

## Direct observations of the chemical shift and electron momentum distributions of core shell in N<sub>2</sub>O

G.L. Su<sup>a</sup>, C.G. Ning<sup>a</sup>, J.K. Deng<sup>a,\*</sup>, X.G. Ren<sup>a</sup>, S.F. Zhang<sup>a</sup>,  
Y.R. Huang<sup>a</sup>, T.C. Yang<sup>a</sup>, F. Wang<sup>b</sup>

<sup>a</sup> Department of Physics and Key Laboratory of Atomic and Molecular NanoSciences of MOE, Tsinghua University, Beijing 100084, PR China

<sup>b</sup> Centre for Molecular Simulation, Swinburne University of Technology, P.O. Box 218, Hawthorn, Melbourne, Vic. 3122, Australia

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### Abstract

Combining a theoretical and experimental investigation of electron momentum spectroscopy (EMS) of the N 1s hole ( $2\sigma^{-1}$  and  $3\sigma^{-1}$ ) orbitals in NNO ( $X^1\Sigma^+$ ), we demonstrate a direct and pronounced manifestation of a chemical shift of the molecule. Evidence from both binding-energy spectra and the corresponding orbital momentum distributions are presented for the chemical shift of 3.4 eV in ionization energy and differences of wave functions of NNO between the terminal N ( $3\sigma^{-1} N_T$ ) and center N ( $2\sigma^{-1} N_C$ ).

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Core orbitals are essentially localized [1]. They usually have approximate atom-localized electronic states such that the electronic structure of specific elements can be studied even in the presence of many other elements. Binding energies and orbital wavefunctions of the electrons are element specific in the core region [2]. The chemical shift of core level binding energies makes it possible to differentiate atoms of the same element located at the nonequivalent sites in a molecule, producing simpler and more novel picture of the molecular structures [3–7]. Local characters of the core orbitals also imply that one can find relationships between the chemical shift and chemical properties with site dependence [1]. A good example is the discovery of the chemical shift of S atoms in thiosulfate [8].

Electron momentum spectroscopy (EMS), based on a binary (e, 2e) ionization reaction, is a powerful and informative experimental tool to study valence-shell electronic structure for atoms, molecules, biomolecules and condensed matter [9–11]. However, except for very few species [12,13], EMS has been rarely used to study core Dyson orbitals of molecules due to experimental difficulties such

as the weakness of the (e, 2e) cross-sections in the core region [12]. The study of chemical shift of core Dyson orbitals has been dominated by theoretical modeling [2,4,5] and has never been studied by EMS. To our best knowledge, the present study is the first reported EMS measurement of the chemical shift of core Dyson orbitals of a molecule. Recent EMS studies of NNO [4,14,15] revealed that the valance shell of NNO has been well predicted using the DFT-BP/TZVP model [15] as confirmed in the experiment [14]. In this Letter, we present an experimental EMS measurement of the N1s core hole states and the core chemical shift of NNO, together with theoretical calculations based on newer models available.

The experiment was performed using the new symmetric non-coplanar electron momentum spectrometer developed at Tsinghua University described previously [16]. In this new EMS spectrometer a double toroidal analyzer (DTA) equipped with a series of conical deceleration lens are used for electron energy and angle analyzing, and electron position detection and data acquisition are realized by using a pair of wedge and strip anode (WSA) position sensitive detectors (PSDs) with a USB multi-parameters data-acquisition system. To study the core states of NNO which are three orders lower in the (e, 2e) cross-sections than the valence orbitals, the count rates were enhanced by raising

\* Corresponding author. Fax: +86 10 6278 1604.

E-mail address: [djk-dmp@mail.tsinghua.edu.cn](mailto:djk-dmp@mail.tsinghua.edu.cn) (J.K. Deng).

the pass energy of the double toroidal analyzer from 100 eV, which is typically used for the higher resolution outer valence studies, to 200 eV. This broadens the range of electron energies observed by each energy-dispersive multichannel detector, from 15 eV in valence-shell measurements [17] to 28 eV in the present core ionization studies. The coincidence energy resolution of 2.0 eV (FWHM) is achieved from the EMS measurements of Helium.

