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MULTIPLET SPLITTING IN 1s HOLE STATES OF MOLECULES*

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ABSTRACT

The binding energies of selected C, N, O, and F 1s electrons in six paramagnetic molecules were measured by x-ray photoemission. A splitting of 1.934(41) eV was observed in the N(1s) line of NF_2, and several other splittings were remeasured or obtained by fitting asymmetric but unresolved lines. Use of the Mg $K\alpha_{12}$ doublet profile in fitting improved the fits markedly. A multiplet hole theory was developed to predict the final-state multiplet splitting. It uses atomic exchange integrals, INDO calculations on an "equivalent-core" final state to obtain spin densities, and Van Vleck's Theorem to account correctly for multiplicity. It gives results in very good agreement with experiment, and it can be used for larger molecules. During photoemission spin density migrates away from the 1s hole in most cases, and electronic charge flows toward this hole, affecting both the 1s splitting and the 1s binding energy. The lower N(1s) binding energy in di-t-butylnitroxide than in NO arises from electron flow to nitrogen from the t-butyl group during photoemission. This inductive effect is closely related to the ease of substitution of nucleophilic groups in unimolecular reactions with tertiary alkyl halides, a phenomenon that must also be understood in terms of final- (or transition-) state properties, rather than simply in terms of the initial state. Inequivalent fluorines in N_2F_4 were identified by an unresolved doublet structure in the F(1s) peak.

I. INTRODUCTION

Atoms or molecules containing unpaired electrons exhibit paramagnetism. The most common species of this kind is the free radical. As might be expected, most free radicals are transient species with very short lifetimes. When formed (generally by thermal decomposition or photolytic means) they undergo interesting addition reactions (e.g. methylene insertion), act as initiators in polymerization processes, and participate in many other reactions of concern to the organic chemist. The electronic structure of these radicals is obviously a subject of great interest. Some paramagnetic species also exist at relatively high concentrations and are therefore amenable to study with photoelectron spectroscopy. There have been several reports of ultraviolet photoelectron spectroscopic studies on free radicals.[1-7] This technique is capable of yielding binding energies of electrons in the outermost molecular orbitals, which are useful in assessing the involvement of the unpaired electron in molecular interactions.

X-ray photoelectron spectroscopy also yields information on the valence electron distribution. The binding energy of a particular core level is related to the electrostatic potential of that level due to the nuclei and the other electrons in the system. Different chemical environments will produce different valence electron distributions and hence different binding energies for core levels of a given atom. This well-known phenomenon is termed the chemical shift.[8]

The core-level spectra of paramagnetic species show an additional interesting feature. In a system containing one or more unpaired spins, the ionization of a core electron leads to at least two final states;[9] one in which the remaining core electron is coupled parallel to the valence spin,

and one in which the spins are antiparallel. The energies of the two final states will not be identical. Thus one expects to see two peaks in the core-level spectrum, separated by the energy difference between the two final states. This phenomenon is termed multiplet splitting of core-level binding energies. It was first reported in molecules by Hedman, et al.,[10] in O_2 and NO, in atoms by Fadley and Shirley,[11] and in transition-metals and salts by Fadley, et al.[12] It has since been studied in transition metal salts[13-18] and in the valence-band spectra of metals.[19-22] Davis and Shirley[23] have also reported work on NO and ditertiary butyl nitroxide. The present paper describes in Sec. II the experimental observation of multiplet splitting in the 1s orbitals of nitrogen, oxygen, and fluorine in the compounds NO_2, NF_2, and $(CF_3)_2NO$. In Sec. III, a theoretical estimate for the magnitude of the splitting based on semi-empirical INDO wavefunctions[24] is presented, and the results are interpreted in Sec. IV in terms of the spin density residing on the ionized center.

II. EXPERIMENTAL

The new species reported in this work are $(CF_3)_2NO$, N_2F_4, NO_2, and NF_2. All samples were run as gases on the Berkeley iron-free double-focusing $\pi\sqrt{2}$ spectrometer, as described earlier.[25] The gases were irradiated by Mg K_α x-rays (primarily the Mg $K_{\alpha_{1,2}}$ spin-orbit doublet, which is unresolved and of energy 1.2536 keV) at typical pressures of approximately 50 microns.

