

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228475373>

Valence Orbital Electron Momentum Spectroscopy For N₂O

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · MARCH 2001

Impact Factor: 2.69 · DOI: 10.1021/jp0031909

CITATIONS

10

READS

12

3 AUTHORS, INCLUDING:



Feng WANG

Swinburne University of Technology

206 PUBLICATIONS 1,595 CITATIONS

SEE PROFILE



Frank P. Larkins

University of Melbourne

196 PUBLICATIONS 2,421 CITATIONS

SEE PROFILE

Valence Orbital Electron Momentum Spectroscopy For N₂OFeng Wang,^{†,§} Michael J. Brunger,^{*,‡} and Frank P. Larkins[†]

School of Chemistry, The University of Melbourne, Victoria 3010, Australia, Department of Physics, The Flinders University of South Australia, GPO Box 2100, Adelaide, SA 5001, Australia, and Department of Chemistry, Sichuan University, Chengdu 610065, Sichuan, China

Received: September 5, 2000; In Final Form: December 11, 2000

Valence orbitals of the ground electronic state of nitrous oxide ($X^1\Sigma^+$) have been studied in configuration space using an ab initio direct multiconfiguration self-consistent field (MCSCF) method and a density functional theory method, which also applied the generalized gradient approximation. The configuration space valence wave functions of the molecule were then transformed to momentum space using the Dirac–Fourier transform. The differential cross sections (i.e., momentum distributions (MDs)) of the valence molecular orbitals (MOs) are calculated in this work using the plane wave impulse approximation. These MDs exhibit excellent qualitative agreement with the available experiments, clearly superior to any previous theoretical calculations. The results from our MCSCF calculations also provide details of the contributions from each of the component atomic orbitals to the valence molecular orbitals. This provides a solid theoretical interpretation for the symmetry and shape (momentum distribution as a function of momentum) of each of the MOs in momentum space. The present work additionally indicates the need for more accurate experimental momentum distributions of N₂O, particularly in the low-momentum region. Theoretical improvements, which might reduce the discrepancies between experiment and theory, are also discussed.

Introduction

Nitrous oxide (N₂O) has been an important subject for many scientific fields including life science,¹ earth science,² atmospheric science,³ and the fuel industry.⁴ It is also a subject of theoretical studies^{5–11} and fundamental experimental studies^{12–16}. However, the unique structure of N₂O, characterized by the two nonequivalent nitrogen atoms, still brings challenges to both theoreticians and experimentalists.

Electron momentum spectroscopy (EMS) is a sensitive and powerful method of obtaining direct information about the electronic structure of matter, atoms, and molecules.¹⁷ It has evolved into a powerful tool for direct and precise measurements of the ionization energy spectrum, and it determines orientationally averaged orbital momentum densities. These orbital momentum densities correspond to individual ionic states, giving a comprehensive “anatomy” of the total momentum density into its individual orbital components in regions where chemical bonding occurs.¹⁸ Most popular computational methods for ground-state properties often employ variational approaches, which give an optimized electronic wave function based on minimization of the total energy. These methods often neglect the important spatial regions of the molecule, such as the valence shells, which contribute significantly less to the total energy than the inner shells but are critically important to chemical bonding.¹⁹ The (e,2e) cross sections measured by EMS emphasize the low-momentum, large r region of the wave function where accuracy is not automatically guaranteed by quantum mechanical calculations. Hence, EMS provides a very strict test

for the computational methods of quantum chemistry for molecules.

Experimental EMS is a well-established and successful probe of the valence-shell electronic structure for a wide range of atomic and molecular targets^{20–28} and of the ionization from excited states of small molecules to their ground states.²⁹ Valence electrons of molecules have dominated chemical research because they are responsible for chemical behavior and most properties such as chemical reactivity and chemical bonding.³⁰ The needs for more accurate experimental and theoretical EMS studies for the N₂O molecule are apparent.

Computational Details

Ab initio calculations applying direct multiconfiguration self-consistent field (MCSCF)^{31,32} methods have been carried out for the ground electronic state of the N₂O molecule. The active CI space was constructed from configurations that distribute electrons in the four occupied valence σ molecular orbitals (MOs) and the first four occupied π MOs plus two virtual 8σ and 9σ and two virtual 3π MOs. The three core MOs remain closed and inactive throughout the calculations. The initial guess for the direct MCSCF calculations was determined from the appropriate preceding SCF calculations. The STO-3G basis set was used in the calculations and the total SCF and MCSCF energies are $-181.190\,578\,34\,E_h$ and $-181.433\,902\,38\,E_h$, respectively.