In our EMS experiment a symmetric non-coplanar kinematic method is used. An incident electron of energy  $E_0$  ( $E_0 = 1600$  eV + binding energies) causes the ionization of the target system and the scattered and ionized electrons are subsequently detected in coincidence at the same kinetic energies and the same polar angles, i.e.  $E_1 \approx E_2$ , and  $\theta_1 = \theta_2 = 45^\circ$ . Within several approximations [9,11], of which the most important are the plane wave impulse approximation (PWIA), and the binary encounter approximation, the triple differential EMS cross-section for randomly oriented molecules is then given [9] by

$$\sigma_{\text{EMS}} \propto g S_j^f \int d\Omega |\psi_j(\mathbf{p})|^2, \quad (1)$$

where the overlap between the ion and target is a one-electron orbital known as the Dyson spin-orbital, which can be approximated by Kohn–Sham or Hartree–Fock orbitals,  $\psi_j(\mathbf{p})$ , in the weak coupling approximation and  $\mathbf{p}$  is known as the momentum of the target electron at the instant of ionization. The integral in Eq. (1) is known as the spherically averaged one-electron momentum distribution (MD).

Ab initio Hartree–Fock (HF) calculations and density functional theory (DFT) calculations, employing the three parameter hybrid functionals, B3LYP [18–20] model were used, together with a triple zeta valence basis set with polarization (TZVP) [21]. The electronic calculations were generated using the GAUSSIAN03 [22] suite of computational chemistry programs and the electron momentum distributions were mapped over into momentum space using the AMOLD code [9].

Nitrous oxide (N–N–O) of the ground state ( $X^1\Sigma^+$ ) is a linear triatomic molecule possessing  $C_{\infty v}$  point group symmetry. It is characterized by its two nonequivalent nitrogen atoms, the terminal nitrogen ( $N_T$ ) and center nitrogen ( $N_C$ ). The N1s core orbitals ( $2\sigma$  and  $3\sigma$ ) of ground state electronic configuration of  $N_T-N_C-O$  is given by

$$\dots (2\sigma)^2 (3\sigma)^2 \dots$$

The core hole orbital ( $2\sigma^{-1}$  and  $3\sigma^{-1}$ ) binding-energy spectra of NNO in the range of 405–414 eV in the EMS measurements at  $\phi = 0^\circ$  and  $\phi = 10^\circ$  angles, respectively, are shown in Fig. 1. The incident energies were 1600 eV plus binding energy. A chemical shift of approximately 3.4 eV for the N1s hole orbitals (the separation of the peak pair in Fig. 1) of NNO has been observed in the spectra, which is in consistent with previous electron spectroscopy for chemical analysis (ESCA) experiment [7] and DFT-

