Resonant double-core excitations with ultrafast, intense X-ray pulses

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ABSTRACT

Intense few-to-sub-femtosecond soft X-ray pulses can produce neutral, two-site excited double-core-hole states by promoting two core electrons to the same unoccupied molecular orbital. We theoretically investigate double nitrogen K-edge excitations of nitrous oxide (N₂O) with multiconfigurational electronic structure calculations. We show that the second core-excitation energy is reduced with respect to its ground state value. A site-selective double core-excitation mechanism using intense few-femtosecond x-rays is investigated using time-dependent Schrödinger equation (TDSE) simulations. The subsequent two-step Auger–Meitner and two-electrons-one-electron decay spectra of the double core-excited states are analysed using a Mulliken population analysis of the multiconfigurational wavefunctions. The change in the electron emission lineshape between the absorption of 1 or 2 photons in the resonant core-excitation is predicted by combining this approach with the TDSE simulations. We examine the possibility of resolving the double core-excited states with X-ray pump-probe techniques by calculating the chemical shifts of the core-electron binding energy of the core-excited states and decay products.

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1. Introduction

The resonant interaction of high-intensity X-ray free electron laser (XFEL) pulses with atoms and molecules on few-to-sub-femtosecond timescales holds promise to a variety of new applications; such as selectively exciting specific local electronic states through the stimulated X-ray Raman process [1–3], enhancing scattering signal images without significant X-ray damage [4–7] and producing coherent superpositions of core-excited states [8]. High intensity XFEL experiments have the potential to induce low probability processes such as valence photoionisation and multi-photon absorption. With intense attosecond pulses, the possibility of sequential absorption before decay processes can be high, and it could significantly impact the efficiency of the stimulated X-ray Raman scattering and enhanced scattering signals.

Early experiments at the Linac Coherent Light Source (LCLS) XFEL used intense femtosecond X-ray pulses for the experimental observation of molecular double-core-hole (DCH) states [9–11], produced through a sequential multi-photon absorption mechanism that creates two vacancies either on a single atomic site (ss) or on...
two sites (ts) of a molecule. Such states were initially described in seminal theory work by Cederbaum et al. [12]. Synchrotron radiation (SR) can also produce ss and ts DCH states with low probability by relying on the change in electronic density induced by the sudden removal of a core electron [13–17], as well as more exotic DCH states through a core-ionisation or core-excitation mechanism [18–28]; recently these states were observed using an XFEL [29]. However, to the best of our knowledge, the formation of neutral excited ss or ts-K-shell DCH states created through sequential core-excitations is unobserved. We note that KL excitations of this form (involving $s$ and $p$-shells) have been observed for argon and the sulfur-containing molecules H$_2$S, SO$_2$ and SF$_6$ [30,31] in SR experiments.

Nitrous oxide (N$_2$O) is a model system for studying neutral excited ts-DCH states, since it is a small molecule with two distinct nitrogen atomic sites with a significant chemical shift in the core electron binding energy (CEBE) of the two nitrogen atoms around 4 eV. Previous SR studies demonstrate selective excitation of the two nitrogen sites due to the large difference of their binding energy [32–40]. Following resonant excitation, the N$_2$O Auger–Meitner decays, where one electron is emitted and another fills the core hole. The high-resolution de-excitation spectrum (often referred to as resonant Auger–Meitner spectroscopy) has been measured following single excitations and reveals significantly different electronic kinetic energy distributions depending on the excitation site [41,42] which was theoretically supported by Fink [43]. A clear signature of the decay of core-excited molecules is from the so-called participator channels, where the electron excited in the first step also participates in the subsequent decay. Because the final state of this decay process is the same as the one following direct valence photoionisation of the ground state, the kinetic energy of these electrons can be easily predicted.

Figure 1(a) shows the generation of a doubly core-excited N$_2$O molecule via ts double nitrogen K-shell excitation to the $\pi^*$ orbital. Scenarios for detecting this state are shown, (b) using time-resolved X-ray photoelectron spectroscopy (TR-XPS) and c-f) through tracking the variety of decay pathways. The double-participator decay in (c) is unique to these states and we will show that its signature is of higher kinetic energy than other pathways. (d) and (e) show the participator and spectator decay processes which are analogous to single-core excited state decay. One intriguing possibility is observing the two-electron-one-electron (TEOE) process shown in (f), where both core holes are filled simultaneously and all the excess energy is carried by a single continuum electron of much higher energy. This process has only been observed previously using SR, for inner-shell vacancies in argon [44] and the CH$_3$F molecule [45]. It was found that the TEOE decay in argon was $10^3$ times less likely to occur than the sequential Auger–Meitner decay [44].

In this work we theoretically investigate the production of ts double core excited states ($K^{-1}K^{-1}V^2$) through sequential inner shell excitations (via single core excited states ($K^{-1}V^1$)) at the nitrogen K-edge in nitrous oxide and characterise the states via the resonant Auger–Meitner decay. Sections 2 and 3 present the calculation details and results discussion, which are both split into four complementary subsections. First, X-ray absorption near edge structure (XANES) spectra detailing the required energetics for the two single-photon excitations yielding the $K^{-1}K^{-1}V^2$ states are discussed in Sections 2.1 and 3.1. Sections 2.2 and 3.2 discuss the electronic population transfer dynamics in the presence of ultrafast x-rays producing the $K^{-1}K^{-1}V^2$ states, modelled by numerically solving the time-dependent Schrödinger equation (TDSE) [46–53]. Sections 2.3 and 3.3 discuss the resonant Auger–Meitner decay of the $K^{-1}K^{-1}V^2$ states, which undergo two-step decay and TEOE processes. Finally, chemical shifts in the core-electron binding energy (CEBE) for the core-excited states and the associated Auger–Meitner decay products are discussed in Sections 2.4 and 3.4, respectively.

2. Theoretical and computational details

The study uses the restricted active space self consistent field (RASSCF) multiconfigurational quantum chemical method [54,55] and its second-order perturbation correction to correlation energy (RASPT2) [56,57]. There are numerous approaches for calculating core-excited states from first principles [58–61], earlier studies of double-core hole states used multiconfigurational self-consistent field (MCSCF) calculations to describe the relaxation of the orbitals in the presence of the core-holes [62]. Auger–Meitner decay rates of single and double core-ionised gas-phase water have also been explicitly calculated by electronic transition rate calculations coupled to ab-initio molecular dynamics [63]. Here we use RASSCF/PT2 as it is a widely used approach for core-hole spectroscopy and provides a flexible and accurate approach to treating single and multiple core-hole states in small gas-phase molecules and transition metal complexes [11,64–67] and recently, the OpenMolcas implementation of this approach has been applied to DCH shake-up spectra [68]. All electron structure calculations in this work were calculated using the OpenMolcas software package [69]. A fixed ground state geometry was used throughout, optimised by density functional theory (DFT) with the B3LYP exchange correlation functional and the 6-311G** basis set. The resulting N$_{\pi}$-N$_{\pi}$ and
Figure 1. (a) Double K-shell excitation from the two nitrogen sites to the $\pi^*$ orbital. (b) Probing the DCH decay with time resolved-X-ray photoelectron spectroscopy (TR-XPS). (c) Double participator decay involving both core-excited electrons. (d) Participator process involving both an inner-shell electron and the core-excited electron. (e) Spectator process involving two inner-shell electrons. (f) Two-electrons-one-electron (TEOE) process involving two electrons simultaneously filling both core-holes and ejecting a single electron.