The molecular geometry of the linear N–N–O molecule, with $C_{\infty v}$ symmetry, was studied at length previously by Wang and Harcourt.⁵ That work included an investigation of the N₂O molecular geometry, using the MCSCF and DFT-BP/TZVP methods, which forms the basis of the present calculations. We note our present, respective, optimized molecular geometries for the MCSCF ($R_{NN} = 1.1197\text{\AA}$; $R_{NO} = 1.1864\text{\AA}$) and DFT-BP/TZVP ($R_{NN} = 1.1453\text{\AA}$; $R_{NO} = 1.2004\text{\AA}$) results are both

* To whom correspondence should be addressed. Fax: 61-8-8201-2905. E-mail: Michael.Brunger@flinders.edu.au.

[†] School of Chemistry, The University of Melbourne.

[‡] Department of Physics, The Flinders University of South Australia.

[§] Department of Chemistry, Sichuan University.

in good agreement with the experimental geometry of Teffo and Chendin.³³

The DFT calculations have been conducted using the same methods we described in our previous studies^{5,6} for the wave functions of N₂O isomers in configuration space. That is, quantum mechanical DFT methods have been employed in the present investigation. These methods apply the generalized gradient approximation (GGA) with a gradient-corrected functional based on the BP exchange-correlation (XC) functionals—Becke 88^{34,35} for the exchange (X)/ Perdew 86³⁶ for the correlation (C). A triple- ζ valence basis set with polarization (TZVP) is used. Such a basis set is specially designed for DFT calculations on molecules,^{37,38} giving the contraction schemes of (7111/411/1) for both N and O atoms. Corresponding to the orbital basis set is an auxiliary basis set called A2.³⁹ It represents the electron density, the XC potential and energy. In the A2 basis set, *s*-, *p*-, and *d*-orbital exponentials were determined separately from an optimization that reproduces, as accurately as possible, the energy from an atomic DFT calculation. The contraction schemes of the A2 basis sets for N and O are (8/4/4), respectively.

The theoretical momentum distributions ((e,2e) cross sections) are simulated for the corresponding experimental EMS conditions.¹⁶ That is, the total energy is assumed to be 1200 eV, and the scattered and ejected electrons make a polar angle of 45° with respect to the incident electron beam. The angular resolution is $\Delta\phi = 1.2^\circ$ and $\Delta\theta = 0.6^\circ$, and the azimuthal angle ϕ is allowed to vary in order to change the momentum (*p*) of the ejected electron.

The ab initio MCSCF calculations were carried out using the MOLPRO96 suite of programs⁴⁰ on a Cray J916 supercomputer. The DFT calculations were performed using the UNICHEM4.0 package,⁴¹ applying the DGAUSS suite of programs. The calculations were made on an SGI-2 workstation and a Cray J90se/82048 computer, employing the computer distribution technique. The PWIA calculations for the theoretical momentum distributions of the MOs were conducted using the AMOLD program package provided by Professor I. E. McCarthy, through a computer interface coded by FW.

Results and Discussion

The valence space configuration for the ground electronic state of the linear N₂O molecule ($X^1\Sigma^+$) is $4\sigma^2 5\sigma^2 6\sigma^2 1\pi_x^2 1\pi_y^2 7\sigma^2 2\pi_x^2 2\pi_y^2$. The inner valence orbitals are of 4σ and 5σ symmetry and the outer valence orbitals of 6σ , $1\pi_x$, $1\pi_y$, 7σ , $2\pi_x$, and $2\pi_y$ symmetry. The properties of the molecule, such as the total energy, geometry, IR spectra, dipole moment and polarizability, Mulliken charge distribution, thermodynamic properties, and so forth, as predicted by the DFT-BP/TZVP method, were reported in our previous papers.^{5,6} The present work will focus on the characteristics of the valence orbitals of the linear N₂O molecule ($C_{\infty v}$).

To interpret the symmetry and momentum distributions (MDs) of the valence MOs in momentum space, we performed calculations using the MCSCF method with STO-3G basis set for the ground electronic state of the molecule. Although this minimal basis set does not provide accurate and quantitative descriptions of the molecular structure, it does reveal the key structural characteristics of the molecule and provides qualitative interpretations. As mentioned in the previous section, in the calculation, there are 12 MOs in the active CI space with a 6:3:3 configuration, that is, 6 orbitals with σ -symmetry ($4\sigma - 9\sigma$) and 3 orbitals ($1\pi - 3\pi$) with π_x - and π_y -symmetry, respectively.