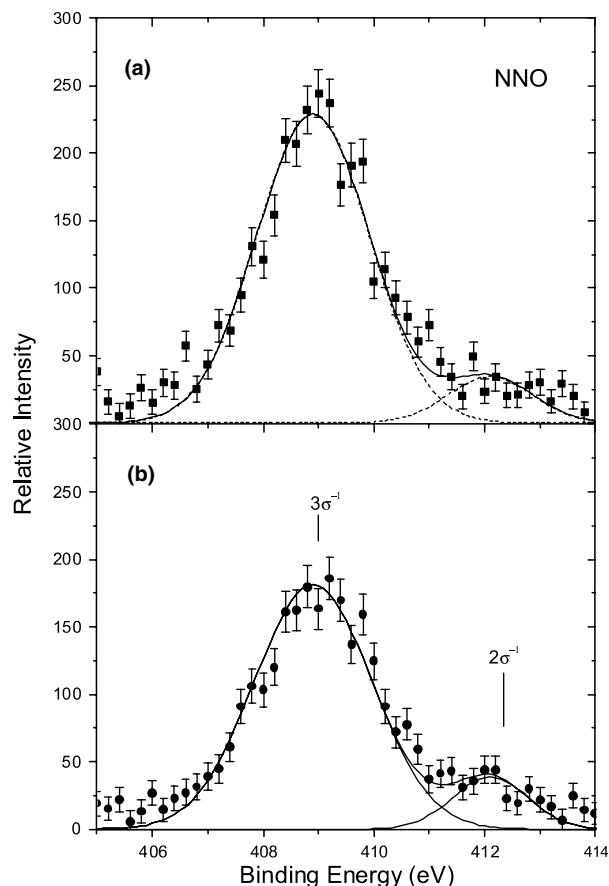


Fig. 1. Binding-energy spectra of  $N_2O$  with 1600 eV plus binding energy at azimuthal angle (a)  $\phi = 0^\circ$  and (b)  $\phi = 10^\circ$ , respectively. The dashed and solid lines represent individual and summed Gaussian fits, respectively.

BP/TZVP prediction of 3.3 eV [4]. Significantly larger intensities at the peak for  $3\sigma^{-1}$  than for  $2\sigma^{-1}$  have been seen in this figure.

The binding (ionization) energies of  $2\sigma^{-1}$  ( $N_C$ ) and  $3\sigma^{-1}$  ( $N_T$ ) orbitals are determined in the present EMS experiment to be 412.2 eV and 408.8 eV, which agree with the earlier ESCA results of 412.5 eV and 408.5 eV [7], respectively. Note that the peak area ratio of the peaks for  $3\sigma^{-1}:2\sigma^{-1}$  was approximately the same in ESCA [7] which was confirmed in theoretical calculations [23]. However, the peak area ratio of the same core hole states is very different in the binding-energy spectra observed in EMS as shown in Fig. 1. This, again, indicates that the angular-correlated EMS binding-energy spectra could further reveal certain anisotropic properties with respect to chemical shift in NNO. Indeed, the derived multipole moment contours (based on the X3LYP/TZVP model) of NNO given in Fig. 2 further support the nonequivalency of the nitrogen atoms in NNO.

NNO can be considered as binary dimmers such as  $N_2 + O$  and/or  $N + NO$ . The N1s Dyson orbitals in either  $N_2$  or  $NO$  can be used as references to study the chemical shift between  $N_T$  and  $N_C$  of NNO. The N1s ionization energies of  $N_2$ ,  $NO$  and NNO revealed in Table 1 and