The spectra of NO_2 and NF_2 were obtained by heating N_2O_4 and N_2F_4, respectively, in a special cell constructed for this purpose. The cell was made of stainless steel and consisted of two chambers. The gas was first admitted into a "preheater" chamber in which thermal decomposition of the dimer took place. This chamber was heated by tantalum wires non-inductively wound inside boron nitride plates. The gas then passed through a constriction and into the second chamber which was maintained at the same temperature. Here it was exposed to the x-rays. The temperature was monitored through the use of a Pt, Pt-Rh thermocouple near the cell.

N_2O_4 exists in equilibrium with NO_2 at room temperature. At the pressures in the gas cell, the decomposition to NO_2 is nearly complete at room temperature.[26] The thermal decomposition $2NO_2 \rightarrow 2NO + O_2$ begins to be important at 150°C and is essentially complete at 600°C. The spectrum of NO_2 in the temperature range 150-170°C (identical to the room temperature spectrum) is shown in Fig. 1. N_2, O_2, and NO are included for comparison. A small amount of NO was observed in the high-temperature spectrum, but the nitrogen 1s line was sufficiently shifted from that in NO_2 to avoid confusion. N_2F_4 also exists in equilibrium with NF_2. The room temperature spectrum of N_2F_4 and one at 180-200°C are shown in Fig. 2. N_2F_4 has been reported to be 99% dissociated to NF_2 at 225°C and 5 Torr total pressure.[27] The dissociation

should therefore be essentially complete under our operating conditions. We conclude that the high-temperature spectrum in Fig. 2 represents multiplet splitting and not a chemical shift between NF_2 and N_2F_4.

The experimental data were analyzed by a least-squares fit to a Lorentzian peak shape with provision made for the spin-orbit splitting of the exciting radiation. In the case of photoemission peaks showing multiplet splitting, the spectra were reproduced with an intensity ratio of the triplet: singlet core doublet of 3.4:1. Prior work has shown that the derived value of the splitting is relatively insensitive as to whether the ratio is taken to be that of the spin multiplicities (3:1) or allowed to vary.[23] The binding energies and splittings so obtained are presented in Table I.

The N_2F_4 was obtained commercially from Air Products and Chemicals, Inc., and the N_2O_4 from Matheson Scientific Co. The $(CF_3)_2NO$ was obtained from Penisular Chem. Research. The N(1s) peak in $(CF_3)_2NO$ indicated the presence of an impurity which seemed to diminish with time. The source of the impurity may be due to sample handling techniques or to a reaction within our gas cell. The splittings reported for this compound therefore represent an upper limit for the magnitude of the multiplet splitting, because the asymmetric peak shapes may possibly reflect impurities as well as the exchange interaction itself.

III. THEORETICAL

In photoelectron spectroscopy the fundamental energy conservation equation is

$$h\nu = E_h - E_i + T \tag{1}$$

where $h\nu$ is the incident radiation energy, E_h is the total energy of the final hole state, E_i is the total energy of the initial state, and T is the kinetic energy of the photoelectron produced. As was mentioned earlier, the ejection of an O(1s) electron in e.g., $O_2(^3\Sigma)$, leads to the final states $O_2^+(^4\Sigma)$ and $O_2^+(^2\Sigma)$. Because these two final states have different energies, there will be two peaks in the O(1s) portion of the O_2 spectrum, split by the difference in the energies of the two final states. If this difference is smaller than the instrumental resolution, a clean separation will not be observed. The intensity of the two peaks, however, should be roughly in the ratio of their spin degeneracies, i.e. 4:2; and even though they may not be distinctly separated in the spectrum, the unresolved total O(1s) peak will show asymmetry due to the different component intensities. A value for the magnitude of the splitting can therefore be derived by careful least squares fitting to the peak profile.

In the example above, the most direct method of calculating the magnitude of the splitting is to determine directly the total energies of the $^2\Sigma$ and $^4\Sigma$ hole states of O_2^+. The difference will yield the multiplet splitting.

It would be convenient, especially for larger molecules, to be able to estimate the magnitude of the splitting without resorting to <u>ab initio</u> hole-state calculations. A particularly useful approach for systems with one or more

unpaired spins is the Unrestricted Hartree-Fock (UHF) formalism.[28,29] This approach treats the many-electron wavefunction as a single Slater determinant with different numbers of α and β spins. The word "unrestricted" means that each one electron orbital is allowed to vary independently. Thus, the spatial part of the one-electron wavefunction of the 1s α electron, e.g., may be different from that of the 1s β electron.