$N\text{c}-O$ bond-lengths were 1.12 and 1.18 Å. Unless stated otherwise, all calculations in this work were calculated with the ANO-RCC-VQZP basis set in combination with the Cholesky-based resolution of the identity auxiliary basis [70]. No point group symmetry restrictions were applied in this work.

2.1. XANES spectra

The ground state, two $N_t$ and $N_c$ $K^{-1}V^1$ states ($1s \rightarrow \pi_x^*$ and $1s \rightarrow \pi_y^*$) and four $K^{-1}K^{-1}V^2$ states (where $K$ is the $N$ 1s orbitals and $V$ is the doubly degenerate $\pi^*$) were initially calculated at the state-averaged (SA-)RASSCF(20,1,2;1,11,1) level of theory. This uses the RASSCF($n,l,m;i,j,k$) notation, where $n$, $l$ and $m$ refer to the total number of active electrons, the maximum number of holes allowed in RAS1 and the maximum number of electrons allowed in RAS3, respectively; $i$, $j$, and $k$ refer to the number of orbitals in the RAS1, RAS2 and RAS3 subspaces, respectively. Both RAS1 and RAS3 contain either the $N_t$ or $N_c$ 1s orbitals and the highly excited state (HEXS) scheme [64], was applied to both RAS1 and RAS3 to generate $K^{-1}K^{-1}V^2$ states. For $K^{-1}V^1$ states, HEXS was applied to either RAS1 or RAS3. Throughout this work, the oxygen 1s orbital (or any core orbital not included in RAS1 or RAS3) was optimised in the Hartree-Fock (HF) level of theory, and the remaining occupied orbitals were in RAS2. The unoccupied $\pi_x^*$, $\pi_y^*$ and Rydberg 3s orbitals were also included in RAS2. Dynamic correlation was included via multi-state restricted active space second-order perturbation theory (MS-RASPT2) [56,57] with an imaginary shift of 0.1 a.u.
The transition dipole moments between the ground to $K^{-1}V^1$ and $K^{-1}V^1$ to $K^{-1}K^{-1}V^2$ states were calculated using the restricted active space state interaction (RASSI) method [71]. A broadening of 0.11 eV [36] and 0.22 eV was applied to the Gaussian lineshapes of the $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ spectra, which assumes the latter decay twice as fast.

### 2.2. Time-dependent Schrödinger equation

The TDSE simulations of the population transfer dynamics of the $K^{-1}K^{-1}V^2$ states were adopted from the procedure previously used in the simulation of stimulated X-ray Raman scattering (SXRS) on NO [3,53]. The time-dependent electronic Hamiltonian, $\hat{H}(t)$, in the presence of an external electric field is given by

$$\hat{H}(t) = \hat{H}_0 + V(t),$$

(1)

where $\hat{H}_0$ is field-free electronic Hamiltonian and $V(t)$ describes the interaction between the molecule and the external field. We solve the time-dependent Schrödinger equation,

$$\frac{i}{\hbar} \frac{\partial}{\partial t} \langle \Psi, t \rangle = \hat{H}(t) |\Psi, t \rangle$$

(2)

for a set of electronic states determined by the state vector,

$$|\Psi, t \rangle = c_i(t) e^{-iE_i t} |g\rangle + \sum_{s=1}^{N_i} c_s(t) e^{-iE_s t} |s\rangle + \sum_{d=1}^{N_d} c_d(t) e^{-iE_d t} |d\rangle.$$  

(3)

In this ansatz for the wavefunction, the ground state is indicated by $|g\rangle$, the single core excited $K^{-1}V^1$ states indicated by $|s\rangle$ and the double core excited $K^{-1}K^{-1}V^2$ states indicated by $|d\rangle$. $E_g$, $E_s$, $E_d$ and $\sigma_{d}$ are the energies of the ground, $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states, respectively. $N_i$ and $N_d$ are the total numbers of the $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states, respectively. The respective equations of motion (EOM) for the ground, $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states are

$$\dot{c}_g(t) = \left( E_g - \frac{i\Gamma_g(t)}{2} \right) c_g(t) + \sum_{s=1}^{N_i} \gamma_{gs}^d(t)c_s(t)$$

(4)

$$\dot{c}_s(t) = \left( E_s - \frac{i\Gamma_s(t)}{2} \right) c_s(t) + \gamma_{gs}^d(t)c_g(t) + \sum_{d=1}^{N_d} \gamma_{sd}^d(t)c_d(t)$$

(5)

$$\dot{c}_d(t) = \left( E_d - \frac{i\Gamma_d(t)}{2} \right) c_d(t) + \sum_{s=1}^{N_i} \gamma_{sd}^d(t)c_s(t).$$

(6)

The first terms are the diagonal matrix elements, containing the energy $E_n$ of the state and its decay width $\Gamma_n$. Here the index $n$ is used for terms applying to either $g$, $s$ and $d$. Unless stated otherwise, all quantities and formulas are expressed in atomic units throughout this section. The second terms are the off-diagonal matrix elements, involving the interaction terms $\gamma_{ij}^d(t)$, which couple the molecular system to the X-ray field within the dipole approximation,

$$\gamma_{ij}^d(t) = D_{ij}^d \mathcal{E}(t) \cos(\omega_x t),$$

(7)

$$\mathcal{E}(t) = E_{\text{max}} e^{-\frac{(t-t_{\text{max}})^2}{2\tau^2}}$$

(8)

$$\sigma_x = \frac{\tau}{2\sqrt{2\ln(2)}}$$

(9)

Here $\omega_x$ is the incident photon energy, $D_{ij}^d$ is the transition dipole moment (TDM) matrix element between states $i$ and $j$, directed by the polarisation vector $\mu$. The electric field $\mathcal{E}(t)$ is described by a Gaussian with a peak height determined by the pulse intensity, $I_{\text{max}}$, which is given by $I_{\text{max}} = E_{\text{max}}^2/8\pi \alpha$, where $E_{\text{max}}$ is the maximum electric field strength, $\alpha$ is fine-structure constant, and $\tau$ is the full-width-half maximum (FWHM) pulse duration. Decay widths contribute to population losses. The ground state has a single population loss mechanism due to photoionisation from the X-ray pulse, such that its decay rate, $\Gamma_g(t)$, is given by

$$\Gamma_g(t) = \Gamma_x(t).$$

(10)