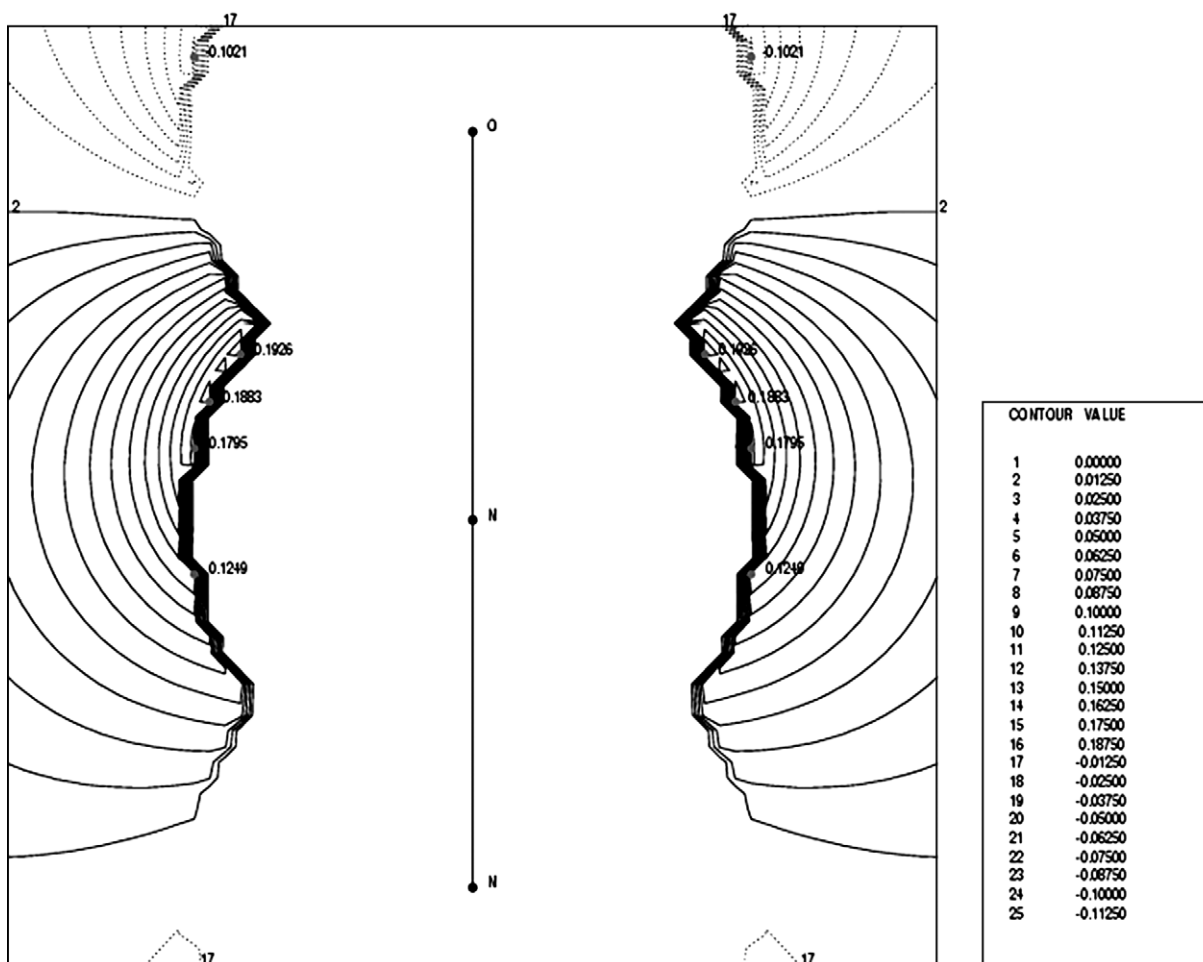


Fig. 2. Derived multipole moment contours of  $N_2O$  ground electronic state based on the X3LYP/TZVP wavefunctions.

Table 1  
Nitrogen N1s ionization energies for NNO and fragments molecules

Cations		Cals./eV	Experiment/eV
$N_2$	$N1s(1\sigma_g)^{-1}$	413.198 <sup>b</sup>	409.938 <sup>c</sup>
	$N1s(1\sigma_u)^{-1}$	413.054 <sup>a</sup>	
NO	$N1s(^3\Pi)$	409.59 <sup>d</sup>	410.3 <sup>e</sup>
	$N1s(^1\Pi)$	410.44 <sup>d</sup>	411.8 <sup>e</sup>
NNO	$N1s(N_T)$	408.68 <sup>f</sup>	408.8 <sup>g</sup>
	$N1s(N_c)$	412.62 <sup>f</sup>	412.2 <sup>g</sup>

<sup>a</sup> Ref. [24] for  $N1s(1\sigma_u)^{-1}$  of  $N_2$ .

<sup>b</sup> Theoretical value for the binding energy difference between  $N1s(1\sigma_g)^{-1}$  and  $N1s(1\sigma_u)^{-1}$  of  $N_2$  is 0.144 eV. [24]. The value of 413.198 eV is estimated using 0.144 eV.

<sup>c</sup> Ref. [25] for  $N1s(1\sigma_u)^{-1}$  of  $N_2$ .