Working within the UHF approach, a simple one-electron picture of the splitting is regained. In the LCAO approximation, both α and β molecular orbitals are expanded in a common basis $\{\chi_\mu\}$ of atomic orbitals

$$\psi_j^\alpha = \sum_\mu C_{j\mu}^\alpha \chi_\mu \quad , \quad \psi_j^\beta = \sum_\mu C_{j\mu}^\beta \chi_\mu \quad . \tag{2}$$

Since Koopmans' Theorem[31] is applicable in the UHF formalism,[32] one obtains as a first estimate of the multiplet splitting (Δ) the difference between the one-electron orbital energies of the α and β spin core electrons. Thus, for a 1s electron

$$\Delta_{1s} = \varepsilon_{1s}^\alpha - \varepsilon_{1s}^\beta \quad , \tag{3}$$

with the one-electron orbital energies defined by

$$\varepsilon_i^\alpha = H_{ii}^\alpha + \sum_j^p (J_{ij} - K_{ij}^\alpha) + \sum_j^q J_{ij} \quad . \tag{4}$$

Here p and q refer to the number of occupied α and β MO's, respectively, and H_{ii} is the core Hamiltonian term

$$H_{ii}^{\alpha} = \langle \psi_i^{\alpha}(1) | -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} | \psi_i^{\alpha}(1) \rangle \quad , \tag{5}$$

which represents the contributions of the kinetic and potential energies of an electron moving in the field of the bare nuclei. J_{ij} and K_{ij} are the usual Coulomb and exchange integrals. They are defined by

$$J_{ij} = \langle \psi_i(1)\psi_j(2) | \frac{1}{r_{12}} | \psi_i(1)\psi_j(2) \rangle \quad ,$$

$$K_{ij}^{\alpha} = \langle \psi_i^{\alpha}(1)\psi_j^{\alpha}(2) | \frac{1}{r_{12}} | \psi_j^{\alpha}(1)\psi_i^{\alpha}(2) \rangle \quad . \tag{6}$$

Recently Basch has pointed out[33] that for core electrons it may be justifiable to assume $\psi_{1s}^{\alpha} = \psi_{1s}^{\beta}$. This assumption leads to

$$\Delta_{1s} = \varepsilon_{1s}^{\alpha} - \varepsilon_{1s}^{\beta} = \sum_j^q K_{1s,j}^{\beta} - \sum_i^p K_{1s,j}^{\alpha} \quad , \tag{7}$$

where the sum is over all occupied molecular orbitals except the core orbitals. Recalling Eqs. (2), one then obtains

$$\Delta_{1s} = \sum_j^q \sum_\mu \sum_\nu c_{j\mu}^{\beta} \, c_{j\nu}^{\beta} \langle \psi_{1s} \, \chi_\mu | \frac{1}{r_{12}} | \chi_\nu \, \psi_{1s} \rangle$$

$$- \sum_j^p \sum_\mu \sum_\nu c_{j\mu}^{\alpha} \, c_{j\nu}^{\alpha} \langle \psi_{1s} \, \chi_\mu | \frac{1}{r_{12}} | \chi_\nu \, \psi_{1s} \rangle \quad . \tag{8}$$

Assuming a valence basis set of atomic orbitals, and that

$$\langle \psi_{1s}\, \chi_\mu | \frac{1}{r_{12}} | \chi_\nu\, \psi_{1s} \rangle = \delta_{\mu\nu} \langle \psi_{1s}\, \chi_\mu | \frac{1}{r_{12}} | \chi_\nu\, \psi_{1s} \rangle \quad , \tag{9}$$

the expression for the splitting then becomes

$$\Delta_{1s} = \sum_\mu \left\{ \sum_j^p (c_{j\mu}^\beta)^2 - \sum_j^q (c_{j\mu}^\alpha)^2 \right\} K_{1s,\mu} \quad , \tag{10}$$

or in the notation of Pople, et al.[34]

$$|\Delta_{1s}| = \sum_\mu \rho_\mu\, K_{1s,\mu} \quad , \tag{13}$$

where ρ_μ is the spin density in atomic orbital χ_μ and $K_{1s,\mu}$ is the exchange integral between χ_μ and the 1s orbital.

