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N1s and O1s double ionization of the NO and N₂O molecules

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Single-site N1s and O1s double core ionisation of the NO and N₂O molecules has been studied using a magnetic bottle many-electron coincidence time-of-flight spectrometer at photon energies of 1100 eV and 1300 eV. The double core hole energies obtained for NO are 904.8 eV (N1s⁻²) and 1179.4 eV (O1s⁻²). The corresponding energies obtained for N₂O are 896.9 eV (terminal N1s⁻²), 906.5 eV (central N1s⁻²), and 1174.1 eV (O1s⁻²). The ratio between the double and single ionisation energies are in all cases close or equal to 2.20. Large chemical shifts are observed in some cases which suggest that reorganisation of the electrons upon the double ionization is significant. Δ -self-consistent field and complete active space self-consistent field (CASSCF) calculations were performed for both molecules and they are in good agreement with these results. Auger spectra of N₂O, associated with the decay of the terminal and central N1s⁻² as well as with the O1s⁻² dicationic states, were extracted showing the two electrons emitted as a result of filling the double core holes. The spectra, which are interpreted using CASSCF and complete active space configuration interaction calculations, show atomic-like character. The cross section ratio between double and single core hole creation was estimated as 1.6×10^{-3} for nitrogen at 1100 eV and as 1.3×10^{-3} for oxygen at 1300 eV. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4853655>]

I. INTRODUCTION

It is well known from numerous studies that core level energies of molecules depend to some extent on the chemical environment in which their individual atoms are situated. The observed energy level changes, referred to as chemical shifts, form a basis for the ESCA (Electron Spectroscopy for Chemical Analysis) method.^{1,2} In some recent investigations of small molecules, it has been found that the chemical shifts are much larger in doubly than in singly core-ionized systems (see, e.g., Refs. 3–12). Double core hole (DCH) electron spectra may therefore provide improved chemical information, especially concerning close lying states. Double core ionisation spectra also give useful information related to the dynamics involved in the photon-molecule interaction when two (or more) electrons are forced to leave the system. An important consequence that needs special theoretical attention is the reorganisation of the electronic structure in the dication.

In the present work, we have studied the closely related NO and N₂O molecules for which single-site 1s double vacancies have been created on both the N and O atoms. The energies of five different double core hole states have thus been determined from coincidence maps incorporating, in principle, the complete information about the transition dynamics. The four electrons emitted have all been detected in coincidence, two primary photoelectrons and two secondary (Auger) electrons. This method of selection minimizes counting of accidental coincidence events.

The study involves calculation of single and double ionization energies of both molecules as well as effects of relaxation and correlation on these quantities. This knowledge allows isolation of the intrinsic chemical effect caused by differences in the electronegativities between the atoms. The relevant theoretical framework, which is similar to that of Refs. 8 and 10, is briefly presented.

Auger electron spectra associated with the decay of the N_t1s⁻², N_c1s⁻², and O1s⁻² dicationic states, where N_t and N_c refer to the terminal and central nitrogen atoms, respectively, and leading to final states carrying four valence vacancies, are presented for the N₂O molecule. To provide theoretical evidence for the interpretation of these Auger spectra CASSCF (complete active space self-consistent field) and CASCI (complete active space configuration interaction) calculations were performed of the Auger kinetic energies and intensities using a theoretical procedure similar to the one described previously for calculations of the corresponding Auger spectra for CH₄, NH₃, and H₂CO.¹²

II. EXPERIMENTAL DETAILS

The experimental studies were carried out at the soft-X-ray undulator beamline U49/2 PGM2 at the electron storage ring BESSY-II in Berlin using the previously described Time-Of-Flight PhotoElectron-PhotoElectron COincidence (TOF-PEPECO) technique,^{13,14} which is based on the “magnetic

bottle” principle.¹⁵ Briefly, photoionisation occurs in the region where an effusive target gas jet from a hollow needle of 1 mm inner diameter crosses the photon beam in the presence of a strong magnetic field produced by a permanent magnet giving a divergent field of approximately 0.7 T. This field reflects and directs almost all emitted electrons into a 2.2 m long flight tube, where they follow the field lines of a weak (10^{-3} T) solenoid. The Lorentz force causes the emitted electrons to spiral around these magnetic field lines up to the end of the flight tube, where they impinge on a micro-channel plate detector containing three plates in Z-stack configuration. The energy resolution for single electrons can be approximated as one part in 50 of the electron energy.