Here,

$$\Gamma_x(t) = \frac{\sigma_{\text{tot}}}{\omega_x} \mathcal{E}^2(t),$$

(11)

where $\sigma_{\text{tot}}$ is the total cross-section for photoionisation at a given photon energy. We use the sum of atomic cross-sections for 2× nitrogen and 1× oxygen performed by the Hartree–Fock–Slater (HFS) method [72] to give a total cross-section of 0.169 mBarn at 400 eV. An additional contribution is included for the core-hole states due to the core-excited state lifetimes, which predominantly undergo Auger–Meitner decay, such that the decay rates for the $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states can be expressed as

$$\Gamma_s(t) = \Gamma_x(t) + \Gamma_a^s$$

(12)

$$\Gamma_d(t) = \Gamma_x(t) + \Gamma_a^d$$

(13)

In this paper, the linewidths of the $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states are 0.11 eV [36] and 0.22 eV, respectively, where we assume the latter decay twice as fast. The former is approximated by N1s$^{-1}$ lifetime in N$_2$ and we justify the approximation of the latter as the $K^{-1}K^{-1}V^2$ state.
is a ts-DCH state which resembles two individual SCH states. Therefore the orbital contraction effect that triples the decay rate of ss-DCH states can be neglected [23,63]. Using these approximated decay rates and by neglecting coherence terms we can evaluate the evolution of the population losses by integrating over the state populations and decay rates,

\[ b_n^b(t) = \Gamma_n^b \int_{-\infty}^{t} df' |c_n(f')|^2 \]

\[ b_n^a(t) = \int_{-\infty}^{t} df' \Gamma_n^a |c_n(f')|^2 \]

where \( b_n^b(t) \) and \( b_n^a(t) \) are the respective Auger–Meitner and photoionisation population loss channels for state \( n \).

The differential EOM's to the TDSE in Equations (4), (5) and (6), were solved numerically using the 4th-order Runge–Kutta algorithm (RK4). A small time step of 5.0 \( \times \) 10\(^{-6} \) fs was used to minimise the population loss due to the RK4 numerical error. Initial conditions of \( \lim_{t \to -\infty} c_n(t) = 1 \), \( \lim_{t \to -\infty} c_{n-1}(t) = 0 \) and \( \lim_{t \to -\infty} c_d = 0 \) were set, with the peak maximum of the pulse at \( t = 1 \) fs. The orbital energies and transition dipole moments used in the TDSE simulations were taken from the XANES spectra RASPT2 calculations discussed in the previous section. To account for the finite bandwidth of the incident X-ray pulse, \( \sigma_x \), we include bandwidth averaging to the quantum state population. In this work, 100 photon energies, \( \omega_j \) in the range of

\[ \omega_j = \omega_x - 3\sigma_x, ..., \omega_x, ..., \omega_x + 3\sigma_x. \]

were applied to a weighting factor,

\[ g(\omega_j, \omega_x) = \frac{\exp\left(\frac{-(\omega_j-\omega_x)^2}{\sigma_x^2}\right)}{\sqrt{2\pi \sigma_x^2}} \]

used on the populations calculated for each sampled photon energy. The TDSE was simulated in the open-source TARANTULA code [73].

### 2.3. Auger–Meitner spectra

For the \( K^{-1}V^1 \) Auger–Meitner decay calculations, initial states were calculated using RASSCF(18,1,1;1,8,2) with either the \( N_11s \) or \( N_c1s \) placed in RAS1. The two unoccupied \( \pi^* \) orbitals were placed in RAS3. For the final cationic doublet states of the \( K^{-1}V^1 \) decay, core-orbitals were removed from RAS1 and 136 states were included in the SA-RASSCF(15,1;0,8,2) and Auger–Meitner spectra calculations. For the \( K^{-1}K^{-1}V^2 \) states, the 4 initial states of the 1st decay step were calculated by SA-RASSCF(20,2,2;2,8,2) and both the \( N_11s \) and \( N_c1s \) orbitals in RAS1 with the doubly excited state (DEXS) scheme applied [64]. For the \( [K^{-1}V^1]^+ \) final cation doublet states of the first step, 317 doublet states were considered using the active space from the \( K^{-1}V^1 \) initial state calculation with one less electron (SA-RASSCF(17,1,1;1,8,2)). For the second \( K^{-1}K^{-1}V^2 \) Auger–Meitner decay step, the initial states are the final states of the first step and 1627 dication singlet final states were used in the SA-RASSCF(14,1,2;0,8,2) calculation. For simplicity only the singlet dicaticonic final states were considered, as triplet states are expected to have a smaller contribution to the Auger–Meitner intensity [74]. The energies of all the states were improved by single state RASPT2 calculations with an imaginary shift of 0.4 a.u.. The configuration interaction (CI) vectors and Mulliken populations used in the determination of the rates discussed below were taken from the RASSCF wavefunctions.

Recent advances in the calculation of molecular Auger–Meitner decay explicitly including the continuum electron wavefunction [75,76] will become too computationally expensive for the two-step decay cascade considered in this work. Therefore we adopt an approximate approach which avoids calculation of the continuum wavefunction, by approximating the calculation of the Auger–Meitner transition amplitudes with the Mulliken populations of the valence-hole orbitals, on the wavefunction of the core-hole initial state [74,77,78]. The approach is also applied to the prediction of the \( K^{-1}K^{-1}V^2 \) TEO spectra and is briefly outlined here. By assuming a two-step process, where the initial excitation is decoupled from the Auger–Meitner decay, the intensities of the latter can be described by Wentzel’s formula,

\[ I_{fi} = 2\pi |\langle \psi_f | \hat{H} - E | \psi_i \rangle|^2 \equiv 2\pi |t|^2, \]

\( \psi_i \) and \( \psi_f \) are the initial and final state wave functions, \( \hat{H} \) is theHamiltonian, \( E \) is the energy of the initial state, and \( t \) is the amplitude of the Auger–Meitner transition. Let’s consider the decay of a core hole orbital in the initial state \( c \) that produces two valence holes in molecular orbital \( v \) and \( w \) and an electron in continuum wavefunction \( k \). \( t \) can be estimated by the Mulliken populations of \( v \) and \( w \) on the atom containing \( c \) in the initial state, noted by \( P_v(C) \) and \( P_w(C) \), respectively.