The index μ runs over all atomic orbitals in the basis set, but because the exchange integrals between orbitals on different centers are typically an order of magnitude smaller than the corresponding one-center contributions, as a first approximation we might sum over only the valence atomic orbitals of the ionized center. The one-electron UHF approach thus gives the multiplet splitting as the difference between 1sα and 1sβ orbital energies. This may be approximated as the exchange integral between atomic orbital μ and the 1s core orbital, weighted by the unpaired spin density in orbital μ and summed over all the valence atomic orbitals on the ionized center.

In the derivation of (13) we have explicitly invoked Koopmans' Theorem. Electronic relaxation accompanying photoemission is therefore neglected. At

first thought one might expect Koopmans' theorem to be a particularly good approximation in this case because the 1sα and 1sβ electrons should be affected very nearly equally by any migration of electronic charge toward the hole. Indeed, since we have already assumed identical wavefunctions for the 1sα and 1sβ orbitals, the "Coulombic" portions of the relaxation repulsions are implicitly assumed identical. The exchange interaction, however, can affect the relaxation energies of the α and β electrons differently. Since the relaxation toward the hole may not be equally partitioned between α and β spins, one must consider the possibility of differential spin migration as an alternative to simply interpreting the splitting in terms of ground-state spin densities.

A third approach involves multiplet hole theory (MHT). This approach, applied to multiplet splitting in transition-metal ions, is the subject of a recent paper by Freeman, et al.[35] MHT recognizes the splitting as the difference in the total energies of the final states, and determines the total energy difference directly, rather than resorting to a one-electron description as presented in the preceding argument. A particularly useful theorem for discussing splitting in s-type core orbitals was given by Van Vleck.[36] It states that the difference in energy between the two final states of spin $(S_k + 1/2)$ and $(S_k - 1/2)$ formed by coupling an s electron to the configuration a^k in an atomic system is given by

$$\Delta_s = (2S_k + 1)\, K_{as} \quad . \tag{14}$$

Here S_k is the spin quantum number of the a^k configuration and K_{as} is the exchange integral between the orbital containing the unpaired spin(s)

and the s orbital being coupled to it. In attempting to generalize (14) to molecular systems, we would require that the splitting be given by the spin multiplicity of the parent configuration times the appropriate exchange integral. For systems such as pi radicals this is very unsatisfactory, since it is well known from ESR experiments that requiring the unpaired spin to reside entirely within a pi symmetry orbital does not satisfactorily explain the experimental observations. The polarization of spin from the pi orbitals into the sigma system can be accomplished through the use of configuration interaction, or by using the UHF approach. The INDO method, based (for open shell systems) on UHF with inclusion of the one-center exchange integrals, has been found to give satisfactory reproduction of the isotropic part of the electron-nuclear hyperfine interaction in ESR results.[34] It would thus seem to be a reasonable method for estimating spin densities in free radicals. Generalizing (14) to be compatible with UHF wavefunctions gives

$$\Delta_{1s} = (2S_k + 1) \sum_{\mu} \rho_{\mu} K_{1s,\mu} \tag{15}$$

Strictly speaking, Eq. (15) is applicable only to the hole-state wavefunctions. It is possible, however, to use the ground-state wavefunctions as approximations to the final-state wavefunctions (in the spirit of Koopmans' Theorem). In this version of the frozen-orbital approach, the valence-orbital spin densities would be obtained from an INDO calculation on the parent molecule, while the MHT "hole state" approach would obtain the spin densities directly from hole state wavefunctions. Since INDO does not include the 1s orbitals in the basis set, a direct hole-state calculation is not possible. The molecular orbitals of the hole state, however, can be rather well approximated by

the "equivalent cores" technique.[38,39] This is based on the fact that a 1s electron shields essentially one unit of nuclear charge from the valence orbitals. Thus the valence orbitals of atomic nitrogen with a hole in the 1s shell closely resemble those of atomic oxygen. In the specific application to this problem, the multiplet splitting in O_2, e.g., would be obtained in the hole-state approach from spin densities and exchange integrals appropriate to FO^+. Since photoemission is a fast process, the molecular geometry used for a calculation on the hole state is the same as that for the parent molecule. The experimental and calculated splittings, along with the geometries used for the calculations, are summarized in Table II. Figure 3 shows a comparison of the MHT and UHF "frozen orbital" theories for Δ_{1s} (Eqs. (15) and (13)) with experiment. The MHT equivalent-core hole state results (Eq. (15)) are compared with experiment in Fig. 4.