After discrimination, a multi-channel, multi-hit, time-to-digital converter card in a local computer records the electron signals. The converter also registers timing signals from the storage ring. The storage ring was operated in single bunch mode, which provides 30-ps light pulses at an inter-pulse spacing of 800.5 ns.¹⁶

Each single photon may lead to the ejection of four electrons, two electrons from the primary process that gives rise to two core holes, and two fast electrons from secondary Auger transitions where valence electrons fill the core vacancies. This process mostly leads to final states with four vacancies in the valence electronic shells. To reduce the rate of accidental coincidences to a negligible level, the total electron count rate was limited to about 1 kHz, compared with a light-pulse repetition rate of 1.25 MHz. In the data extraction, double core hole formation, whose cross-section is exceedingly small, was identified by coincident detection of all four expected electrons within the limited arrival time ranges allowed, within conservative margins, by energy conservation. Data were acquired typically for several (3.5–7) hours.

The measured flight times are related to the kinetic energies by the following formula:¹³

$$E = \frac{D^2}{(t - t_0)^2} - E_0. \quad (1)$$

D contains the fixed flight length and E_0 and t_0 are calibration parameters taking into account instrumental offsets in energy and flight-time, respectively. In the present investigation, they were obtained from known energies of the xenon atom, for which spectra were recorded separately. The parameter values for the photon energy 1100 eV were obtained as: $D = 3700 \text{ ns}\sqrt{\text{eV}}$; $E_0 = 0.37 \text{ eV}$; $t_0 = 23.9 \text{ ns}$.

The parameter values for the photon energy 1300 eV were obtained as follows:

$$D = 3700 \text{ ns}\sqrt{\text{eV}}; \quad E_0 = 0.42 \text{ eV}; \quad t_0 = 23.5 \text{ ns}.$$

The sample gases were obtained commercially with a stated purity of > 99%. The purity was checked throughout the studies by recordings of photoelectron spectra.

III. THEORETICAL DETAILS

As in Ref. 10, ionization energies of single and double core-hole states of NO and N₂O molecules were obtained by Δ -self-consistent field (Δ SCF) and complete active space self-consistent field (CASSCF) methods, where ionization en-

ergies are obtained as energy difference of a neutral and core-ionized states calculated separately. In these calculations, the 1s core orbitals were kept frozen, while valence orbitals were optimized for each electronic state.

Following the work of Ref. 12, Auger electron spectra were calculated based on the two-step Auger decay mechanism of a double core hole state: the 1st Auger transition leads from the DCH state to core-valence-valence (CVV) ionized states and the 2nd Auger transition from the CVV to quadruply-ionized valence (VVVV) ionized states. The energies of the DCH, CVV, and VVVV states were obtained by the full-valence CASCI method based on state-averaged CASSCF^{17,18} molecular orbitals (MOs).

The relative Auger intensities were evaluated using Wentzel’s formula¹⁹ with the full-valence CASCI wave functions of the DCH, CVV, and VVVV states. The two-electron integrals involving the Auger electron orbital were approximated using the population of MOs.^{12,20} Further details of the calculation procedure are described in Ref. 12.

The energies and wave functions of the DCH, CVV, and VVVV states were evaluated at the experimental equilibrium geometries of the neutral N₂O molecule.²¹ We used C_{2v} symmetry in the calculations, although the geometries of this molecule correspond to C_{∞v} symmetry. The cc-pVTZ basis set²² was employed. As active orbitals in the CASSCF and CASCI calculations, we used a total of 12 valence orbitals for the N₂O molecule. Important orbitals such as σ , σ^* , π , and π^* are all included in this active orbital space. The 1s core orbitals were kept frozen during all the CASSCF orbital optimizations, using those obtained by the Hartree–Fock calculation on the neutral molecule. For each of the N₂O N₁s^{−1}, N_c1s^{−1}, and O1s^{−1} CVV states, 5000 doublet states were calculated by the CASCI method. The MOs were obtained by the CASSCF calculations with state averaging over the lowest 15, 15, and 16 electronic states for the N₁1s^{−1}, N_c1s^{−1}, and O1s^{−1} CVV states, respectively. For the VVVV states, 8000 singlet states and 8000 triplet states were obtained by the CASCI calculations. The state-averaged CASSCF calculations were performed for the lowest 18 states for the singlet, and 22 states for the triplet spin multiplicities. Auger intensities were calculated for all the possible DCH-CVV transitions, i.e., 5000 transitions for each DCH decay. For the CVV-VVVV Auger transitions, the CVV states having finite DCH-CVV Auger intensities were selected, and then Auger intensities were calculated for all the possible pairs of CVV and VVVV states. For example, in the case of the N₁1s^{−2} DCH decay, Auger intensities were calculated for 4 500 000 transitions in the CVV-VVVV Auger decay, although only a small fraction of these transitions contributes to the total Auger intensity.

