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HOLE LOCALIZATION EFFECTS IN MOLECULAR INNER-SHELL EXCITATION

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Introduction

Ab initio calculations of valence shell ionization potentials have shown that orbital relaxation and correlation differences usually make contributions of comparable magnitude. In marked contrast to this observation is the situation for deep core ionization, where correlation differences (~ 1 eV) play a relatively minor role compared to orbital relaxation (~ 20 eV). Theoretical calculations have shown that this relaxation is most easily described if the $1s$ -vacancy created by a K -shell excitation is allowed to localize on one of the atomic centers.¹ For molecules possessing a center of inversion, this means that the molecular orbitals that best describe the final state do not transform as any irreducible representation of the molecular point group.

This point has been thoroughly investigated for the case of $1s \rightarrow \pi^*$ excitation in molecular nitrogen.² In this previous study, we found that the $1s^{-1}\pi^*$ excited states could be adequately described at the level of single-excitation configuration-interaction using broken symmetry orbitals, the dominant effect being the relaxation of the outer valence orbitals in the presence of a localized $1s$ -hole. The calculations gave two quasi-degenerate molecular states of ${}^1\pi_g$ and ${}^1\pi_u$ symmetry; we also obtained the generalized oscillator strengths³ for these transitions as a function of momentum transfer.

Recent experimental work by Shaw, King, Read and Cvejanovic⁴ and by Stefani and coworkers⁵ has prompted us to carry out further calculations on N_2 , as well as analogous investigations of $1s_N \rightarrow \pi^*$ excitation in NO and N_2O . The generalized oscillator strengths display a striking similarity and point to the essential correctness of the localized hole picture for N_2 . The theoretical calculations are briefly described in the next section, followed by a summary of the results and comparison to experiment, followed by a short discussion.

Theoretical Calculations

The wavefunctions used in this study were all based on limited configuration interaction expansions with molecular orbitals obtained from SCF calculations on the ground state of the molecule. The N_2 calculations have been described in detail previously.² The basis sets chosen for the N_2 , NO and N_2O calculations were all based on a (5s/3p) contraction of a (9s/5p) set of primitive gaussian functions⁶. These were augmented with two d_π polarization functions as well as one additional diffuse p-function. For the N_2 calculations, "localized" 1σ orbitals are constructed by taking

$$1\sigma_{L,R} = 1\sigma_g \pm 1\sigma_u.$$

The calculations are then carried out in a reduced symmetry ($C_{\infty v}$). Because the 1σ orbitals have a very small overlap with the remaining molecular orbitals, the latter can still be classified by g or u symmetry, as can the total molecular wavefunctions, when a balanced set of reference configurations are used. Starting with the four reference configurations,

$$(1\sigma_R^2 1\sigma_L^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g), \quad 1, 3\Pi$$

$$(1\sigma_R^2 1\sigma_L^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_u), \quad 1, 3\Pi$$

$$(1\sigma_R^2 1\sigma_L^2 2\sigma_g^2 2\sigma_u^2 3\sigma_u^2 1\pi_u^4 2\pi_g), \quad 1, 3\Pi$$

$$(1\sigma_R^2 1\sigma_L^2 2\sigma_g^2 2\sigma_u^2 3\sigma_u^2 1\pi_u^4 2\pi_u), \quad 1, 3\Pi$$

we include all single excitations relative to each configuration. Note that the orbitals we have labelled $2\pi_{g,u}$, which are unoccupied in the N_2 ground state, are chosen by inspecting the virtual orbitals and selecting those which have the largest spatial overlap with the atomic nitrogen 2p.

The calculations on NO and N_2O were similarly executed. The distinguishability of the nuclear centers, of course, obviates the need for explicit construction of localized core orbitals. The N_2O ground state is linear (we used $R_{NN} = 2.128$ a.u. and $R_{NO} = 2.243$ a.u.) and has the configuration: $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi_{NN}^4 2\pi^4), \quad 1\Sigma^+$. The $1s_N \rightarrow \pi^*$ singlet states were obtained by including all single excitations relative to the configurations $(1\sigma^2 2\sigma 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 2\pi^4 3\pi), \quad 1\Pi$ and $(1\sigma^2 2\sigma^2 3\sigma 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 2\pi^4 3\pi), \quad 1\Pi$. As in the case of N_2 , the 3π orbital was chosen, after inspection of the virtual orbitals, to be an antibonding $2p_\pi$ orbital. The 2σ and 3σ orbitals correspond to the central and outer nitrogen $1s$ orbitals, respectively. We label these N_C and N_T .

The MO calculations were carried out at the equilibrium internuclear separation of 2.173 a.u. The ground state configuration is $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi)^2 \Pi$. The reference configurations for the spin-allowed nitrogen core-excited states were obtained by moving an electron from the 2σ orbital into the partially occupied 2π orbital. The configuration-interaction calculations included all single excitations relative to these reference configurations and were carried out for the nitrogen core-excited states of ${}^2\Sigma^+$, ${}^2\Sigma^-$ and ${}^2\Delta$ symmetry.