TABLE 1: Dominant Configurations and Their Coefficients of the N–N–O Molecule ($X^1\Sigma^+$) Using Direct MCSCF/STO-3G Method^a

valence	space	config ^b	CI coeffs
$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^0 9\sigma^0$	$1\pi_x^2 2\pi_x^2 3\pi_x^0$	$1\pi_x^2 2\pi_x^2 3\pi_x^0$	0.927
$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^0 9\sigma^0$	$1\pi_x^2 2\pi_x^2 3\pi_x^0$	$1\pi_y^2 2\pi_y^2 3\pi_y^0$	−0.141
$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^0 9\sigma^0$	$1\pi_x^2 2\pi_x^0 3\pi_x^2$	$1\pi_x^2 2\pi_x^0 3\pi_x^2$	−0.141
$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^0 9\sigma^0$	$1\pi_x^2 2\pi_x^1 3\pi_x^{-1}$	$1\pi_x^2 2\pi_x^1 3\pi_x^{-1}$	0.100
$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^0 9\sigma^0$	$1\pi_x^2 2\pi_x^{-1} 3\pi_x^1$	$1\pi_x^2 2\pi_x^{-1} 3\pi_x^1$	0.100
$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^0 9\sigma^0$	$1\pi_x^2 2\pi_x^{-1} 3\pi_x^1$	$1\pi_y^2 2\pi_y^{-1} 3\pi_y^1$	−0.070
$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^0 9\sigma^0$	$1\pi_x^2 2\pi_x^1 3\pi_x^{-1}$	$1\pi_x^2 2\pi_x^1 3\pi_x^{-1}$	−0.070
$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^0 9\sigma^0$	$1\pi_x^2 2\pi_x^2 3\pi_x^0$	$1\pi_x^2 2\pi_x^2 3\pi_x^0$	−0.056
$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^0 9\sigma^0$	$1\pi_x^2 2\pi_x^2 3\pi_x^0$	$1\pi_y^2 2\pi_y^2 3\pi_y^0$	−0.056

^a The active CI space is 6:3:3—6 σ symmetry orbitals, 3 π_x and 3 π_y symmetry orbitals and 3 closed shell orbitals (core orbitals). ^b Here, 1 means spin up and −1 means spin down.

TABLE 2: Mulliken Population Analysis for the N–N–O Ground State Using the Direct MCSCF/STO-3G Wavefunctions

symmetry	N _t	N _c	O
σ	1.996(1s) 1.282(2s) 1.049(2p _z)	1.998(1s) 1.769(2s) 1.030(2p _z)	1.998(1s) 1.884(2s) 0.989(2p _z)
π_x, π_y	1.277(2p _x , 2p _y)	1.130(2p _x , 2p _y)	1.595(2p _x , 2p _y)

TABLE 3: Mulliken Population Analysis for the N–N–O Ground State Using the Direct MCSCF/STO-3G Wavefunctions by Basis Function Type^a

unique atom	s	p	total	charge
N _t	3.278	3.604	6.882	+0.118
N _c	3.766	3.289	7.055	−0.055
O	3.883	4.180	8.063	−0.063

^a N_t refers to the terminal nitrogen atom, whereas N_c refers to the center nitrogen atom.

Table 1 reports the most important configurations ($c_i \geq 0.05$) of the ground electronic state. All the configurations in the ground state exhibit π -electron excitations while the σ -electrons remain “undisturbed”. The dominant valence configuration is given by $4\sigma^2 5\sigma^2 6\sigma^2 1\pi_x^2 1\pi_y^2 7\sigma^2 2\pi_x^2 2\pi_y^2$, which yields the CI coefficient of 0.927. This configuration in fact is the Hartree–Fock (HF) configuration for the ground state of the N–N–O molecule and has been confirmed by a number of experiments including photoelectron spectroscopy,⁴² and binary¹⁵ and dipole⁴³ (e,2e) coincidence spectroscopy. As a result, Table 1 indicates that those methods using single determinant wave functions, such as the DFT-BP method, can be expected to yield reasonably accurate calculations.

Tables 2 and 3 give the Mulliken population analysis for the ground state of N₂O using the MCSCF/STO-3G method. In particular, Table 2 presents the population analysis by atoms while Table 3 is by basis function type. In the calculations, the N–N–O molecule lies along the *z*-axis (as the molecular axis), so that the $2p_z$ AOs do not form chemical bonds in the same manner as do the $2p_x$ and $2p_y$ AOs. For example, as clearly shown in Table 2, the $2p_z$ electrons bond “head-on” to form σ -MOs, like the other *s* electrons, and the $2p_x$ and $2p_y$ orbitals overlap “shoulder-on” to form π -MOs. On the other hand, the two nitrogen atoms are not equivalent, as the contributions from the terminal nitrogen atom (N_t) to the molecule are different from those from the center nitrogen atom (N_c). For instance, the $2p$ ($2p_x$ or $2p_y$)-electrons of the N_t atom make a larger contribution to the π MOs (N_t:N_c = 1.277:1.130), whereas the N_c atom is more populated (N_c:N_t = 3.766:3.278) by the *s*-electrons than the N_t atom (see Table 3). Table 3 also presents