This approach is discussed in details for both resonant and non-resonant Auger–Meitner processes elsewhere [74,78,79]. The expression used in this work for multi-reference wavefunctions are shown below,

\[ t_{vw} = (cv|kw) \approx KP_v(C) \quad (v = w) \]
\[2t_{vw} = \sqrt{\frac{1}{2}} \{ (cv|kw) + (cw|kv) \} \]
\[\approx \sqrt{\frac{1}{2}} K[P_v(C) + P_w(C)] \quad (v \neq w). \] (20)

where \((cv|kw)\) are the usual two electron repulsion integrals \([78]\). These formulas apply to the production of the doublet states in the \(K^{-1}V^1\) and first step of the \(K^{-1}K^{-1}V^2\) state decay. They can also be applied to the second step of the \(K^{-1}K^{-1}V^2\) decay yielding singlet dicationic states. By assuming \(K\) in Equations (19) and (20) to be constant for all pairs of \(v\) and \(w\) \([74,78]\), the Auger–Meitner intensity between multiconfigurational initial and final state wavefunctions can be approximated by the expression below,

\[I_n \propto 2\pi |t_n|^2 = 2\pi \sum_{v \leq w} C_{j,v,w} t_{vw}^2. \] (21)

The \(C_{j,v,w}\) coefficients are determined by the products of the CI expansion coefficients between the initial and final states corresponding to the creation of holes in MOs \(v\) and \(w\). This simplified approach is readily applicable to estimate multistep Auger–Meitner decay cascades in molecules and has been previously applied to double core ionised decay cascades \([74]\). In this work we apply it to the two-step decay cascade of the double core excited states, where the intensities of the second step are normalised with respect to the corresponding first step. For example, starting from the \(K^{-1}K^{-1}V^2_M\) state, the intensity of the decay from the corresponding SCH cation states (\(\langle K^{-1}V^2_{p,M} \rangle\)) to the set of all possible valence dication states (\(\langle K^2V^2 \rangle_{Q}^{++P}\)) is labelled as (\(I([K^{-1}V^2]_{p,M}^{+M}, [K^2V^2]_{Q}^{++P})\)) and normalised via,

\[\sum_Q I([K^{-1}V^2]_{p,M}^{+M}, [K^2V^2]_{Q}^{++P}) = I(K^{-1}K^{-1}V^2_{M}, [K^{-1}V^2]_{p,M}^{+M}). \] (22)

The TEOE spectra intensity is also calculated using this approach, however the sum of the Mulliken populations on both atomic sites is used. All Auger–Meitner spectra were computed in the open-source AUGER-POP code \([80]\).

### 2.4. Core-electron binding energy chemical shifts

Accurately and efficiently attaining CEBE shifts has advanced rapidly in recent years due to the work of Besley and others \([81–89]\). In this work, attaining O and N 1s chemical shifts for valence, \(K^{-1}V^1\) and \(K^{-1}K^{-1}V^2\) states within a consistent level of theory is non-trivial as single, double and triple core-hole states are required. Fortunately OpenMolcas RASSCF calculations provide a flexible approach to multiple core-hole states as HEXS and DEXS can be applied to either RAS1, RAS3 or both in combination with restricting the maximum number of electrons in RAS3. The \(N_t, N_c\) and O 1s binding energies of the ground, valence cation and dication states were calculated by \(\Delta\text{RASPT2}(18,1,2;1,11,1,0), \Delta\text{RASPT2}(17,1,2;1,11,0)\) and \(\Delta\text{RASPT2}(16,1,2;1,11,0)\), respectively, where the core orbital under question was placed into RAS1 and HEXS used to calculate core-hole with \(N_{\text{dec}} - 1\) active electrons in the same active space.

The \(N_{t/c}\) ss-DCH binding energies of neutral and cation \(N_{t/c}\) \(K^{-1}V^1\) states were calculated by \(\Delta\text{RASPT2}(20,2,2;1,11,1)\) and \(\Delta\text{RASPT2}(19,2,2;1,11,1)\), respectively. The initial state was generated by using HEXS on the desired \(N_{t/c}\) core hole in RAS1 (the other \(N_{t/c}\) was in RAS3). The ss-DCH binding energy was calculated by applying DEXS to RAS1 of the N-1 wavefunction. To calculate ts-DCH binding energies, HEXS was applied to both the RAS1 and RAS3 subspaces. This same approach was applied to the O1s ts-DCH binding energies.

In order to calculate the binding energies of the \(N_{t/c}\) \(K^{-1}K^{-1}V^2\) state, a triple core-hole final state is required. The initial state was calculated by \(\text{RASPT2}(20,2,2;1,11,1)\) where HEXS is applied to both RAS1 and RAS3 each containing either the \(N_t\) or \(N_c\) orbitals. The binding energy is calculated by applying both DEXS to RAS1 and reducing the maximum number of electrons in RAS3 to 1. This yields a \(\text{RASPT2}(19,2,1;1,11,1)\) calculation. To calculate the O1s binding energy, the initial state was prepared by a \(\text{RASPT2}(22,2,2;1,11,1)\) calculation with both \(N_t\) and \(N_c\) orbitals in RAS1 with DEXS applied. The O1s orbital was in RAS3 and the maximum number of electrons in RAS3 was also changed from 2 to 1. Dyson orbital norms are also provided in Table 4 of Section 3.4, these are calculated by the RASSI program in OpenMolcas. For the \(K^{-1}K^{-1}V^2\) state binding energies, different active spaces are used for the N and N-1 wavefunctions, which is not applicable to the RASSI method, therefore the wooverlap code \([90]\) was used to calculate these Dyson norms.

### 3. Results and discussion

The present work studies the formation of \(K^{-1}K^{-1}V^2\) states during resonant interaction with an intense few-to-sub-femtosecond X-ray pulse. \(N_2O\) represents a model system containing two distinct atomic centres of the same element (N) with a significant chemical shift of about 4 eV. In following we present the calculated RASPT2 energetics of the two-step XANES process in Section 3.1, TDSE simulations of the production of the
following core-excitation at the other nitrogen site to the same $\pi^*$ orbital, compared to the ground state values. This can be understood as the result of the stabilisation (lower energy) of valence shells due to a higher charged core, while the CEBE remains essentially the same in the still neutral molecule (except for the second electron at the same site of the first core-excitation). This effect can be quantified by looking at the RASSCF canonical orbital energies shifts, between the ground and $K^{-1}V^1$ states. In the $N_tK^{-1}V^1$ state, the $N_t$ 1s orbital energy shifts by $+0.37$ eV and the $\pi^*$ shifts by $-5.46$ eV and in the $N_c$ $K^{-1}V^1$ state, the $N_c$ 1s orbital energy shifts by $-0.87$ eV and the $\pi^*$ shifts by $-6.74$ eV. This effect is demonstrated by the spectra and energy level diagrams (not to scale) in Figure 2(a,b), respectively.