IV. DISCUSSION

It is clear from Table II that the MHT hole state approach is far superior, on the average, to the other two approximate models, giving an rms deviation of only 0.32 eV in ΔE, vs 0.77 and 0.64. The superiority of this approach is even more obvious when the systematic nature of the deviations from experiment is considered, as shown in Figs. 3 and 4. The MHT hole-state predictions "track" experimental values, being $\sim 0.3 \pm 0.1$ eV low, while the other two models give predictions that are much more erratic. In discussing the results, we shall first concentrate on those species which show marked splittings, rather than only asymmetric peak shapes. These will be sufficient to deduce the general failures or successes of the methods employed. The remainder of the splittings, being smaller, are more subject to the limitations imposed by the fitting procedure and hence less definitive.

The experimental splitting of the N(1s) line in NF_2 is the largest found to date. The MHT "hole state" calculation is in excellent agreement with experiment in this case. The "frozen orbital" MHT approach does a reasonable job, but is somewhat smaller. One reason for this can be seen in the spin density migrations of Fig. 5. The INDO method places most of the α spin on the nitrogen in NF_2. When ionization of the N(1s) electron takes place, the molecular orbitals rearrange to place more total electron density on the nitrogen as well as donating further α spin to the nitrogen center. Thus the frozen-orbital method underestimates the amount of spin density on the nitrogen in the final state. The other contribution arises from the equivalent-cores approach. The dominant contribution to the calculated splitting comes from the spin density in the p orbitals and hence from the 1s-2p atomic exchange integral for nitrogen. In the "hole state" approach one uses the exchange integral for

oxygen, which is $\sim$ 0.6 eV larger than that for nitrogen. The increase in predicted splitting in the hole state case, then, arises from increased spin density on the ionized center, as well as an increase in the magnitude of the exchange integral. The "frozen orbital" UHF expression which gives the splitting as the difference in one-electron orbital energies is nearly a factor of 3 in error.

The splitting of the O(1s) peak in O_2 is also again well described by the MHT "hole state" approach. Bagus and Schaefer[42] have performed direct "localized hole" ab initio calculations on O_2^+. By examining the total energy of the $^4\Sigma_g^-$ and $^2\Sigma_g^-$ states of O_2^+ produced by ionization of a $1\sigma_g$ electron, they deduced a value of 0.61 eV for the splitting in O_2. Since they included a very large basis set of Slater functions (7s, 6p, 3d, and 2f on each atom), the reason for their discrepancy with experiment is difficult to understand. The "frozen-orbital" MHT approach fails miserably for this molecule, being in error by nearly a factor of 3. It is evident from Fig. 5 that spin migration plays a very important role in this case. Here, unlike NF_2, the majority spin (α) migrates away from the center being ionized. The larger value for the spin density in the ground state more than compensates for the reduced value of the exchange integral in the frozen orbital approach, thus greatly overestimating the magnitude of the splitting. For O_2, the "frozen orbital" UHF method does a reasonable job.

The final peak showing a marked splitting is N(1s) in NO. "Hole State" MHT predicts 0.96 eV vs 1.41 experimentally. The "frozen orbital" MHT does slightly better here, while the UHF expression is again nearly a factor of 3 in error. Bagus and Schaefer,[43] as well as Schwartz,[44] have performed ab initio calculations on the NO molecule. Schwartz calculated the splitting as

$(2S_k + 1) K_{ij}$, where i is the core σ orbital of interest and j is the 2π Mo in NO (i.e. Eq. (14)). Double zeta quality wavefunctions were used to construct the ground state of NO. This version of Koopmans' Theorem yielded a value of 1.26 eV for the N(1s) and 0.77 eV for the O(1s) splittings. Bagus and Schaefer (using the same basis set as in O_2) found frozen orbital splittings of 1.23 for N(1s) and 0.73 for O(1s), while the direct hole-state calculation gave N(1s) = 1.35 eV and O(1s) = 0.48 eV. They concluded that while frozen-orbital calculations are in qualitative agreement with experiment, the direct hole-state approach is in nearly quantitative agreement.