TABLE 4: Contributions to the N–N–O Valence MOs from Related AO^a

MOs	Occ	orbital energies eV	Coefficients							
			N _i (2s)	N _i (2p _z)	N _c (2s)	N _c (2p _z)	O(2s)	O(2p _z)	Σc_{2s}^2	$\Sigma c_{2p_z}^2$
4σ	2	42.0(38.7)	0.543	−0.020	0.263	−0.141	0.461	0.146	0.577	0.042
5σ	2	37.0(35.0)	0.147	0.443	0.394	−0.164	−0.492	−0.086	0.419	0.231
6σ	2	19.7(20.1)	0.541	−0.235	−0.496	−0.157	−0.730	0.411	1.071	0.247
7σ	2	16.1(16.5)	−0.100	−0.428	0.726	0.525	−0.319	0.301	0.638	0.542
			N _i (2p _x ,2p _y)	N _c (2p _x ,2p _y)	O(2p _x ,2p _y)					
1π _x (1π _y)	2	19.4(18.3)	0.683	0.369	0.393					
2π _x (2π _y)	2	10.0(12.9)	−0.124	−0.580	0.811					

^a Experimental ionization energies¹⁶ are in parentheses.

the total population of the individual atoms to the N₂O molecule. The overall contributions from the individual atoms of N_i, N_c, and O to the N₂O molecule are atom-dependent, with the N_i atom positively charged and the N_c and O atoms negatively charged. Note that a Mulliken population analysis for the ground state of N₂O using the DFT-BP/TZVP method was also made. The results from this approach were entirely consistent with those presented in Tables 2 and 3 and so we do not discuss them further.

Table 4 provides detailed information on the valence MOs of the N₂O ground electronic state, in configuration space, using the MCSCF/STO-3G method. The calculated orbital energies qualitatively agree with the experimental ionization energies.¹⁶ As pointed out by Wang and Larkins^{44,45} and other authors, the direct relationship between the orbital energies and the ionization energies of a molecule is an approximation due to orbital relaxation. That is, the actual orbital energies of a molecule are not exactly the same as the corresponding ionization energies. Table 4 also presents the coefficients of the MOs, in terms of a linear combination of atomic orbitals (LCAO) approach, with only the dominant contributions ($\geq |0.25|$) being highlighted. The inner valence 4σ MO is almost purely from contributions of the 2s AOs of the three atoms, with the N_i 2s AO of 0.543, the N_c 2s AO of 0.263 and the O 2s AO of 0.461. The total ratio of the ($\Sigma_i c_{i,2s}^2$):($\Sigma_i c_{i,2p_z}^2$) is 0.577:0.042.

For the other inner valence 5σ MO, apart from the contributions made by the 2s AOs of the N_c (0.394) and O (−0.492) atoms, the contribution from the 2p_z AO of the terminal nitrogen N_i is significant (0.443), whereas the 2s AO contribution of the N_i atom is of negligible importance. The 2s:2p_z ratio of 0.419:0.231 indicates that the 2p_z contributions cannot be ignored. As a result, the formation of the 5σ MO is not dominated by the s-AOs alone and indeed the 2p_z contribution has been observed for the 5σ MD measurement in EMS experiments.^{15,16} In a similar vein, contributions from 2p_z AOs to the 6σ MO cannot be neglected. This is reflected in the ratio of 2s to 2p_z for the 6σ MO being given by 1.071:0.249. However, due to the CI coefficients for each AO being different in the 6σ MO compared to the 5σ MO, both in magnitude and in phase (positive values and negative values), the resulting MD of the 6σ MO should not necessarily be expected to be similar to the 5σ MO. This is also confirmed by the EMS experiments.^{15,16} These ratios for the 5σ and 6σ MOs, in general, are still dominated by the 2s AOs. However, with the additional important contributions from the 2p_z AOs, we therefore expect the MDs of these MOs (in momentum space) to exhibit a distorted s-type symmetry. Evidence for this expectation being fulfilled is also provided by the EMS data of Minchinton et al.¹⁶

The outer valence 7σ MO of the N₂O molecule illustrates a different situation. Contributions from the 2p_z AOs are signifi-

cant, with a competitive 2s to 2p_z ratio of 0.638:0.549. As in general, the s-type symmetry is totally symmetric and p-type symmetry is antisymmetric,⁴⁶ the significant contributions from the 2p_z AOs are able to alter the shape of the 7σ cross section in momentum space. Consequently, it is reasonable that the 7σ MO exhibits more of a p-type symmetry than an s-type symmetry.

For the π MOs, it is obvious from Table 4 that the 1π_x and 1π_y MOs are dominated by the contributions from the N_i 2p_x and 2p_y AOs, respectively, whereas the 2p_x and 2p_y AOs of the N_c and O atoms, particularly the O atom, make significant contributions to the 2π_x and 2π_y MOs.