To enable sequential core-excitations $N_2O$, Figure 2(a,b) show that a pulse centred at 401 eV with a bandwidth of around 2 eV should selectivity excite the $N_t$ ($\approx 401$ eV) then $N_t$ ($\approx 402$ eV) K-shell electrons to the $\pi^*$. The alternative double core-excitation scheme ($N_t$ then $N_t$) requires a first photon at $\approx 405$ eV and a second photon at $\approx 398$ eV and is much less probable.

3.2. Electronic population transfer dynamics

We examine how the pulse conditions proposed by the previous subsection can produce $K^{-1}K^{-1}V^2$ states via a sequential core-excitation mechanism using TDSE simulations described in Section 2.2. First we discuss the time and intensity scan of the incident pulse to determine optimal conditions for producing a high yield of the $K^{-1}K^{-1}V^2$ states. Figure 3 (a) shows the total $K^{-1}K^{-1}V^2$ population at 6 fs with a pulse centred at 1 fs with durations of 1.0, 1.5, 2.0 and 2.5 fs. For each pulse duration, we sampled across 28 intensity points between $1 \times 10^{16}$ and $1 \times 10^{19}$ W/cm$^2$. The sampled high-intensity range shows a sensitivity to the total $K^{-1}K^{-1}V^2$ population, as seen by the multiple peaks in the population across the intensity range. This is due to the complex interplay of Rabi-cycling and pulse duration as the results are not averaged over the focal volume [53]. The maximum $K^{-1}K^{-1}V^2$ population in Figure 3(a) is approximately 10% of the total population and is generated by a 1.5 fs pulse with $4 \times 10^{17}$ W/cm$^2$ intensity. This is close to the intensity of the two-photon cross-section saturation fluence of the ground to $N_tK^{-1}V^1$ and $N_tK^{-1}V^1$ to $^1\Delta K^{-1}K^{-1}V^2$ excitation’s at $5.11 \times 10^{17}$ W/cm$^2$. The results show that the optimal conditions for the $K^{-1}K^{-1}V^2$ production are for pulse duration’s between 1 and 2 fs and intensities between $1 \times 10^{17}$ and $1 \times 10^{18}$ W/cm$^2$. At higher intensities, the $K^{-1}K^{-1}V^2$ population will be reduced due to the valence

Table 1. RASPT2 calculated excitation energies for producing $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states through sequential core-excitations. $K^{-1}K^{-1}V^2$ states using an ultrashort intense pulses in Section 3.2. Sections 3.3 and 3.4 look at the characteristic Auger–Meitner decay spectra and core electron binding energies of the $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states, respectively.

| Transition | $\Delta$RASPT2 | Experiment |
|------------|----------------|------------|
| $K^{-1}V^1N_t$ | 400.74 | 401.13 |
| $K^{-1}K^{-1}V^2 : N_t \rightarrow N_t^1 \Delta$ | 402.17 | - |
| $K^{-1}K^{-1}V^2 : N_t \rightarrow N_t^2 \Sigma^-$ | 402.62 | - |
| $K^{-1}K^{-1}V^2 : N_t \rightarrow N_t^2 \Sigma^+$ | 403.68 | - |

Note: Experimental $K^{-1}V^1$ taken values from ref [41]. Scheme 1 and 2 correspond to the top and bottom panels in Figure 2(a), respectively.
photoionisation. On the other hand, lower intensities will not sufficiently drive the two-photon process.

For pulse durations longer than 2.5 fs, the production of $K^{-1}K^{-1}V^2$ will compete with the decay of intermediate $K^{-1}V^1$ states. Furthermore, a sufficiently large bandwidth is required to first excite the $N_1$ $K^{-1}V^1$ state at 401 eV then the $K^{-1}K^{-1}V^2$ states at 402-403 eV. In particular, pulses with a duration of the 1-2 fs will provide a bandwidth of approximately 1-2 eV to drive this two-photon transition. Figure 3(a) shows the effect of the pulse bandwidth for a duration of 1.5 fs, sampled across a 1.2 eV FWHM bandwidth with a central photon energy of 401 eV. The bandwidth causes a small drop in the population transfer to the $K^{-1}K^{-1}V^2$ states, which may result from the increased detuning from resonance, but maintains the same overall the trend and sensitivity with respect to the intensity between $1 \times 10^{17}$ and $1 \times 10^{18}$ W/cm$^2$.

Figure 3(b–d) show the population transfer dynamics for producing $K^{-1}K^{-1}V^2$ states under an intensity of $4 \times 10^{17}$ W/cm$^2$ and 1.5 fs pulse duration. The simulation includes the bandwidth averaging applied in (a) but no focal volume averaging. The results are averaged over linear $x$ and $y$ pulse polarisations and the molecular bond lies in the $z$ axis. Figure 3(b) shows the time-evolution of the ground and $K^{-1}V^1$ state populations, Figure 3(c) shows the $K^{-1}K^{-1}V^2$ state evolution and Figure 3(d) shows the total Auger–Meitner and photoionisation population losses. The decay widths of the $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states are 0.11 and 0.22 eV, respectively, this can be observed by the steeper gradient of the $K^{-1}K^{-1}V^2$ state population decline. The $K^{-1}K^{-1}V^2$ decay width is based on the assumption that the these states will decay twice as fast. Despite this, the yield of $K^{-1}K^{-1}V^2$ states is comparable to the $K^{-1}V^1$ states after the Rabi-cycling period. Figure 3(d) shows that Auger–Meitner decay is the dominating loss mechanism in which the $K^{-1}K^{-1}V^2$ states contribute to more. The first step of the $K^{-1}K^{-1}V^2$ decay leads to SCH cation states ($[K^{-1}V^1]^+$), these are also produced by the valence photoionisation of the $K^{-1}V^1$ states, which is shown to be a smaller population loss channel in Figure 3(d). In Section 3.4 we show that these states have ss-DCH ionisation values that are resolvable within 100’s attosecond TR-XPS probe bandwidths, however this will not provide a direct observation of the $K^{-1}K^{-1}V^2$ states due to the competing photoionisation of the $K^{-1}V^1$ intermediates.

