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SPLITTING IN NITROGEN AND OXYGEN 1s PHOTOELECTRON PEAKS IN TWO PARAMAGNETIC MOLECULES: SPIN DENSITY IMPLICATIONS*

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Multiplet splitting of core-level peaks in x-ray photoelectron spectra, arising from exchange interactions between unpaired core and valence electrons, has been reported previously for molecular O_2 and NO[1,2] and for compounds of Mn and Fe.[3,4] In every case the magnitude of the multiplet splitting, ΔE, was found to be in good agreement with approximate theoretical estimates,[5] and it was concluded that the splitting was qualitatively understood. Better theoretical values for ΔE (NO) are now available, however. These values were derived from "frozen orbital" Hartree-Fock calculations on NO itself[6,7] and also from direct Hartree-Fock calculations[7] on the four NO^+ final states that can be formed by removing a single 1s electron from $NO(^2\Pi_{1/2})$. In this note we report high-precision experimental values for $\Delta E(NO)$. In addition, values of ΔE are reported for di-t-butylnitroxide. These latter data illustrate the efficacy of x-ray photoelectron spectroscopy in measuring spin density distributions in polyatomic free radicals.

All samples were run as gases on the Berkeley iron-free double-focusing $\pi\sqrt{2}$ spectrometer, as described earlier.[8] The current stepping interval of 0.1mAmp was equivalent to 0.14 eV for the N 1s peak and 0.13 eV for the O 1s peak. Sufficient data were taken to achieve good statistical accuracy (i.e., up to 6000 counts in the peak channel). At least two spectra were taken for each case, to demonstrate reproducibility. Careful least-squares fits were made, using both Gaussian and Lorentzian peak shapes, in order to extract values of ΔE from the unresolved peaks. The values of ΔE so obtained were essentially independent of the peak shape chosen. They were also insensitive to whether the doublet intensity ratio was fixed at 3 or allowed to vary. The final values, which are quoted in Table I, were all derived from Lorentzian fits, with the intensity ratio fixed at 3. A comparison run on N_2 gas gave a symmetrical N 1s peak of width 0.974 ± 0.025 eV FWHM.

The NO splittings given in Table I show good agreement with the Hartree-Fock final state calculations,[7] which are, however, 0.06 eV (or three standard deviations) low in each case. The frozen orbital calculations[6,7] also give fairly good estimates for ΔE, although the final state calculations are distinctly favored by our data.

In a free atom whose valence electrons are coupled to spin S, the multiplet splitting of the 1s peak can be estimated as

$$\Delta E = (2S + 1)H_x,$$

where H_x is the 1s electron-valence electron exchange integral. In a free radical the unpaired electrons are bound in molecular orbitals that are distributed over the atoms. In the crudest approximation, using an LCAO basis set and neglecting all two-center integrals (including overlap), the total population of unpaired electrons can be approximately partitioned among the atoms, with a fraction f_i assigned to the <u>ith</u> atom. In this approximation we would expect multiplet splitting

$$\Delta E^i \cong f_i H_x^i (2S+1)$$

for the <u>ith</u> atom. Using this relation, and assuming that $H_x^N \simeq H_x^O$, we may infer from Table I that most of the unpaired spin in the $p\Pi$ antibonding orbital of NO is on the N atom. With some refinement, multiplet splittings may give a more direct measure of spin density distributions than do hyperfine structure constants.

The splittings in di-t-butylnitroxide, when compared to those in NO, suggest that the spin density on the oxygen atom is essentially unchanged, but that the N atom loses spin density in the larger molecule, apparently to the alkyl groups. This is not surprising, as the unpaired electron is presumably in a delocalized antibonding orbital. By contrast the large reductions in binding energy of both the N 1s and the O 1s electrons in di-t-butylnitroxide demonstrate quite conclusively a net flow of electron charge from the alkyl group to the NO group. This conclusion is corroborated by increases in the binding energies of 1s electrons in the tertiary carbon atoms, as compared to the usual values of 290.2 eV for the tertiary alkyl carbon, indicating oxidation of these carbon atoms.

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FOOTNOTES AND REFERENCES

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Table I. Binding Energies and Splittings of 1s Electrons (in Electron Volts).

Case[a]	Binding Energy	Linewidth (FWHM)	Measured Splitting, ΔE	ΔE from Final State Calculations	ΔE from Frozen Orbital Estimates		ΔE (expt) Hedman, et al.
$\underline{\mathrm{N}}\mathrm{O}(^1\Pi)$	411.5(5)[b]	0.93(2)[c]	1.412(16)	1.35[d]	1.23[d]	1.26[e]	1.5
$\underline{\mathrm{N}}\mathrm{O}(^3\Pi)$	410.1(5)						
$\mathrm{N}\underline{\mathrm{O}}(^1\Pi)$	543.6(5)	0.91(2)	0.530(21)	0.48[d]	0.73[d]	0.77[e]	0.7
$\mathrm{N}\underline{\mathrm{O}}(^3\Pi)$	543.1(5)						
dtb $\underline{\mathrm{N}}\mathrm{O}(^1\Pi)$	406.9(5)	1.13(4)	0.539(42)				
dtb $\underline{\mathrm{N}}\mathrm{O}(^3\Pi)$	406.4(5)						
dtb $\mathrm{N}\underline{\mathrm{O}}(^1\Pi)$	536.7(5)	0.88(3)	0.448(26)				
dtb $\mathrm{N}\underline{\mathrm{O}}(^3\Pi)$	536.2(5)						
Methyl C	290.3(5)	1.16(5)					
Tertiary C	291.4(5)						

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[a] The atom losing a 1s electron is underlined. Assumed final-state symmetry is denoted paranthetically, and "dtb" means "di-tertbutyl".

[b] Standard deviation in the last digit is given paranthetically. Absolute values of binding energies are accurate to only 0.5 eV.

[c] In fitting each group, linewidths were constrained to be equal.

[d] Ref 7

[e] Ref. 6