Although the MCSCF/STO-3G calculations have been very useful in analyzing the contributions of the AOs to the respective σ- and π-MOs, they are not expected to provide a very accurate description of the wave function at large *r*.⁴⁶ As it is precisely at large *r*, or small *p* in momentum space, where EMS is most sensitive, we have therefore performed the (e,2e) cross section calculations using the DFT-BP/TZVP method. Note there is significant evidence already available in the literature⁴⁷ that attests to the utility of the BP/TZVP basis for calculating (e,-2e) cross sections.

Electron momentum spectroscopy experiments have proven that DFT wave functions possess an appropriate shape for the Dyson orbitals (e.g., Ref 28), in momentum space. The azimuthal angle ϕ , which is what is varied in experimental EMS, is quite simply related to the momentum *p* in a standard symmetric noncoplanar EMS geometry.²² Theoretical MDs, for the valence MOs of the N₂O molecule, can then be calculated using the PWIA.²²

In momentum space, the overlap function for s-symmetry AOs is considered as a square of the momentum space wave function,²²

$$|\psi_s(p)|^2 \propto (1 + p^2)^{-4}$$

Hence, to the first order, if an orbital is essentially dominated by “s-type” symmetry, it exhibits a maximum cross section (i.e., MD) at *p* = 0.0 a.u.—it has a cosine-function-like shape. Similarly, an orbital has “p-type” symmetry if it is characterized by a minimal cross section at *p* = 0.0 a.u., that is, if it has a sine-function-like shape.²² However, in molecules, the “s-type” and “p-type” symmetry of the MOs are dependent on the corresponding symmetry of the AOs. Thus, for simple molecules, π MOs almost always correspond to “p-type” symmetry but for σ MOs, it may correspond to either “s-type” symmetry or “p-type” symmetry, depending on the particular MO’s formation process.

Theoretical spherically averaged electron momentum profiles have been obtained for each of the valence orbitals of N₂O (X¹Σ⁺). Figures 1 and 2 present these momentum profiles for

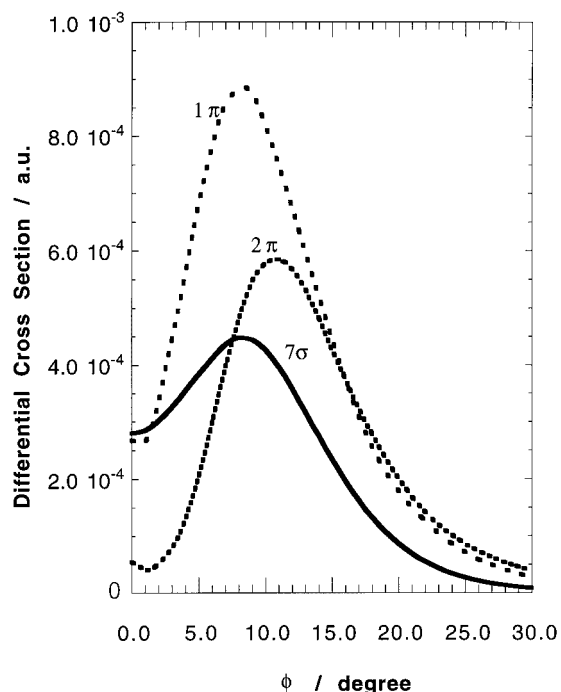


Figure 1. Momentum distributions of the MO wave functions with "p-type" symmetry. The curves are from our DFT-BP/TZVP calculations with (7111/411/1) contraction schemes for both N and O atoms.

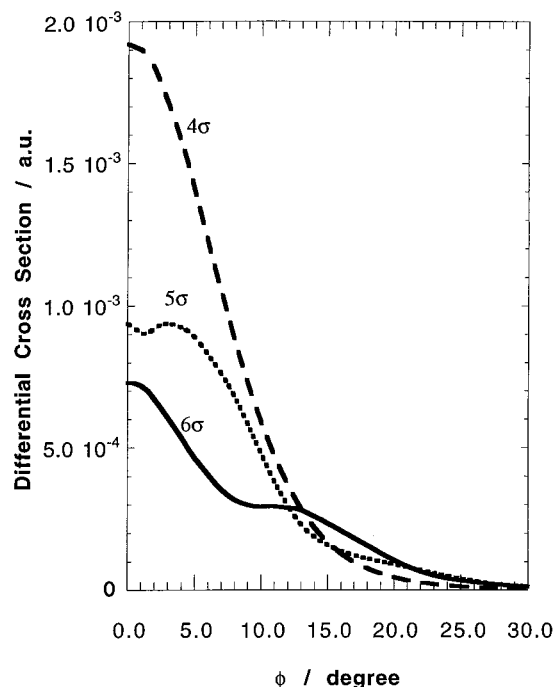


Figure 2. Momentum distributions of the MO wave functions with "s-type" symmetry. The curves are from our DFT-BP/TZVP calculations with (7111/411/1) contraction schemes for both N and O atoms.