<sup>d</sup> Ref. [24] for NO.

<sup>e</sup> Ref. [7] for NO.

<sup>f</sup> Ref. [6] for N1s of NNO.

<sup>g</sup> This work for N1s of NNO.

Fig. 3 indicate the relationship of the chemical shifts among the N1s Dyson orbitals of NNO and its fragmental species. The N1s Dyson orbitals terminal nitrogen,  $N_T$ , of NNO behaves more like the N1s Dyson orbitals of molec-

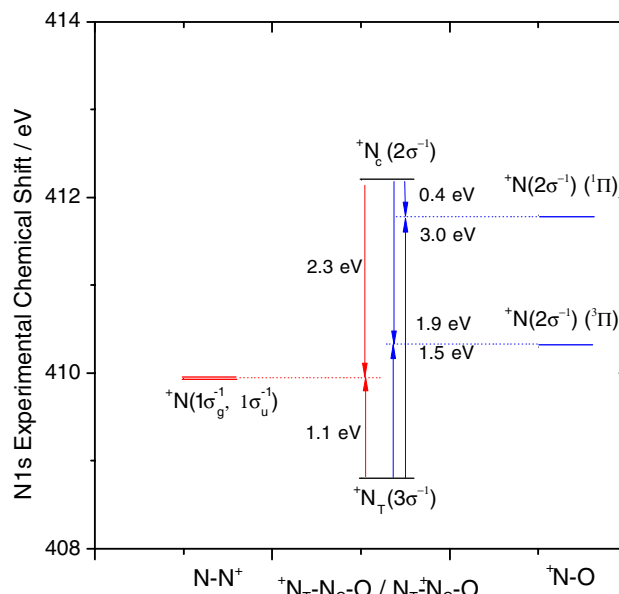


Fig. 3. Ionization energy diagram of chemical shifts among the N1s Dyson orbitals of  $N_2O$  and its fragmental species.

ular nitrogen,  $N_2$ , as  $N_T$  only interacts with  $N_C$  through bond in NNO, like the N–N interactions except that  $N_T$  and  $N_C$  are not equivalent in NNO. The ionization energy of the center nitrogen,  $N_C$ , prefers the  $N1s$  Dyson orbitals in NO, rather than those in NN. However, the bonding of  $N_C$  with oxygen lifts up the ionization energy of the  $N1s$  Dyson orbital of  $N_C$  in NNO, whereas the bonding with  $N_C$  causes an ionization energy drop in the  $N1s$  Dyson orbital of  $N_T$  in NNO. Fig. 3 demonstrates that the  $N1s$  Dyson orbitals of the species all exhibit individual chemical environment dependent chemical shift.

The experimental momentum profiles of the  $N1s$  Dyson orbitals of NNO have been extracted by deconvolution of a series of sequentially obtained angular-correlated binding-energy spectra. In the momentum distribution simulation, the Dyson orbitals obtained using two models, that is, RHF/TZVP and B3LYP/TZVP, have been mapped over to momentum space individually. The experimental conditions that the incident electron energies of 1600 eV plus the binding energy and the effects of the finite spectrometer acceptance angles of  $\Delta\theta \approx \pm 0.7^\circ$  and  $\Delta\phi \approx \pm 1.9^\circ$  were incorporated in the simulation. The experimental  $N1s$  Dyson orbital momentum distributions (MDs) are compared with the calculations in Fig. 4. Noted that the theoretical momentum distributions of the  $2\sigma^{-1}$  and  $3\sigma^{-1}$  orbitals have been normalized to their corresponding experimental distributions, respectively.

Both the  $3\sigma^{-1}$  and  $2\sigma^{-1}$  Dyson orbital MDs measured have been well described by the HF/TZVP and B3LYP/TZVP models as shown in Fig. 4. However, it is noted that small discrepancies between the experimental and theoretical distributions of  $3\sigma^{-1}$  orbital are observed. It may involve various effects such as the core relaxation and screening effects. It is also possible that the error from the independent particle model: the simulation produces the ground electronic state orbitals whereas the measured is the single electron hole state.