The CASSCF calculations were performed using the MOLPRO program package,²³ while the SCATCI module in the UK R-matrix codes²⁴ was used for the CASCI calculations.

IV. RESULTS

Time-of-flight coincidence spectra associated with double core ionization of the NO and N₂O molecules are presented below and show the total coincidence intensity as a

TABLE I. The Δ SCF and CASSCF results for single core-hole ionization energies along with the corresponding experimental data. R refers to the relaxation energy and C to the correlation energy. The theoretical values for NO are taken from Ref. 11. “av” denotes weighted average. S and T represent singlet and triplet, respectively. All values are given in eV.

Mol.	Character	$-\varepsilon_i$	Δ SCF			CASSCF				Expt. (Ref. 25)	
			IE	av	$R(S^{-1})$	IE	av	$RC(S^{-1})$	$C(S^{-1})$	IE	av
N ₂ O	N _t 1s ⁻¹	427.230	410.475		16.755	409.046		18.184	1.429	408.5	
	N _c 1s ⁻¹	431.293	415.151		16.142	412.921		18.372	2.230	412.5	
	O1s ⁻¹	562.226	541.940		20.286	541.977		20.249	-0.037	541.4	
NO	N1s ⁻¹ , S	427.819	413.777	412.741	15.078	411.895	410.867	16.952	1.874	411.5	410.5
	N1s ⁻¹ , T		412.396			410.525				410.1	
	O1s ⁻¹ , S	563.112	543.854	543.485	19.627	544.125	543.757	19.355	-0.272	543.6	543.2
	O1s ⁻¹ , T		543.362			543.634				543.1	

function of the sum of the energies of the two electrons emitted in the primary process initiated by the incident photon. The relevant ionization energies determined from these spectra are given in Tables I (single ionization) and II (double ionization). The single core ionization energies, denoted IE, were taken from Refs. 25 and 26 and are included in the present paper for the purpose of systematic comparison, especially with respect to chemical shifts. In addition, coincidence maps have been obtained, which show the coincidences versus the kinetic energies of the two electrons liberated by the incident photon. An example of such a map is shown along with the corresponding spectrum for the N1s double ionization of NO.

Theoretical values of the IE and DIE (double ionization energy) have been obtained using Δ SCF and CASSCF methods. The relevant energies are provided in Tables I and II along with the experimental IEs and DIEs. In particular, influences of relaxation and correlation are identified and quantified with respect to the individual charge states.

Note that these theoretical values for the N₂O molecule are different from those given in Ref. 10, because the geometry of the N₂O molecule used in Ref. 10 was not optimal, and we recalculated these values using the proper molecular geometry in this work. In these tables, the theoretical values for the orbital energies (ε_i), and the relaxation and correlation energies (RC , R , C) are shown. It is important to know that these values for the N₂O molecule in Ref. 10 also contain errors because of the incorrect geometry. The definition and meaning of these energies are explained as follows:

TABLE II. The Δ SCF and CASSCF results for single-site double core-hole ionization energies (DIEs) and static correlation energies C , in eV. The theoretical values for NO are taken from Ref. 11.

Molecule	Character	Δ SCF	CASSCF		Expt. (this work)
		DIE	DIE	C	
N ₂ O	N _t 1s ⁻²	896.949	895.228	1.721	896.9
	N _c 1s ⁻²	907.518	904.086	3.432	906.5
	O1s ⁻²	1172.354	1172.434	-0.080	1174.1
NO	N1s ⁻²	904.855	902.947	1.908	904.8
	O1s ⁻²	1176.435	1177.704	-1.269	1179.4