the complete valence space for the N₂O molecule in its ground state. The symmetry of the MOs, classified by either pure "s-type" or "p-type" symmetry, applies to molecules that do not exhibit significant electron correlation. Alternatively, the MOs may not possess "pure" s- or p-type symmetry as reflected in the AOs. Under these circumstances, the shape of the MDs, in momentum space, will be distorted, depending on the specific configuration interactions. Consequently, in Figure 2, only the innermost valence 4σ MO exhibits "pure" s-type symmetry. The momentum profiles of the other valence σ orbitals respectively

possess a somewhat distorted s-type shape as the momentum (ϕ) changes. The π orbitals generally present p-type symmetry, except in the low momentum region ($\phi \leq 2.0^\circ$), where the π MDs exhibit a small local maximum at $\phi = 0.0^\circ$ ($p \approx 0.0$ a.u.). Nonetheless, Figures 1 and 2 strongly suggest configuration interaction (CI) in the MOs. As is evident from our previous papers,^{5,6} orbital interactions among the core MOs make significant contributions to N₂O isomerization, which causes the frozen core (FC) approximation to fail to predict the stability of the N₂O isomers.^{5,6} Interactions among the valence MOs can therefore be expected to be more significant, which is confirmed in Figures 1 and 2.

The EMS related studies, both experimental^{15,16} and theoretical,^{48–50} were made some 20 years ago. The original experimental data¹⁶ were collected using single channel coincidence techniques, and the energy resolution was a modest 1.8 eV (fwhm). Consequently, there is a manifest need for a new experimental EMS investigation into this system. This new study should employ now standard multiparameter coincidence techniques²² and also be made with improved energy resolution (< 1 eV fwhm). Such an investigation would significantly improve the quality of the measured binding energy spectra (and thus the MDs) and would also enable a less ambiguous deconvolution of the various valence orbitals than was encountered in the original work.¹⁶ In addition, the original theoretical MD calculations were made with quite crude basis sets,^{48,49} and so therefore, we would expect our DFT-BP/TZVP calculations to provide a more accurate description for the experimental MDs.

Unfortunately, the experimental MD data of Minchinton et al.¹⁶ are not available in digital form and in this paper, we can only make a more qualitative comparison of the shapes of our valence MD profiles with those plotted in Figures 2 and 3 of Ref 16. The approximate ratio of the maximum experimental cross sections¹⁶ of the valence MOs 2 π :7 σ :1 π :6 σ :5 σ :4 σ is 15:35:20:22:15:30, whereas this ratio in the present work is approximately 14:10:18:16:15:30. At this level of comparison, we can see that the agreement is quite good, with the exception of 6 σ and 7 σ MOs and in particular the latter.

To provide a clear picture of the valence MO distortion, our Figures 1 and 2 present the MDs for the "p-type" symmetry MOs and the "s-type" symmetry MOs of the N₂O molecule, respectively. In Figure 1, the shape and the positions of the maximum cross sections of the 2 π and 1 π MOs essentially agree with the experiment.¹⁶ For example, our ratio of the maximum cross sections for the 2 π and 1 π MDs is 3:4, which is the same as in the experiment.¹⁶ In this work, the positions (momenta) of the maximum cross sections for 2 π and 1 π are $\approx 11.0^\circ$ and 8.0° , respectively, which agree well with the experimental determinations of ≈ 0.9 a.u. and 0.7 a.u., respectively. However, the present theory cross sections of the 1 π and 2 π MO wave functions apparently behave as a "pure p-type" symmetry (as ϕ decreases), until they reach a local minimum at approximately $\phi = 1.0^\circ$ and then start to weakly rise in strength again (see Figure 1). The experimental cross sections¹⁶ at small ϕ are not very clear: the 2 π MD data of Minchinton et al. exhibit quite a lot of scatter, whereas the 1 π MD of Minchinton et al. does appear to possess a shallow local minimum at small ϕ . Clearly, further detailed experimental measurements, armed with advanced EMS instruments, are also needed in the small momentum regions of the π MDs of the N₂O molecule.

Perhaps the most challenging MO in the valence space of the N₂O molecule is the 7 σ MO. As discussed previously, the contributions to the 7 σ MO from the 2s AOs and 2p_z AOs of

the N_t , N_c and O atoms are very competitive (see Table 4). This, in turn, causes the distortion of its MO wave function and a large contribution from the $2p_z$ AOs results in a "p-type" symmetry due to the totally symmetric s AOs. The present calculated cross section for the 7σ MO (see Figure 1), and the experimental 7σ MD have confirmed such conclusions. However, it is also noted that even though the general shape of the theoretical and experimental 7σ cross sections agree qualitatively, apparent discrepancies in detail are still seen in this case. Such discrepancies probably originate from three sources: First, the PWIA reaction mechanism description may be inappropriate in this situation, a distorted wave impulse approximation (DWIA)²² level calculation being needed instead in the study of the 7σ MO. Second, our DFT-BP/TZVP method uses a single determinant wave function, and the degree of the electron correlation effect included is unknown. Therefore, the calculated wave function in momentum space may not reflect the key characteristics of the 7σ MO with sufficient accuracy. Third, the quality of the experimental 7σ measurements could be improved with modern day coincidence techniques.