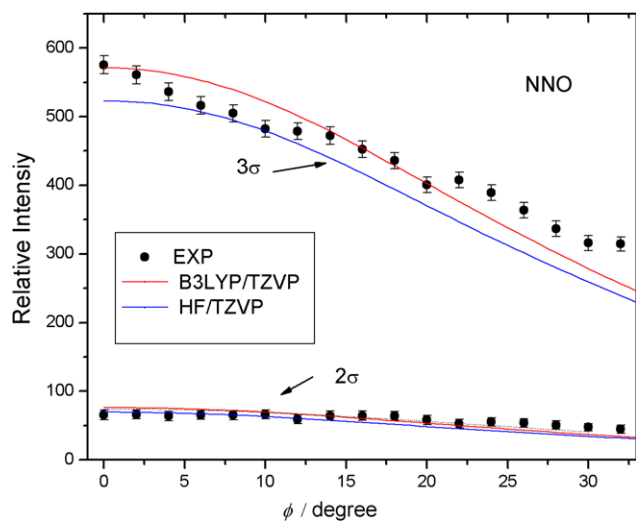


Fig. 4. The theoretical and experimental momentum profiles for the  $2\sigma$  and  $3\sigma$  Dyson orbitals of  $N_2O$ .

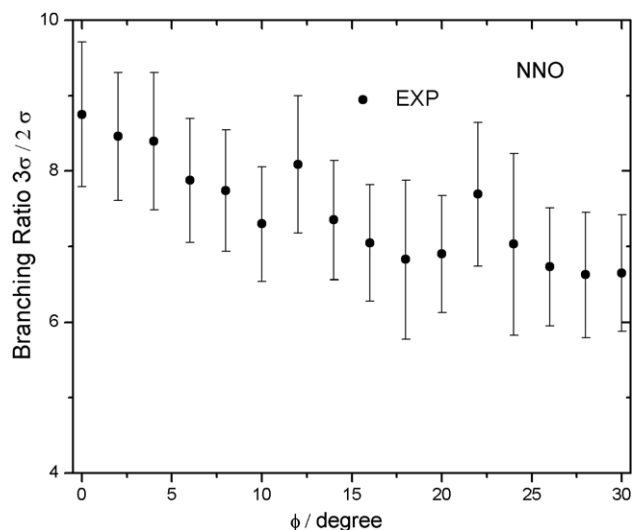


Fig. 5. The 1600 eV non-coplanar symmetric (e, 2e) branching ratios of  $3\sigma:2\sigma$  plotted as a function of the azimuthal angle.

In order to compare the differences of  $3\sigma$  and  $2\sigma$  Dyson orbital MDs clearly, the ratio of  $3\sigma:2\sigma$  area cross-section is plotted in Fig. 5 as a function of the azimuthal angle. From Fig. 5, it could be seen that not only the intensities of the momentum distributions of the  $2\sigma$  and  $3\sigma$  orbitals are much different, but also the ratio of  $3\sigma:2\sigma$  cross-section depends on the azimuthal angle. The ratio of  $3\sigma:2\sigma$  cross-section decreases with the increase of the azimuthal angle. Therefore, the differences of the wave functions of  $N1s$  in NNO could be observed clearly by the corresponding electron MDs ratio.

In summary, this work presents the first such EMS experimental applications to study chemical shift and MDs in the core shell of NNO. The chemical shift of the  $N1s$  Dyson orbitals, i.e.,  $2\sigma^{-1}$  ( $N_C$ ) and  $3\sigma^{-1}$  ( $N_T$ ) of NNO have been observed both in the binding-energy spectra and the corresponding electron momentum distributions in EMS. It demonstrates that EMS is capable of observing the chemical shift of the binding energy and the corresponding differences of wave functions, the heart and soul of quantum chemistry [26].

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