The limited CI calculations we have carried out were aimed at treating correlation effects in the initial and final states on an equal basis. The appropriate choice of reference configurations for the excited states and the restriction to single excitation CI incorporates the dominant relaxation effects and gives transition energies of essentially ASCF quality which, for these systems, should be accurate to roughly 1 eV. The use of CI wavefunctions employing a common set of orthonormal molecular orbitals also simplifies the calculation of properties such as the generalized oscillator strengths, which were obtained for all the spin-allowed transitions.

Results

Table I summarizes the results of our theoretical calculations on the nitrogen $1s \rightarrow \pi^*$ excited states of N_2 , N_2O and NO. For N_2 , the calculated vertical singlet-triplet energy splittings are .94 and .89 eV for the ${}^{1,3}\Pi_u$ and ${}^{1,3}\Pi_g$ states, respectively. This can be compared to the .82 eV difference in energy between the $v = 0$ levels measured by Shaw, et al.⁴. These investigators^{4,7}, however, see no evidence of separate Π_g and Π_u states. The g-u splittings we obtain are ~.1 eV, which is less than the natural (Auger) decay width of the states and therefore, presumably, unresolvable.

In N_2O , we find two ${}^1\Pi$ states separated by 4 eV. This splitting comes about from the difference in the binding energies of the $1s$ electrons residing on two non-equivalent nitrogen centers.⁸ The calculated transition energies for these states are in excellent agreement with the experimental values obtained by Bianconi et al.⁹ using monochromatized synchrotron radiation. There is also good agreement between the calculated optical oscillator strengths and the experimental value of .11 obtained by Stefani and coworkers⁵.

The calculated results for NO provide an interesting example of the equivalent nucleus model of K-shell excitation. According to this model, the effect of a K-shell vacancy is to essentially increase the positive charge of the nuclear core by one.¹⁰ There should then be a correspondence between the core-excited states of NO and the valence states of O_2 . The core-excited ${}^2\Sigma^-$, ${}^2\Delta$ and ${}^2\Sigma^+$ states of NO we have calculated have as their analogues the $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ valence states of O_2 . Although the ordering of the calculated NO states is the same as the corresponding O_2 states, the energy differences are slightly different.

Table I Summary of nitrogen ($1s^{-1}\pi^*$) excited states.

Species	Transition Energy	Oscillator Strength
$N_2 (1s^{-1}1\pi_g), 1\pi_u$	399.06 (400.86 ^a)	.236 (.195 ^b)
$(1s^{-1}1\pi_g), 1\pi_g$	399.12	---
$(1s^{-1}1\pi_g), 3\pi_u$	398.12 (400.02 ^c)	---
$(1s^{-1}1\pi_g), 3\pi_g$	398.23	---
$N_2O (1s^{-1}3\pi), 1\pi$	400.6 (401.16 ^d)	.090(.11 ^e)
$(1s^{-1}3\pi), 1\pi$	404.7 (404.92 ^d)	.119
$NO (1s^{-1}2\pi^2), 2\Sigma^-$	397.7	.061
$(1s^{-1}2\pi^2), 2\Delta$	397.8	.038
$(1s^{-1}2\pi^2), 2\Sigma^+$	399.0	.019

^a $1\pi_{g,u}$ unresolved, ref. 7

^b R. B. Kay, Ph. E. VanderLeeuw and M. J. VanderWiel, J. Phys. B 10, 2513 (1977)

^c $3\pi_{g,u}$ unresolved, ref. 4

^d ref. 9

^e ref. 5

Stefani and coworkers have measured the generalized oscillator strengths for the nitrogen $1s \rightarrow \pi^*$ transitions in N_2 , NO and N_2O . Figure 1 compares our calculated results with the experimental data for the case of N_2 . Note that the data is in excellent agreement with the summed $1\pi_u$ and $1\pi_g$ GOS values, pointing to the enhancement of the dipole-forbidden transition at values of the momentum transfer greater than 1 a.u. Figure 2 compares the summed GOS results for N_2 , NO and N_2O to the experimental values. The shapes of the GOS are indistinguishable in the three molecules.

Discussion

The nitrogen $1s \rightarrow \pi^*$ excited states in N_2 , NO and N_2O are quite similar and are well described by limited configuration-interaction wavefunctions that include the effect of orbital relaxation following creation of a $1s$ vacancy. For the case of N_2 , localized $1s$ orbitals must be used to describe this relaxation properly. (Analogous calculations using $g-u$ symmetrized orbitals give transition energies in error by 12-13 eV.²) The N_2 molecule with a $1s$ -hole behaves like a heteropolar molecule, although the overall symmetry of the wavefunctions we calculate correspond to $D_{\infty L}$. Similar considerations are expected to apply to $1s$ -vacancy production in any molecule containing atoms in equivalent locations.

Fig. 1 GOS for $1s \rightarrow \pi^*$ excitation in N_2 . Upper curve: summed $X^1\Sigma_g^- \rightarrow ^1\Pi_u$ and $X^1\Sigma_g^- \rightarrow ^1\Pi_g$; lower curve: $X^1\Sigma_g^- \rightarrow ^1\Pi_u$ only. Experimental data from reference 5. Theoretical data arbitrarily normalized to experiment at $k=1.0$ a.u.

Fig. 2 Comparison of calculated total and experimental GOS for $1s \rightarrow \pi^*$ excitation in N_2 , N_2O and NO . Experimental data from reference 5.

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