Figure 2 gives the cross sections of the valence MOs dominated by "s-type" symmetry. As the MOs move from the inner valence space to the outer valence space, interaction among the valence MOs is enhanced. For example, the innermost valence 4σ MO exhibits "pure s-type" symmetry as the $2s$ AO contributions are dominant, and the interaction from the $2p_z$ AOs can be neglected (see Table 4). However, significant contributions from both s and p AOs are observed as the MO moves from the inner valence space to the outer valence space, as shown for the 5σ and 6σ MOs. It should be emphasized that contrary to the previous theoretical results,¹⁶ which gave the 5σ MO a "pure p-type" symmetry (see Figure 3 of Ref 16), the present MD for the 5σ MO does show a local minimum in the low-momentum region of the cross section. This phenomenon is confirmed in the corresponding measurement of Minchinton et al.¹⁶

Conclusions

Electronic structure for the valence space MOs of the N_2O molecule, in the ground electronic state ($X^1\Sigma^+$), has been investigated using the quantum mechanical direct multiconfiguration self-consistent field method and the density functional theory method. In addition, we have observed in this study theoretical electron momentum spectroscopy by applying the plane wave impulse approximation. The momentum distributions for the 2π , 1π , and 7σ MOs exhibit "p-type" symmetry as their wave functions are dominated by contributions from p AOs of the component atoms, whereas the 6σ , 5σ , and 4σ MOs can be considered to be dominated by s AOs, although the 6σ and 5σ MOs also display strong distortion. Theoretical electron momentum spectroscopy demonstrated that configuration interactions and electron correlation effects can be elucidated from consideration of the cross sections in momentum space, at least qualitatively.

The present work demonstrated the need for a new and more accurate experimental EMS measurement, particularly to detail the electronic information underlining the low-momentum region $\phi \leq 5^\circ$. To quantitatively predict and interpret the valence structure of the N_2O molecule, theoretical investigations using methods at a higher level, such as multireference configuration interaction methods, DFT methods with multideterminant wave functions and distorted wave impulse approximation methods, should be conducted. More comprehensive and accurate theoretical calculations at this higher level of theory would be

warranted when more detailed and accurate experimental data become available.

Acknowledgment. The work is supported by the Australian Research Council (ARC). Professor Ian E. McCarthy is acknowledged for providing the AMOLD program package and for useful discussions. F.W. wishes to thank the high performance computing and communication center (HPCCC), CSIRO for access to their computing facilities.