Figure 3(c) shows the production of a superposition of the $K^{-1}K^{-1}V^2$ states including the $1\Sigma^-$ state and the $1\Delta_y$, which is the sum of population of $1\Delta_x$ and $1\Delta_y$ states. The $1\Sigma^-$ states are not produced as a result of the transition dipole phase effect [91]. Since the transition dipole moment phases are not uniquely defined, this leads to the difference in the $1\Delta_x$ and $1\Delta_y$ populations despite the results being averaged over $x$ and $y$ linearly polarised pulses. During the lifetime of the $K^{-1}K^{-1}V^2$ state,
Figure 3. TDSE simulations producing $K^{-1}K^{-1}V^2$ states through sequential core-excitation’s in N$_2$O at the nitrogen K-edge to the doubly degenerate $\pi^*$ orbital. The simulations are based on matrix elements from on MS-RASPT2 wavefunctions. In all subplots the pulse is centred at 1.0 fs and the central photon energy is 401 eV. (a) The total $K^{-1}K^{-1}V^2$ state population at 6 fs as a function of the pulse duration and intensity. Bandwidth averaging (BW Avg.) is applied to 1.5 fs. In (b)–(d) the pulse duration and intensity are 1.5 fs and $4 \times 10^{17}$ W/cm$^2$ and the results are averaged over a 1.2 eV bandwidth. (b) Time evolution of the ground and $K^{-1}V^1$ state populations. (c) Time evolution of the $K^{-1}K^{-1}V^2$ state populations. (d) Time evolution of the population loss channels.

There will be a charge oscillation between the electron configurations of the doubly occupied $\pi^*$ configurations. It was previously demonstrated that a circularly polarised IR streaking field can detect the charge oscillation of a $K^{-1}V^1$ core excited superposition in NO molecules [8]. This streaking detection technique may be applicable to probe the charge oscillation in $K^{-1}K^{-1}V^2$ of N$_2$O.

### 3.3. Auger–Meitner spectra

This subsection investigates the possibility of observing $K^{-1}K^{-1}V^2$ states through Auger–Meitner spectroscopy. Following resonant excitation, the decay of N$_2$O can produce electrons with different kinetic energies depending on the excitation site [41,42]. Figure 4 presents Auger–Meitner decay spectra, where the electron energies were determined at the RASPT2 level of theory and intensities were approximated by the CI coefficients and Mulliken populations from the RASSCF wavefunctions, as discussed in Section 2.3. Due to the large number of possible final states for the $K^{-1}K^{-1}V^2$ decay, we do not consider the shake-off effects in this work, however, we note that shakeup states, which can play an role in DCH spectroscopy [92], will be considered in future work. To check the validity of our approach, which omits the continuum electron wavefunction, we compare our simulated $K^{-1}V^1$ spectra to experiment in Figure 4 and show that they are in qualitative agreement. This is supported by the state analysis of the calculated spectrum which forms a one-to-one mapping with the experimental peaks. Whilst the solid black lines in Figure 4(c,d) correspond to the calculated stick spectrum of the $K^{-1}V^1$ states, the vertical red lines spanning across all 4 panels correspond to transitions with the orbital assignments given in Table 2. Dot-dashed lines show participator decay and dotted lines show spectator decay. A clear signature of the calculated and experimental $K^{-1}V^1$ decay spectra in Figure 4 comes from participator channels. However the calculations indicate this only applies to participator peaks involving the $2\pi$ and $1\pi$ orbitals, as the
Figure 4. Comparison of the RASPT2 Auger–Meitner decay spectra against experiment for the $K^{-1}V^1$ states. Left (a) and (c)) and right (b) and (d)) columns show Auger–Meitner processes filling the $N_c$ and $N_t$ 1s core holes, respectively, where (a) and (b) show the experimental [41] and (c) and (d) show the calculated spectra. The calculated results also show the spectra for the first step in the $K^{-1}K^{-1}V^2$ state decay. An analysis on some of the states contributing to peaks in the spectra is based on the calculated results and shown by the vertical lines. Dot-dashed: participator channels, dotted: spectator channels. Assignments to molecular orbitals are given in Table 2. The red dashed vertical lines indicate the kinetic energies of the double participator transition unique to $K^{-1}K^{-1}V^2$ states. 1.7 eV and 3.4 eV FWHM Gaussian broadening is applied to the $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ spectra, respectively.

Table 2. RASPT2 calculated kinetic energies (KE) for Auger–Meitner decay transitions of the $K^{-1}V^1 : N_c$ and $K^{-1}V^1 : N_t$ states highlighted by the vertical lines in Figure 4 and the associated binding energies for the final states with respect to the ground state.

| Channel | $KE_{K^{-1}V^1 : N_c}$ | $KE_{K^{-1}V^1 : N_t}$ | BE |
|---------|-------------------------|-------------------------|----|
| Double Participator | $\pi^* - \pi^*$ | 394.5 | 390.5 | – |
| Participator | $\pi^* - 2\pi$ | 391.1 (392.0) | 387.1 (388.3) | 13.6 |
| $\pi^* - 7\sigma$ | 388.4 (388.5) | 384.4 (384.8) | 16.3 |
| $\pi^* - 1\pi$ | 386.1 (386.7) | 382.1 (383.0) | 18.5 |
| $\pi^* - 6\sigma$ | 383.3 (384.8) | 379.2 (381.1) | 21.4 |
| Spectator | $2\pi - 2\pi$ | 385.0 | 381.0 | 19.6 |
| $2\pi - 1\pi$ | 381.1 | 377.1 | 23.6 |
| $2\pi - 7\sigma$ | 380.2 | 376.2 | 24.5 |
| $2\pi - 6\sigma$ | 376.3 | 372.3 | 28.3 |
| $7\pi - 6\sigma$ | 376.1 | 372.1 | 28.6 |
| $7\pi - 1\pi$ | 374.1 | 370.1 | 30.6 |
| $1\pi - 1\pi$ | 373.5 | 369.5 | 31.2 |

Notes: The double participator energies for the $K^{-1}K^{-1}V^2$ state decay (dashed vertical lines Figure 4) are also shown. The participator values (dot-dashed vertical lines in Figure 4) are compared against experimental values from ref [41], which are shown in parentheses.

7$\sigma$ and 6$\sigma$ transitions lie between the peaks in the theory and experiment, which can be seen at 388.4 383.3 eV for $K^{-1}V^1 : N_c$.

Unique to the $K^{-1}K^{-1}V^2$ states is the double-participator decay shown by the red vertical dashed line. Its signature is having a higher kinetic energy than other pathways, as shown by the solid red lines in Figure 4 at 394.5 and 390.5 eV for $N_c$ and $N_t$, respectively. The highest energy participator peaks for the $K^{-1}V^1$ decay are at 391.1 and 387.1 eV, respectively. However, our calculations indicate that the signal from the double participator peak is small and the dominant signal comes from other pathways. This might be an underestimation from the population analysis method as the $2\pi$ participator peak for the $K^{-1}V^1 : N_t$ state is much lower than the experimental value and previous theoretical calculations using the one-centre approximation [43]. This underestimation by the population analysis can be partly attributed to the relatively low electron population in the $\pi^*$ orbital with respect to the other valence occupied orbitals, which is shown in Table 3. Future calculations with higher levels of theory [76] will further verify this finding.