A possible source of error not mentioned thus far within the MHT expressions (as well as the UHF) is the possibility of two-center exchange integrals contributing significantly in Eq. (15). If a substantial amount of spin density which might have a sizable exchange interaction with the 1s hole resides in an orbital on an adjacent center, the calculated splittings should increase. We could find no reasonable approximate scheme for estimating the magnitudes of the two center integral. Instead, they were calculated directly using a program kindly furnished by Prof. Schaefer.[45] The recalculated splittings, with inclusion of two-center exchange integrals, are also listed in Table II. In no case did the correction amount to more than 0.05 eV. While it was found that some of the integrals were rather large (0.218 eV for F(1s)---N($2p_\sigma$) at R = 1.15 Å) most of the unpaired spin was usually in a p_π orbital for which the exchange integral with a 1s orbital on the adjacent center was nearly zero. A plot of the exchange integrals vs internuclear distance is shown in Fig. 6. As one might expect, the exchange integral between a 1s orbital and an adjacent-center n = 2 orbital is directly proportional to the square of the overlap integral, as shown in Fig. 7. For the convenience of

future workers in this area we have included in Figs. 6 and 7 enough information to permit estimates of (1s) - (adjacent center n = 2) exchange integrals either directly (Fig. 6) or from overlap integrals (Fig. 7).

In the remainder of the molecules studied, the "hole state" MHT approach is generally better. Here the experimental splittings are smaller, and although there are isolated cases of better agreement with UHF and "frozen orbital" MHT, the hole state method is the only one which avoids gross inconsistencies (e.g. Δ(O 1s) in DTBNO) and gives the qualitatively correct ratio of magnitudes for two core peaks in a single molecule. Considering the approximations inherent in the INDO approach and in the "equivalent cores" technique for the hole state, it is rather remarkable that this very approximate method does as well as it does. It appears, however, that this approach has predictive power that can be applied rather directly to other chemically-interesting free radicals, while the other two approaches really have only qualitative value.

The phenomenon of spin migration accompanying photoemission is obviously very important. For all cases studied in this analysis (with the exception of NF_2), there is a decrease in spin density on an atom when its nuclear charge is increased by one (corresponding to inner shell ionization). This occurs in spite of the fact that the net electronic population on the atom always increases by 0.5 to 1 electron. In general, upon core ionization the bonding orbitals increase in electron density at the ionized atom, whereas the contribution of the ionized center in the anti-bonding orbitals tends to decrease. Although spin migration arises from the relaxation mechanisms of the entire set of α and β molecular orbitals, as a first step in understanding the phenomenon one is

naturally led to consider those processes occurring in the highest occupied α molecular orbital, which contains the unpaired electron. Since, in the molecules studied in this work, the highest occupied molecular orbital is antibonding in character, its contribution to the electron density at the ionized center in the hole state decreases. Thus spin density seems to migrate away from the hole. The apparent anomaly in NF_2 must reflect a more subtle rearrangement of the α and β wavefunctions which lie "deeper" than the highest occupied MO.

The absolute values of the binding energies deserve comment. Figure 1 shows a steady increase in the N(1s) binding energy from N_2 to NO to NO_2. Chemical intuition would predict such an ordering as negative charge is successively drawn away from the nitrogen through oxidation. The N(1s) binding energy in NF_2 is greater than that for NO_2, in agreement with the relative electronegativities of fluorine and oxygen. The O(1s) binding energy decreases from O_2 to NO to NO_2. The intuitive approach used above would predict the O(1s) binding energies as $O_2 > NO \approx NO_2$. We believe the rather substantial (∿ 2 eV) shift between NO and NO_2 is, in large part, due to electron density migration toward the hole in the final state. Although this "extra atomic relaxation" also affects the N(1s) shifts, the increased oxidation of the nitrogen in NO_2 (vs NO) apparently overrides the relaxation effect, and the N(1s) binding energy is greater for NO_2.

The N(1s) and O(1s) peaks in $(CF_3)_2NO$ and $((CH_3)_3C)_2NO$ are of special interest. They are both shifted toward lower binding energies relative to NO. This may be interpreted in terms of inductive electron donation by the alkyl groups during photoemission. The fact that the N(1s) and O(1s) binding energies are lower for the di-tertiary butylnitroxide than bis-trifluoromethyl nitroxide is qualitatively in line with the organic chemists' concept of strong inductive