The IE for the formation of a single-core vacancy S^{-1} , at a core orbital S , can be represented as

$$IE(S^{-1}) = -\varepsilon_S - RC(S^{-1}), \quad (2)$$

where ε_S is the orbital energy and $RC(S^{-1})$ is a contribution to the IE due to relaxation $R(S^{-1})$ and correlation $C(S^{-1})$ effects. It can be decomposed in the form of a sum as

$$RC(S^{-1}) = R(S^{-1}) + C(S^{-1}). \quad (3)$$

The orbital energy term in the IE expression represents the initial state effect, whereas the RC term describes the final state effect, which represents relaxation of the valence electron density induced by creation of the core-hole. Similarly, the DIE for core-hole vacancies S_i^{-1} and S_j^{-1} , at core orbitals of atomic site i and j , can be decomposed as

$$DIE(S_i^{-1}, S_j^{-1}) = -\varepsilon_{Si} - \varepsilon_{Sj} - RC(S_i^{-1}, S_j^{-1}) + E_{RE}, \quad (4)$$

$$RC(S_i^{-1}, S_j^{-1}) = RC(S_i^{-1}) + RC(S_j^{-1}) + NRC(S_i^{-1}, S_j^{-1}). \quad (5)$$

Here, E_{RE} is the repulsion-exchange energy of two vacancies, which can be represented by the two-electron integral $V_{SiSiSiSi}$ ($i = j$) or $V_{SiSiSjSj}$ ($i \neq j$). These two-electron integrals can be well approximated by simple formulas as given in Refs. 8 and 10. The relaxation correlation term $RC(S_i^{-1}, S_j^{-1})$ is decomposed into a sum of single core-hole RC terms and the remaining non-additive term $NRC(S_i^{-1}, S_j^{-1})$, where the NRC is called excess generalized relaxation energy, ERC , in the single-site DCH case ($i = j$), and interatomic generalized relaxation energy, IRC , in the two-site DCH case ($i \neq j$).

As exemplified in Sec. VIII below, important properties of the system studied can be extracted from measuring the energy difference as follows:

$$\Delta E = DIE(S_i^{-1}, S_j^{-1}) - IP(S_i^{-1}) - IP(S_j^{-1}). \quad (6)$$

As discussed in Ref. 10, in the case of single-site double core holes ($S_i = S_j$), ΔE takes on the form

$$\Delta E1(S^{-2}) = -ERC(S^{-1}, S^{-1}) + V_{ssss}. \quad (7)$$

Here, subscripts i and j of the core orbital S are omitted for simplicity. Values for V_{ssss} have been calculated both for

FIG. 1. A spectrum of the N1s double ionization of NO using a photon energy 1100 eV derived from four-fold electron coincidences.

NO and N₂O; NO N1s: 112.300 eV; O1s: 129.023 eV; N₂O N₁1s: 112.210 eV; N_c1s: 112.174 eV; O1s: 128.970.

V. THE NO MOLECULE

Figure 1 shows a N1s double core hole spectrum of the NO molecule recorded using the photon energy 1100 eV. It reveals one single line at the binding energy 904.8 eV obtained as the energy difference between 1100 eV and the sum of the kinetic energies of the two emitted photoelectrons. This core DIE is thus 2.20 times the energy for N1s single ionization (410.5 eV).²⁶ Studies of valence double ionization of several small molecules have given consistent ratios of DIE to IE,²⁷ which proved useful for predictive purposes. If the ratios of DIE to IE for core holes also prove to be consistent over a range of molecules, they may be valuable for similar purposes. Table III summarises this ratio obtained experimentally and theoretically for all the states considered in this study.

Both the Δ SCF and CASSCF methods give energies in good agreement with the experimental values with differences of the order of a couple of eV or less for both the IE and DIE (Tables I and II), which applies generally to the cases studied here. The ratio DIE/IE is also very close to the experimental counterparts, which is another demonstration of the accuracy of the calculations.

As concerns chemical shifts, it is interesting to compare with the N1s IE and DIE of the N₂ molecule, for which the values 409.93 eV²⁶ and 902.55 eV⁴ have been reported previously. For NO, the N1s ionization energy is 0.57 eV higher compared to N₂, whereas the single-site double core ionization energy increases by 2.25 eV, which is substantially larger.

TABLE III. The ratio between DIE and IE for NO and N₂O.

Molecule	Orbital	DIE/IE		
		Exp	Δ SCF	CASSCF
N ₂ O	N ₁ 1s	2.20	2.19	2.19
	N _c 1s	2.20	2.19	2.19
	O1s	2.17	2.16	2.16
NO	N1s	2.20	2.19	2.20
	O1s	2.17	2.16	2.16

FIG. 2. An intensity map of the N1s double ionization of NO using the photon energy 1100 eV. The horizontal and vertical axes represent the kinetic energy of each of the two N1s electrons. The data points are lying on a straight line between the points at approximately (0, 195.2 eV) and (195.2, 0 eV).