The qualitative agreement shown in Figure 4 enables our calculations to provide a reasonable estimation of the two-step $K^{-1}K^{-1}V^2$ decay cascade. Figure 5(a,b) show the decay processes where the $N_c$ and $N_t$ core holes
are filled, respectively. The first step involves the 4 neutral singlet $K^{-1}K^{-1}V^1$ DCH states each decaying to 316 doublet cationic $[K^{-1}V^1]^+$ single core-hole (SCH) states. These states will then undergo a second decay step to either singlet or triplet dicationic valence states. In our calculation we have included 1627 potential final singlet dicaticonomic states and exclude the triplet states to reduce the cost of the calculation, which are expected to have a smaller contribution to the Auger–Meitner intensity [74]. The $K^{-1}V^1$ decay has two initial states as either the $\pi_0^*$ or $\pi_1^*$ orbital can be singly occupied and there are 4 initial states for the first step $K^{-1}K^{-1}V^2$ decay, therefore both steps of $K^{-1}K^{-1}V^2$ decay have been weighted by a factor of 0.5.

By using a central photon energy of 401 eV, there is an increased selectivity for starting the sequential core-excitations via a core-hole in $N_2$, according to the energetics found in Figure 2 and Table 1. The shape of the Auger–Meitner spectrum should therefore be very sensitive to the intensity of the X-ray pulse as the additional channels involving $N_c$ core hole decay will only appear when the second core-excitation occurs to form the $K^{-1}K^{-1}V^2$ state superposition. In Figure 5(c), we predict the change in spectral shape with respect to the intensity. Here, the Auger–Meitner spectra from an unfocused (low-intensity) beam, is compared to the case of a focused (high-intensity) beam, which are determined by combining the spectra in Figure 5(a,b), where the sum of each contributing spectra are normalised to the corresponding Auger–Meitner populations extracted from the TDSE simulation in Figure 3(b,c,d) at 10 fs, which provides a good approximation to the total Auger–Meitner yield detected. Intensities of $1 \times 10^{16}$ W/cm$^2$ and $4 \times 10^{17}$ W/cm$^2$ (representing linear and non-linear interaction regimes) were used for the unfocused and focused lineshapes, respectively.

Figure 5(a,b) illustrates that the second step of the $K^{-1}K^{-1}V^2$ decay results in the creation of a broad background signal, which is not resolvable, but should not hinder observation of the first steps due to the relatively low intensity which is dependent on the intensities of the first step. Additionally, since the Auger–Meitner spectra often fall on top of valence photoemission lines, it is important to further analyse the resonant features either from angular distribution of the emitted electrons [39] or by scanning the incident photon energy over a small range. Throughout this work we have considered a fixed nuclear geometry and expect relatively little nuclear motion during the core-hole lifetimes. However it has been observed experimentally that Auger–Meitner spectroscopy can be sensitive to nuclear motion within the lifetime of the core-excited state [93] and previous studies have shown that the $K^{-1}V^1$ states in $N_2O$ adopt a bent geometry [33].

Furthermore, we examine a TEOE process (see the schematic in Figure 1(d)) that involves the simultaneous collapse of two electrons to fill both core vacancies in the $K^{-1}K^{-1}V^2$ states and the emission of a single electron to form valence cation states. Our calculated spectrum in Figure 5(d) shows that TEOE results in a large energy transfer to the single continuum electron, yielding significantly higher kinetic energies (700–800 eV) compared to the energies of other Auger–Meitner electrons, if this energy range is experimentally detectable then the TEOE electrons will provide a clear signature of the $K^{-1}K^{-1}V^2$ state observation.

### 3.4. Core-electron binding energy chemical shifts

While the deexcitation spectrum should provide a clear signature of the production of neutral excited ts-DCH states, it is unlikely to be sensitive to the dynamics of these states after their formation. To further establish their existence and gain a first glance of the complex decay states, we predict chemical shift values of these excited states which can be measured with TR-XPS. In practise, an attosecond pulse would be necessary to resolve the decay steps with lifetimes between 3 and 5 fs. Therefore, chemical shifts must approximately exceed 5 eV to be resolvable within 100’s attosecond pulse bandwidths, even if techniques such as spectral ghost imaging (spook spectroscopy) present some promising avenues [94] for high energy resolution with attosecond x-rays. Table 4 shows the predictions for the chemical shifts at the three atomic sites between the neutral ground, $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states and the associated intermediate and final states of the Auger–Meitner decay, calculated by $\Delta$RASPT2 as described in Section 2.4. In cases where the removal of an electron yields multiple spin states, only the low-spin cases are presented as the spin multiplicity has a minor effect on the chemical shifts. Also, the values in Table 4 represent lower bounds to the chemical shifts as they only consider the ground state of each particular low spin species in the core-excitation and Auger–Meitner decay.

| MO      | $K^{-1}V^1$ | $K^{-1}V^1$ | $K^{-1}V^1$ | $K^{-1}V^1$ |
|---------|-------------|-------------|-------------|-------------|
| $\pi_0^*$ | 0.202       | 0.204       | 0.395       | 0.324       |
| $2\sigma$ | 0.262       | 1.126       | 0.027       | 1.098       |
| $7\sigma$ | 0.237       | 1.452       | 0.434       | 1.397       |
| $1\pi$   | 1.355       | 0.565       | 1.156       | 0.303       |
| $6\sigma$ | 0.423       | 0.215       | 0.445       | 0.225       |
| $5\sigma$ | 0.582       | 0.829       | 0.731       | 0.779       |
| $4\sigma$ | 0.560       | 0.267       | 0.634       | 0.373       |

Table 3. RASSCF Mulliken populations of the valence molecular orbitals (MO’s) on the core-hole containing atom in the $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ states.
Figure 5. Comparison of the $K^{-1}V^1$ against the $K^{-1}K^{-1}V^2$ first and second ($K^{-1}K^{-1}V^2_{1s}$ and $K^{-1}K^{-1}V^2_{2nd}$) steps of the Auger–Meitner decay processes calculated with RASSCF/PT2 wavefunctions and the Mulliken population analysis method to estimate the intensity. (a) and (b) Auger–Meitner processes filling the $N_c$ and $N_t$ 1s core holes, respectively, a 0.5 weighting factor was applied to the $K^{-1}K^{-1}V^2_{1s}$ and $K^{-1}K^{-1}V^2_{2nd}$ spectra as there are 4 initial $K^{-1}K^{-1}V^2$ states as opposed to the two initial states for the $K^{-1}V^1$ decay. (c) Estimated change in Auger–Meitner line-shape between an unfocused and focused beam. Both line shapes contain all the spectra in (a) and (b) and the sum of the each contributing spectra are normalised to the corresponding Auger–Meitner populations extracted from the TDSE simulation in Figure 3(b,c,d) at 10 fs (close to the maximum Auger–Meitner yield). Intensities of $1 \times 10^{16}$W/cm$^2$ and $4 \times 10^{17}$W/cm$^2$ (representing linear and non-linear interaction regimes) were used for the unfocused and focused line-shapes, respectively. (d) TEOE spectra (Figure 1(d)), as both core-holes are filled simultaneously, the sum of the Mulliken populations on both the $N_c$ and $N_t$ atoms are used. 1.7 and 3.4 eV FWHM Gaussian broadening was applied to the $K^{-1}V^1$ and $K^{-1}K^{-1}V^2$ (incl. TEOE) spectra, respectively.