electron donation by a tertiary-butyl group. Tertiary carbons can stabilize positive charge more readily than secondary carbons, and they in turn more readily than primary carbons.[47] This is the basis of the general rule concerning the order of reactivity of aklyl halides in S_N1 reactions. Since the intermediate in these reactions is a carbonium ion, those species which tend to stabilize the carbonium ion transition state react more rapidly. Because tertiary carbons can stabilize the transition state more effectively than secondary, etc., the order of reactivity found is $3^\circ > 2^\circ > 1^\circ$. This process can only be properly understood in terms of charge transfer between the initial (ground) state and the final (or transition) state; a discussion that includes the initial state alone is simply not adequate. The same is true in explaining core-level binding-energy shifts. This point is made especially cogently by the results of INDO calculations on NO, DTBNO, and $(CF_3)_2NO$, presented in Table III. On the basis of ground state properties alone one would not expect a large shift in the N(1s) binding energies from NO to DTBNO: the observed shift arises almost entirely from electron transfer from the t-butyl groups to the nitrogen atom in the final hole state (extra atomic relaxation). This transfer enhances the loss of the N(1s) electron since it stabilizes the positive ion in the final state. The relationship between core-level binding energy shifts and other chemical properties (such as basicity) suggests that further study is warranted.

Based on experience with other fluorine compounds, the FWHM of the F(1s) peak in N_2F_4 seems to be somewhat large (1.6 eV vs 1.4 eV in NF_2). We found that the fit was much better when two peaks (with the same width as the fluorine in NF_2) were used to construct the peak profile than when one

peak was used. (The weighted variance obtained from fitting our best set of data with one peak was 2.94 vs 1.88 for two peaks. This trend was qualitatively reflected in two other data sets.) There has been considerable discussion in the literature[27,48-52] as to the structure of N_2F_4. It now appears that two rotamers exist in equilibrium with one another. The gauche conformation (dihedral angle $\sim 70°$) and the trans conformation appear to constitute an approximately 1:1 mixture.[50] The unusual width of the F(1s) peak and the improved fit with two lines would be consistent with the presence of two rotamers, but we do not regard this as very strong evidence. The shift deduced from fitting the spectrum with two peaks of equal intensity ratio and a FWHM of 1.40 eV is presented in Table I.

V. CONCLUSIONS

Multiplet hole theory on the "equivalent cores" INDO ions satisfactorily describes the magnitude of core level splitting in paramagnetic molecules. It was found that one can qualitatively predict trends in the multiplet splitting in terms of the amount of unpaired spin density residing on the atom in question, provided that spin migration accompanying photoemission is considered. For molecules in which migration plays an important role, Koopmans' theorem estimates are inapplicable. A priori determination of the direction of spin migration is not well understood. However, in the cases studied here the general rule is that spin tends to migrate away from the ionized center, in opposition to the direction of charge flow.

Although the present technological level of instrumentation does not permit studies of the much greater number of radicals that exist in small concentrations, further refinements may make the technique of general use in the study of free radicals. XPS measurements are complementary to the spin density distributions obtained from ESR studies.

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FOOTNOTES AND REFERENCES

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Table I. 1s Electron Binding Energies and Multiplet Splittings (eV)

Molecule[a]	Binding Energy[b]	Linewidth (FWHM)	Multiplet Splitting[c]
$\underline{N}_2F_4$	412.5(5)[d]	1.02(4)	
$N_2\underline{F}_4$	694.1(5)[e] 694.6(5)[e]	1.40(8)[f]	
$\underline{N}F_2$	414.4(5)[g] 412.5(5)[g]	0.82(4)	1.934(41)
$N\underline{F}_2$	695.3(5)[g] 694.5(5)[g]	1.40(8)	0.720(8)
$\underline{N}O_2$	413.3(5)[d] 412.6(5)[d]	0.94(3)	0.702(35)
$N\underline{O}_2$	542.0(5)[h] 541.3(5)[h]	0.97(4)	0.666(41)
$(CF_3)_2\underline{N}O$	408.9(5)[o] 408.4(5)[o]	1.1(1)	0.5(1)
$(CF_3)_2N\underline{O}$	540.6(5)[o] 539.8(5)[o]	1.3(1)	0.8(1)
$(C\underline{F}_3)_2NO$	695.3(5)[o] 694.7(5)[o]	1.59(8)[i]	0.6(1)
$(\underline{C}F_3)_2NO$	299.7(5)[o] 299.3(5)[o]	1.00(8)[j]	0.4(1)
$\underline{O}_2$	544.2(5)[k] 543.1(5)[k]	0.80(31)	1.122(25)
$\underline{N}O$	411.5(5)[ℓ] 410.1(5)[ℓ]	0.81(3)	1.421(24)
$N\underline{O}$	543.6(5)[ℓ] 543.1(5)[ℓ]	0.80(4)	0.548(49)
DTB$\underline{N}$O[m]	407.2(5)[d] 406.6(5)[d]	1.03(12)	0.590(70)
DTBN$\underline{O}$[m]	537.0(5)[n] 536.4(5)[n]	0.76(5)	0.525(45)

(continued)

Table I. (continued)

[a]The ionized atom is underlined. The cases O_2, NO, and DTBNO have been reported previously. In this work they were redone incorporating the $K_{\alpha_{1,2}}$ doublet in the fitting procedure.