In addition to the sharp line at 904.8 eV in Fig. 1, a more or less continuous structure extends over a region up to at least 950 eV in the spectrum. The origin of the structure is uncertain, but the major part is attributed to real but unwanted coincidences with secondary electrons arising from wall collisions. So, we attempt no further interpretation.

Figure 2 shows the corresponding coincidence map where each data point is defined by the kinetic energies of the two core electrons, e_1 and e_2 , separately represented on the horizontal and vertical axes, respectively. As can be seen, coincidences associated with the total kinetic energy sum 195.2 eV form a clear straight line between the points on the horizontal and vertical axes with this energy. It may be noted that the distribution of excess energy between the two photoelectrons is effectively continuous with some tendency to favour pairs that have different energies, one high and one low.

Figure 3 shows the double ionization O1s spectrum of the NO molecule using the photon energy 1300 eV. A sharp line in the spectrum represents O1s double core ionization. The DIE, determined from this line in a similar way as for N1s, is 1179.4 eV. The corresponding O1s binding energy (IE) is 543.2 eV,²⁶ which means that the ratio between the double and single core ionization energies is in this case 2.17. The theoretical value is nearly the same, 2.16.

FIG. 3. A spectrum of the O1s double ionization of NO at the photon energy 1300 eV.

The IE and DIE can be compared with the corresponding energies for O₂ to investigate the magnitude of the chemical shifts. For O₂, the energies are 543.86 eV²⁶ (weighted average of the ⁴Σ and ²Σ states) and 1179.2 ± 0.8 eV,⁴ respectively, which means that the IE and DIE of NO are chemically shifted by 0.66 eV and 0.2 eV, respectively. The shifts are small as expected from consideration of electro-negativities. In view of the error limits of ±0.8 eV considered for the double ionization energy, the value 0.2 eV is not significant.

In the corresponding map (not shown), the coincidences connected to the formation of the O1s⁻² dication in its ground electronic state form a clear straight and continuous line between the axis points at 120.6 eV (1300–1179.4 eV). As in the case of the nitrogen atom there is a preference for emission of two electrons having widely different energies.

VI. THE N₂O MOLECULE

The N₂O molecule contains two types of atoms, N and O, but the two nitrogen atoms are chemically different, and there is an observable shift between the N1s energies. There will thus be 3 different ionization energies associated with single-site double core vacancies as well as for single core vacancies.

Figure 4 shows the N1s double ionization spectrum of the N₂O molecule using the same photon energy as for NO (1100 eV). The spectrum shows two well-defined lines, one associated with the terminal nitrogen atom (N_t) and the other with the central nitrogen atom (N_c). The double ionization energies obtained from these lines are 896.9 eV and 906.5 eV, respectively, in fairly close agreement with the theoretical energies. The energy of the central atom is fairly close to that of the NO molecule (cf. Table I), whereas as much as 9.6 eV towards lower binding energy shifts the energy of the terminal atom. The corresponding single ionization energies are 408.5 eV and 412.5 eV, respectively,²⁶ with a chemical shift between the nitrogen atoms of 4.0 eV, less than half of that of the double core holes. This observation is in qualitative agreement with previous studies, where double core hole electron spectra are found to exhibit much larger chemical shifts than single ionization spectra.^{3–12} The ratio between the double and single ionization energies is for both the terminal and central nitrogen atoms 2.20, the same as obtained for the NO

FIG. 4. A spectrum of the N1s double ionization of N₂O at a photon energy 1100 eV. Two lines are observed at around 900 eV corresponding to ionization from the terminal and central nitrogen atoms as indicated.

FIG. 5. A spectrum of the O1s double ionization of N₂O at a photon energy 1300 eV.

molecule. The theoretical values are very close, 2.19, for both the central and terminal atoms.

About 20 eV above the N_c line there is an indication of additional structure, which could possibly reflect strong shake-up transitions. Further experimental investigations with better statistics will be needed to clarify the origin of this structure.

In the corresponding coincidence map (not shown), the double core hole states are represented by two straight lines, which intersect the horizontal and vertical axes at 203.1 and 193.5 eV, respectively. In addition to these two lines, a faint line is found which intersects the axes at about 180 eV. This feature corresponds to the weak diffuse structure in Fig. 4 at about 925 eV.

