory. All calculations were performed at the CVS-ADC(2)x/6-311++G** level of theory and with all other nuclear degrees of freedom kept fixed.



FIG. 7. (a) Pre-edge XAS for the S_1 state of CO₂ along the bending angle θ . (b) Potential energy surfaces of the S_0 , S_1 , and S_2 states of CO₂ along the bending angle θ calculated at the ADC(2) level of theory. All calculations were performed at the CVS-ADC(2)x/6-311++G** level of theory and with all other nuclear degrees of freedom kept fixed.

lower energies as the S_1 state reaches its local minimum and then begins to increase in energy.

VII. CORE EXCITATION AS A PROBE OF NON-ADIABATIC DYNAMICS

To be a useful probe of excited state non-adiabatic dynamics, the XAS needs to be sensitive to both the electronic and structural dynamics. As discussed in Sections VI B and VI C, for all systems considered in this work, the calculated XAS was indeed found to be sensitive to these degrees of freedom.

For ethylene, ammonia, water, and carbon dioxide, both the bound and continuum parts of the calculated XAS were found to vary significantly as a function of the initial electronic state. Significantly, for all systems considered (with the exception of CO_2) the bound parts of the excited state XAS are dominated by single transitions that map directly onto the character of the initial state. In the single configuration limit, these transitions would correspond to excitation of a core-level electron into the lowest singly occupied orbital of the initial state. Therefore, we suggest that the pre-edge part of the XAS may act as a fingerprint of the electronic character of the initial state in many cases. For this reason, we chose to focus our attention on the pre-edge part of the spectrum.

We also predict that the pre-edge part of the XAS will be sensitive to large amplitude structural motions in electronically excited states. This is exemplified in the calculated pre-edge S_1 -state XAS of ethylene as a function of the torsional degree of freedom φ and of CO₂ along the bending coordinate θ . We identify three potentially inter-related effects that might give rise to a significant modulation of the pre-edge XAS: (1) A change in the vertical energy difference between the initial and final states of the dominant transition (due to either differences in first or second derivative of the PESs of the initial and final

states) may give rise to energy shifts in the spectrum. (2) Intersections between PESs and any non-adiabatic processes mediated by them should result in large shifts in the pre-edge XAS in accord with the corresponding change in electronic structure of the initial state. (3) Strong vibronic coupling between excited states may result in the electronic character of the initial state changing significantly as the corresponding coupling modes are displaced, resulting in an evolution of the number and/or identities of the final states. Effect (1) (modulation of the vertical energy difference between the initial and final states) is present in the calculated spectra for both ethylene and CO₂. For CO₂, however, this effect is also intimately linked to effect (3) (strong vibronic coupling), as the negative curvature of the S_1 PES responsible for this change in excitation energy is a direct result of the pseudo-Jahn-Teller effect. Finally, and perhaps most distinctly, effect (2) (crossing of initial state PESs) is also present in the calculated spectra of both ethylene and CO₂. In both cases, a discontinuous change in the electronic character of the S_1 state results in large shift of the spectrum on account of the corresponding change in the identities of the final states.

VIII. CONCLUSIONS

The aims of the work presented here are two-fold: (i) to establish the accuracy of core photoionization crosssections obtained through the application of Stieltjes imaging to the Lanczos pseudo-spectrum of the CVS-ADC(2)x representation of the electronic Hamiltonian and (ii) to determine whether the XAS is likely to be a good probe of excited state non-adiabatic molecular dynamics.

Through comparison to experimental ground state XAS for few small molecules, we have shown that the ground state XAS may be accurately and tractably calculated using the CVS-ADC(2)x method in combination with the Stieltjes imaging method. In agreement with previous studies, the CVS-ADC(2)x oscillator strengths and excitation energies accurately reproduce the bound part of the XAS. Additionally, we showed for the first time that the continuum part of the XAS may also be accurately calculated via the application of Stieltjes-Chebyschev moment theory to the CVS-ADC(2)x Lanczos psuedospectrum.

Having established that the CVS-ADC(2)x method accurately reproduced ground state XAS, we extended the calculation to excited state XAS, with an aim of assessing core-excitation as a probe of excited state non-adiabatic dynamics. To be a useful probe of excited state non-adiabatic dynamics, the XAS is required to be sensitive to both the electronic character of the molecular wavefunction and the nuclear geometry. That is, to both electronic and structural dynamics. The calculations presented here suggest that the XAS may indeed be sensitive to both. With regard to the electronic character of the wavefunction, we found that the calculated XAS vary significantly as a function of the initial electronic state. In particular, we observed that the bound part of the calculated spectrum maps directly onto the electronic character of the initial state, with a single dominant transition corresponding in a single configuration framework to excitation from a core orbital into the lowestlying singly occupied orbital of the initial state. This interesting result led us to emphasize the bound part of the XAS as a new spectroscopic signature of excited state dynamics. Furthermore, the bound part of the XAS is predicted to vary significantly as a function of the nuclear geometry, as exemplified by the bound XASs calculated for ethylene and carbon dioxide along nuclear degrees of freedom pertinent to their excited state dynamics (along the torsional angle for ethylene and along the bending angle for carbon dioxide). In both cases, the bound part of the XAS varied significantly due to variations in the vertical energy differences between the initial and final states and, importantly, due to the crossings of PESs. For the case of carbon dioxide, the bound part of the calculated XAS was found to be sensitive to changes in the electronic character of the initial state resulting from the pseudo-Jahn-Teller effect.

The calculations presented here suggest that XAS will be sensitive to both the electronic and nuclear degrees of freedom and, as such, has significant potential as a spectroscopic probe of excited state non-adiabatic dynamics. To investigate this suggestion more concretely, we believe that it will be necessary to calculate time-resolved XAS via the coupling of XAS calculations to wavepacket propagation calculations. In our future studies, we will combine our excited state XAS method with quantum dynamics calculations performed using, for example, the *ab initio* multiple spawning method.^{47,48}

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