References and Notes

- (1) Remsen, L. G.; Pagel, M. A.; McCormick, C. I.; Fiamengo, S. A.; Sexton, G.; Neuwelt, E. A. *Anesthesia & Analgesia* **1999**, *88*, 559.
- (2) Alm, J.; Saarnio, S.; Nykanen, H.; Silvola, J.; Martikainen, P. J. *Biogeochem.* **1999**, *44*, 163.
- (3) Rahn, T.; Zhang, H.; Wahlen, M.; Black, G. A. *Geophys. Res. Lett.* **1998**, *25*, 4489.
- (4) Liu, H.; Gibbs, B. M. *Fuel* **1998**, *77*, 1579.
- (5) Wang, F.; Harcourt, R. D. *J. Phys. Chem. A* **2000**, *104*, 1304.
- (6) Wang, F.; Larkins, F. P.; Brunger, M. J.; Michaelwicz, M. T.; Winkler, D. A. *Spectrochim. Acta A* **2001**, *57*, 9.
- (7) Chakraborty, D.; Lin, M. C. *J. Phys. Chem. A* **1999**, *103*, 601.
- (8) Yan, G.; Xian, H.; Xie, D. *Chem. Phys. Lett.* **1997**, *271*, 157.
- (9) Zuniga, J.; Alacid, M.; Bastida, A.; Requena, A. *J. Chem. Phys.* **1996**, *105*, 6099.
- (10) Harcourt, R. D. *THEOCHEM* **1995**, *342*, 51.
- (11) Harcourt, R. D.; Hall, N. *THEOCHEM* **1995**, *342*, 59. Harcourt, R. D.; Hall, N. *THEOCHEM* **1996**, *369*, 217.
- (12) Maki, A. G.; Wells, J. S.; Vanek, M. D. *J. Mol. Spectrosc.* **1989**, *138*, 84.
- (13) Teffo, J.-L.; Chendin, A. *J. Mol. Spectrosc.* **1989**, *135*, 389.
- (14) Hishikawa, A.; Iwamae, A.; Hoshina, K.; Kono, M.; Yamanouchi, K. *Res. Chem. Intermed.* **1998**, *24*, 765.
- (15) Fantoni, R.; Giardini-Guidoni, A.; Tiribelli, R.; Camilloni, R.; Stefani, G. *Chem. Phys. Lett.* **1980**, *71*, 335.
- (16) Minchinton, A.; Fuss, I.; Weigold, E. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *27*, 1.
- (17) Leung, K. T. In *Theoretical Models of Chemical Bonding, Part 3*; Maksic, Z. B., Ed.; Springer: Berlin, 1991.
- (18) Chuaqui, M. H.; Mei, L.; Mathers, C. P.; Allison, M. L.; Ying, J. F.; Leung, K. T. *J. Chem. Phys.* **1995**, *102*, 90.
- (19) Mei, L.; Chuaqui, M.; Mathers, C. P.; Ying, J. F.; Leung, K. T. *J. Chem. Phys.* **1994**, *101*, 3558.
- (20) McCarthy, I. E.; Weigold, E. *Rep. Phys.* **1976**, *C27*, 275.
- (21) McCarthy, I. E.; Weigold, E. *Rep. Phys.* **1988**, *51*, 299.
- (22) McCarthy, I. E.; Weigold, E. *Rep. Phys.* **1991**, *54*, 789.
- (23) Brion, C. E. In *Correlations and Polarization in Electronic and Atomic Collisions and (e,2e) Reactions*; Eds.; Teubner, P. J. O.; Weigold, E.; Institute of Physics Conference Series 122, 1992; p 171.
- (24) Byron, F. W., Jr.; Joachain, C. J. *Rep. Phys.* **1989**, *C179*, 211.
- (25) Lahmam-Bennani, A. *J. Phys. B: At. Mol. Phys.* **1991**, *24*, 2401.
- (26) Coplan, M. A.; Moore, J. H.; Doering, J. P. *Rev. Mod. Phys.* **1994**, *66*, 986.
- (27) Fan, F. W.; Chen, X. J.; Zhou, S. J.; Zheng, Y.; Brion, C. E.; Frey, R.; Davidson, E. R. *Chem. Phys. Lett.* **1997**, *276*, 346.
- (28) Rolke, J.; Cann, N.; Zheng, Y.; Hollebone, B. P.; Brion, C. E.; Wang, Y. A.; Davidson, E. R. *Chem. Phys.* **1995**, *201*, 1.
- (29) Lerner, N.; Todd, B. R.; Cann, N. M.; Zheng, Y.; Brion, C. E.; Yang, Z.; Davidson, E. R. *Phys. Rev. A* **1997**, *56*, 1393.
- (30) van der Put, P. J. *The Inorganic Chemistry of Materials*; Plenum Press: New York and London, 1998.
- (31) Knowles, P. J.; Werner, H.-J. *J. Chem. Phys.* **1985**, *82*, 5053.
- (32) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259.
- (33) Teffo, J.-L.; Chendin, A. *J. Mol. Spectrosc.* **1989**, *138*, 84.
- (34) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (35) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 2574.
- (36) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (37) Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280.
- (38) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.
- (39) Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 4993.
- (40) MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, M. J. O. Deegan, F. Ecket, S. T. Elbert, C. Hampel, R. Lindh, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schuetz, H. Stoll, T. Thorsteinsson, and D. L. Cooper, 1996.

- (41) UniChem 4.0, Chemistry Codes, Oxford Molecular Group, 1997.
- (42) Brundle, C. R.; Turnrt, D. W. *Int. J. Mass Spectrosc. Ion Processes* **1969**, 2, 195.
- (43) Brion, C. E.; Tan, K. H. *Chem. Phys.* **1978**, 34, 141.
- (44) Wang, F.; Larkins, F. P. *J. Phys. B: At. Mol. Phys.* **1998**, 31, 1649.
- (45) Wang, F.; Larkins, F. P. *J. Phys. B: At. Mol. Phys.* **1998**, 31, 3513.
- (46) Weigold, E.; McCarthy, I. E. *Electron Momentum Spectroscopy*; Kluwer Academic/Plenum Publishers: New York, 1999; pp 112–115.
- (47) Adcock, W.; Brunger, M. J.; McCarthy, I. E.; Michalewicz, M. T.; von Niessen, W.; Wang, F.; Weigold, E.; Winkler, D. A. *J. Am. Chem. Soc.* **2000**, 122, 3892.
- (48) Snyder, L. C.; Basch, H. *Molecular Wave Functions and Properties*; Wiley-Interscience: New York, 1972.
- (49) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, 51, 2657.
- (50) Domcke, W.; Cederbaum, L. S.; Schirmer, J.; von Niessen, W.; Brion, C. E.; Tan, K. H. *Chem. Phys.* **1979**, 40, 141.