Figure 5 shows the O1s double ionization spectrum of the N₂O molecule at the photon energy 1300 eV. A single line is observed, as expected, corresponding to the O1s⁻² electronic ground state. The DIE is determined to be 1174.1 eV in the same way as for the nitrogen atoms, and for the case of NO. This energy is 5.3 eV lower than the corresponding value for NO, which is a comparatively large chemical shift. Since the single O1s ionization energy is 541.4 eV,²⁶ the ratio between the double and single ionization energies is 2.17 (cf. Table I). This is identical with the corresponding value for NO, whereas the theoretical value is 2.16. The O1s⁻² double core hole state is, in the corresponding coincidence map (not shown), represented by a straight line that cuts the horizontal and vertical axes at 125.9 eV. The plateau observed in the binding energy range between 1190 and 1230 eV in Fig. 5 may suggest the presence also of true coincidences associated with shake-up and shake-off transitions.

At 1100 eV photon energy, the ratio of fourfold coincidences from DCH formation to twofold coincidences from single core hole formation at the N atom was $4.08 \pm 0.2 \times 10^{-4}$. In view of the measured collection efficiency of $0.5 \pm .05$, assumed to be independent of electron energy over the range involved, this implies a real cross-section ratio between double and single ionization of $1.6 \pm 0.2 \times 10^{-3}$ at this photon energy. Similarly for the O atom, the estimated cross-section ratio is $1.3 \pm 0.2 \times 10^{-3}$ at 1300 eV photon energy. Because the true collection efficiency is likely to be lower for the high energy photoelectrons from SCH formation, these ratios should be taken as upper limits.

VII. AUGER ELECTRON SPECTRA OF N_2O

Figure 6 shows an Auger electron spectrum recorded for N_2O between 300 eV and 500 eV at the photon energy 1100 eV coincident with electron pairs from creation of the initial double core hole state at 896.9 eV (terminal N). All Auger electron spectra of N_2O were obtained using a window of ± 2 eV for the photoelectrons. It exhibits three broad features centred at about 350 eV, 420 eV, and 480 eV. However, only the features at 350 eV and 420 eV can be ascribed to Auger transitions, while the structure at higher energies is apparently due to accidental coincidences involving scattered electrons present in the spectrometer and, most likely, electrons from the $\text{O}1s^{-1}$ normal Auger process. The present calculations and those made previously for NH_3 ,¹² both predict kinetic energies around 350 eV and 420 eV for Auger electrons from $\text{N}1s^{-2}$ states.

The spectrum calculated in the present study, and shown along with the experimental data in Fig. 6, was obtained by associating each transition with a Gaussian of full width at half maximum of 5 eV, which gives a reasonable band width in comparison with the experimental curve with peak maxima at 350 eV and 420 eV. Each of these peaks is associated with weaker and broader structures at lower energy.

As suggested in the theoretical part, the Auger transitions may formally be represented as a two-step process, where in the first step one of the inner shell vacancies is filled by a valence electron and another valence electron is forced to leave the system ($\text{DCH} \rightarrow \text{CVV}$). In the second step, the remaining inner shell hole is filled by a valence electron and still another valence electron leaves the system, which has now four valence holes ($\text{CVV} \rightarrow \text{VVVV}$). Many different final electronic states can be formed by combination of four valence holes, and all these states are expected to contribute at different energies to the spectrum of Fig. 6. The hole-states may involve vacancies distributed in various ways among the valence electrons. The energies 420 eV and 350 eV represent average energies for the $\text{DCH} \rightarrow \text{CVV}$ and $\text{CVV} \rightarrow \text{VVVV}$ processes, respectively, involving primarily outer valence electrons. The

FIG. 6. A coincident Auger spectrum of the N_2O molecule showing transitions from the double N_t1s^{-2} inner shell vacancies to final states containing four valence holes. The photon energy used to create the inner shell vacancies was 1100 eV. Dotted and solid lines show a calculated Auger electron spectrum of the N_2O molecule using the CASSCF and CASCI methods. The spectrum incorporates transitions from N_t1s^{-2} double inner shell vacancies to a final state containing four valence holes.

FIG. 7. Energy levels, transitions, and charge states involved in the emission of Auger electrons from N_2O after hole production on the terminal nitrogen atom.

accompanying features centred at about 400 eV and 330 eV probably reflect final states primarily connected to inner valence vacancies. Figure 7 shows an energy level diagram with the transitions and various charge states involved in the Auger processes considered.