Between the neutrally charged species, less than 1 eV chemical shifts in the O K-edge binding energies were predicted around 541 eV, which likely prevents them from being resolved within the hundreds of attoseconds pulse bandwidths currently available at XFEL light sources. Furthermore, there is an overlap between the valence cation final states ($[K^2V^1]^+$) from the $K^{-1}V^1$ Auger–Meitner decay and the single-core-hole cation intermediate ($[K^1V^2]^+$) states from the first step in the $K^{-1}K^{-1}V^2$ state decay of about 2 eV around 553 eV. Unresolvable chemical shifts within hundreds of attoseconds pulse bandwidths also occur for the single, two-site (ts) double and single-site double CEBE’s for the neutral species at the N K-edge. On the other
Table 4. RASPT2 calculated CEBE values in eV for the products of the sequential core excitation and subsequent Auger–Meitner decay processes.

| Species | O-1s | Nt-1s SCH | Nc-1s SCH | Nt-1s ss-DCH | Nt-1s ts-DCH | Nc-1s ss-DCH | Nc-1s ts-DCH |
|---------|------|-----------|-----------|-------------|-------------|-------------|-------------|
| Neutral |      |           |           |             |             |             |             |
| G       | 541.41 (0.64) | 408.25 (0.65) | 412.35 (0.70) | –            | –           | –           | –           |
| K−1V1Nt | 541.30 (0.01) | –            | –           | 475.80 (0.00)| –           | –           | 411.52 (0.32)|
| K−1V1Nc | 540.58 (0.00) | –            | –           | –            | 407.77 (0.00)| 479.99 (0.00)| –           |
| K−1K−1V2(avg.) | 541.37 (0.22) | –            | –           | 476.11 (0.16)| –           | 480.15 (0.29)| –           |
| Cation  |      |           |           |             |             |             |             |
| [K−1V1]+ | 554.62 (0.00) | 420.59 (0.30)| 422.34 (0.36) | –            | –           | –           | –           |
| [K−1V1]+; Nt | 553.29 (0.31) | –            | –           | 487.75 (0.61)| –           | –           | 424.51 (0.34)|
| [K−1V1]+; Nc | 552.45 (0.28) | –            | –           | 420.39 (0.31)| 492.01 (0.69)| –           | –           |
| Dication |      |           |           |             |             |             |             |
| [K−1V1]++ | 566.12 (0.00) | 433.26 (0.33)* | 433.04 (0.45)* | –           | –           | –           | –           |

* triplet cation used

Notes: The values represent TR-XPS values at the O K-edge and N K-edge. Due to the nature of the K−1V1 and K−1K−1V2 states the N K-edge values consider SCH and DCH states. The DCH state probes can either be single-site (ss) or two-site (ts). Only the CEBE’s of the lowest spin ground state configurations are shown for simplicity. Dyson norms of the transitions are shown in parentheses.

hand, our calculations indicate that probing the nitrogen sites through the ionisation of half-empty orbitals is more promising. Specifically, the binding energy of a ss-DCH at either the central or terminal nitrogen site is significantly different in the [K−1V1]+ states produced following the first decay step of the K−1K−1V2 states when compared with the K−1V1 or K−1K−1V2 neutral molecules. The 10 to 20 eV shift is easily resolvable, even with the large bandwidth of a 100’s of attosecond probe pulse. Furthermore, the Dyson orbital norms of these transitions, shown in the parentheses of Table 4, are relatively large compared to other transitions and this provides an estimation of the strength of the TR-XPS measurement within the sudden approximation. These transient states will have a short (≈ 3 fs) lifetime but the TDSE simulations presented in Figure 3 show that the population produced by the K−1K−1V2 decay is significantly higher than the population produced by valence photoionisation of the K−1V1 states by the pulse. Furthermore, by extending the delay between the pump and probe pulses, one could additionally probe the dissociation and fragmentation of the di-cationic states produced from Auger–Meitner decay.

4. Conclusions

We have simulated the production of K−1K−1V2 states by selective sequential double core excitations at the N K-edge of N2O to the doubly degenerate π* orbitals and have shown a number of possible avenues for detecting these states by exploiting the contemporary capabilities of XFEL facilities. The simulations are based on RASSCF/PT2 multiconfigurational quantum chemical calculations, which offer accurate prediction of multiple hole states in samll gas-phase molecules. The XANES spectra of the sequential double core-excitation was predicted using RASPT2 calculations, showing excellent agreement to experiment for the K−1V1 excitation energy and providing a reliable estimate for the energetics of the K−1K−1V2 state production. We found that the second core-excitation energy from the adjacent, unexcited nitrogen atom is approximately 2 eV lower than its original ground state excitation energy. As a result, a 1-fs pulse centred at 401 eV with a 2-eV bandwidth would enable the production of neutral double core-excited states preferably via a sequence of N1s excitation followed by N2 1s excitation and suppress the opposite sequence. This is supported by the TDSE simulations that demonstrate a femtosecond pulse can produce a high yield of K−1K−1V2 states involving a superposition of 1Δ and 1Σ states.

We show that by examining the pulse intensity dependence of the site-selective Auger–Meitner decay spectra, the change of spectra lineshape can reveal a signature of the K−1K−1V2 states. Furthermore, the high kinetic energies (≈ 700–800 eV) of the TEOE electrons will provide an additional direct signature of the K−1K−1V2 states. The RASPT2 calculations show that most of the core ionisation energies of core-excited states, decay intermediates and final states overlap within hundreds of attosecond pulse bandwidths (≈ 5 eV) and therefore not resolvable. The exception is the ss-DCH ionisation energies of the single core-excited cation ([K−1V1]+) states, in which the CEBE differ by more than 5 eV with respect to other states. Also, our TDSE simulations demonstrate that Auger–Meitner decay of the K−1K−1V2 states is the dominant pathway for producing [K−1V1]+ states in comparison to the pathway of the valence photoionisation of the K−1V1 states.

We have produced a clear theoretical demonstration of the potential to produce and detect these states in ultrafast, intense XFEL experiments. Experimental validation would provide important insights into the presence of
sequential resonant interactions for future experiments inducing and tracking molecular dynamics with such pulse conditions.

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