Figure 8 shows the corresponding experimental and calculated Auger spectra associated with a double $1s$ vacancy on the central nitrogen atom. The main features are essentially the same as in Fig. 6. Differences can be observed particularly on the low kinetic energy sides both in the experimental and theoretical spectra indicating differences in the transition probability for the central and terminal nitrogen atoms.

The coincident Auger spectrum recorded at the ionisation energy 1174.1 eV, associated with the $\text{O}1s^{-2}$ state, is shown in Fig. 9. The spectrum exhibits two broad features centred at about 560 eV and 480 eV. They are due to $\text{DCH} - \text{CVV}$

FIG. 8. A coincident Auger spectrum of the N_2O molecule showing transitions from the double N_c1s^{-2} inner shell vacancies to final states containing four valence holes. The photon energy used to create the inner shell vacancies was 1100 eV. Dotted and solid lines show a calculated Auger electron spectrum of the N_2O molecule using the CASSCF and CASCI methods. The spectrum incorporates transitions from N_c1s^{-2} double inner shell vacancies to a final state containing four valence holes.

FIG. 9. A coincident Auger spectrum of the N_2O molecule showing transitions from the double $\text{O}1s^{-2}$ inner shell vacancies to final states containing four valence holes. The photon energy used to create the inner shell vacancies was 1300 eV. Dotted and solid lines show a calculated Auger electron spectrum of the N_2O molecule using the CASSCF and CASCI methods. The spectrum incorporates transitions from $\text{O}1s^{-2}$ double inner shell vacancies to a final state containing four valence holes.

and CVV – VVVV Auger transitions as can readily be proved by extracting spectra at other energies than 1174.1 eV, that is, away from the energy of the $\text{O}1s^{-2}$ configuration. In fact, the intensity is substantially reduced already at 1169 eV using the photoelectron window of ± 2 eV as used for the Auger spectrum of Fig. 9. In this figure, also the theoretical spectrum is presented. As can be seen, it is in very good agreement with the experimental data.

VIII. DISCUSSION

The observed chemical shifts of various signs and magnitude give insights into the electronic structure and dynamics of these closely related systems. In the first place, the $\text{N}1s$ single ionization energy of NO is 0.6 eV higher than for N_2 . This may clearly be an effect of the slightly higher electronegativity of oxygen than of nitrogen, which leads to a small charge transfer from the nitrogen to the oxygen atom. In the case of N_2O , the $\text{N}1s$ shifts are larger and have opposite signs both in single and double core ionization. For N_c1s , the shift in single ionization compared to N_2 is +2.6 eV, whilst for N_t1s it is –1.4 eV.

As mentioned above, the effect is expected to become more pronounced in the double core ionization spectra, which is indeed observed. The total energy difference between N_c1s and N_t1s is 4 eV in the single ionization and 9.6 eV in the double ionization spectra of N_2O . It is interesting to note that the ratio between 9.6 and 4.0 is 2.4, which is close to the ratio 2.2 between the ionisation energies themselves. In respect to the chemical shift, the central atom behaves like the N atom of NO, though the shift is enhanced in N_2O . The terminal atom is, however, strikingly different.

The peculiar chemical shifts in N_2O described above may partly reflect an increasing importance of reorganisation in N_2O , where more electrons can participate in the movements than in NO or N_2 . This reorganization results in a final state energy shift expressed by the R value or RC value in Table I; apparently, both R and RC are larger for N_2O com-

pared to NO and for O than for N atoms. The larger relaxation effects in N_2O than N_2 or NO may be attributed to the different number of atoms in the molecule.

As clearly demonstrated by the orbital energies, the different behaviour of the N_t and N_c levels is primarily an initial state effect. The $\text{O}1s$ level is shifted by 1 eV to lower energy compared to NO, and the electronic charge needed for this shift is supplied by both nitrogen atoms, but unequally. Most of the charge comes from N_c , whilst N_t provides approximately the same amount as the nitrogen atom in NO.

Figure 10(a) is a summary of the energy levels of the single ionisation energies obtained from Koopmans' theorem (ϵ_i), CASSCF calculations, and experiments. The splitting of the N_t1s and N_c1s levels as an initial state effect is clearly seen. Relaxation and correlation influence the behaviour relative to the NO $\text{N}1s$ level to some extent, as can be seen by considering its location in the Koopmans' approximation and in the CASSCF data, but the electronegativity effect still dominates.

The chemical shift argument applies also in the $\text{O}1s$ case (upper part of the figure) where the lowest energy is observed for N_2O for which more charge can be transferred than for NO. A slight effect due to relaxation and correlation is observed in the way that the splitting in the Koopmans' energy is smaller than for CASSCF or experimentally. It obviously influences the result quantitatively but does not alter the main conclusions from the electronegativity model.

In Fig. 10(b), the corresponding results for the dications are shown. In particular, the splitting between the N_t1s and N_c1s levels is increased by a factor 2 compared to the cation. The NO $\text{N}1s$ level is close to N_c1s but still lower in energy as for the cation. A rather large difference of more than 1 eV in the correlation energy contributes to move these levels close to each other. Concerning the $\text{O}1s$ levels, the splitting between NO and N_2O is much larger than for the cation, following the general trend that dicationic chemical shifts are substantially larger than the cationic.

Some interesting observations can be made from Table III. The first is the consistency between the values; the ratio DIE/IE is always close to 2.2. This value is the same as obtained for valence double ionization.²⁷ The second is a small difference between the nitrogen and oxygen atoms. Whereas for nitrogen it is 2.20 (2.19 theoretically), the value for oxygen is 2.17 (2.16 theoretically). This difference of only 1.5% would seem to be too small to be experimentally observable, but since the same difference is found for the theoretical energies, it possibly has some significance. It means that the relaxation is larger for oxygen than for nitrogen, which is not unlikely considering the number of electrons and its higher electronegativity.

In applying Eqs. (6) and (7) to our experimental and theoretical data, the results of which are summarized in Table IV, a substantially larger value for the generalized relaxation energy ERC of the double core hole states in N_2O is found for the oxygen edge compared to the nitrogen edges. We note that $\text{ERC}/2$ essentially reflects the R value in Table I, i.e., by measuring both IP and DIP we can extract the relaxation energy $R \cong \text{ERC}/2$, which represents the final state energy shift, separately from the initial state shift. A

FIG. 10. Energy level diagrams showing (a) calculated (Koopmans' and CASSCF) and experimental ionisation energies for the O1s and N1s levels of NO (dotted lines) and N₂O (full lines); (b) calculated (CASSCF) and experimental energies for the O1s⁻² and N1s⁻² levels of NO (dotted lines) and N₂O (full lines).

similar tendency is found for the NO case. Further experimental studies along these lines would be of interest, in particular of molecules containing also other atoms than nitrogen and oxygen as theoretically proposed in Ref. 10.

As mentioned before, having information on both IE and DIE, we can separate the relaxation effect and the initial state-bonding effect. This separation is useful for understanding the chemical implications of the energy shifts. In the present example of N₂O, the difference of ~4 eV between IE(N_i1s⁻¹) and IE(N_c1s⁻¹) mostly stems from the initial-state-bonding shift because the difference of the relaxation energy (<1 eV) is smaller, although not negligible.

TABLE IV. The energy difference ΔE (cf. Eq. (6)) and the generalized relaxation energy ERC/2 for the 1s edges of NO and N₂O.

Molecule		ΔE (eV)		ERC/2 (eV)	
		Expt.	Theor.	Expt.	Theor.
N ₂ O	N _i 1s	79.9	77.14	16.2	17.54
	N _c 1s	81.5	78.24	15.3	16.97
	O1s	90.1	88.48	19.4	20.25
NO	N1s	83.9	81.21	14.2	15.55
	O1s	93.0	90.19	18.0	19.42

As can be seen from the spectra, the lines corresponding to double ionization from nitrogen are in all cases much broader than those connected to oxygen. This is primarily caused by the dependence of the resolution of the spectrometer on the kinetic energy of the electrons. The larger kinetic energy of the electrons coming from N1s shells gives larger line widths than obtained for O1s. Other factors that may be of importance for the line widths is the statistics, which is not sufficient for determining line widths with high accuracy, and the vibrational profile, which may vary substantially between the different electronic states.

The N₂O DCH Auger spectra obtained by the experiment and calculation agree reasonably well, as shown in Figs. 8 and 9. This agreement suggests that the two-step Auger decay picture assumed in the theoretical calculation may be adequate. However, this assumption should be verified by more accurate experimental measurements or theoretical calculations in the future.

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