[b]Standard deviation in the last digit is given parenthetically.

[c]Fits were obtained by constraining the linewidths to be equal.

[d]Referenced to N_2.

[e]Referenced to F 1s of CH_3F. Splitting in F 1s line believed to be due to inequivalent fluorines in N_2F_4 (see text) and not the presence of any NF_2.

[f]FWHM constrained to be the same as that in NF_2 in obtaining fit.

[g]Absolute binding energies for NF_2 were obtained from the observed shifts from N_2F_4 when both were referenced to neon, coupled with the N_2F_4 absolute binding energies referenced as in d and e.

[h]Referenced to O_2.

[i]FWHM constrained to be that of F 1s in CF_3H in obtaining a fit.

[j]FWHM constrained to be that of C 1s in CF_3H in obtaining a fit.

[k]Ref. 8.

[ℓ]Ref. 23.

[m]Abbreviation is for ditertiary butyl nitroxide.

[n]Referenced to H_2O.

[o]Referenced to neon.

Table II. Comparison with Calculated Splittings[40] (eV)

Molecule		Experiment	"Hole State" MHT	"Hole State" + two center exchange	"Frozen orbital" MHT	"Frozen orbital" UHF
NF_2[a]	$\Delta_{N\ 1s}$	1.93	1.85	1.85	1.40	0.70
	$\Delta_{F\ 1s}$	0.72	--[d]	--[d]	0.11	0.05
NO_2[b]	$\Delta_{N\ 1s}$	0.70	0.62	0.64	0.86	0.43
	$\Delta_{O\ 1s}$	0.67	0.27	0.32	0.54	0.27
O_2[b]	$\Delta_{O\ 1s}$	1.12	1.05	1.05	2.91	0.96
NO[b]	$\Delta_{N\ 1s}$	1.42	0.96	0.96	1.04	0.52
	$\Delta_{O\ 1s}$	0.55	0.35	0.35	0.63	0.31
DTBNO[c]	$\Delta_{N\ 1s}$	0.59	0.20	0.20	0.46	0.23
	$\Delta_{O\ 1s}$	0.53	0.16	0.17	1.34	0.67
RMS deviation of each theory			0.320	0.310	0.768	0.636

[a]INDO calculation used geometry from M. D. Harmony and R. J. Myers, J. Chem. Phys. 35, 1129 (1961).

[b]Geometry from L. E. Sutton, ed. Tables of Interatomic Distances and Configuration in Molecules and Ions (London, The Chemical Society, Burlington House, 1958).

[c]Ditertiary butyl nitroxide; R(N-O) = 1.28 Å; R(N-C) = 1.47 Å, R(C-C) = 1.52 Å, R(C-H) = 1.1 Å; ∠ ONC = 115°; ∠ NCC = 109.45°; ∠ CCH = 109.45°; the tertiary carbons, the nitrogen atom and the oxygen were assumed to lie in the same plane.

(continued)

Table II. (continued)

[d]It is not possible to perform an "equivalent cores" hole state calculation in this case since it would involve the neon atom which is not accounted for in the INDO parameterization.

Table III. Nitrogen atom valence electron density in the ground state and the corresponding hole state.

Molecule[a]	P_N(valence electron density)	ΔP_N
NO	4.96	
N^*O	5.5	0.54
$((CH_3)_3C)_2NO$	4.99	
$((CH_3)_3C)_2N^*O$	5.94	0.95
$(CF_3)_2NO$	5.15	
$(CF_3)_2N^*O$	6.03	0.88

[a]The "hole state" case is denoted by an asterisk.

FIGURE CAPTIONS

Fig. 1. Nitrogen and oxygen 1s peaks in diamagnetic N_2; paramagnetic O_2; paramagnetic NO; and the paramagnetic species NO_2 (150 - 170°C).

Fig. 2. Nitrogen and fluorine 1s peaks in NF_2 (180 - 200°C) and room temperature N_2F_4. Vertical bars indicate binding energies in F_2 and N_2.

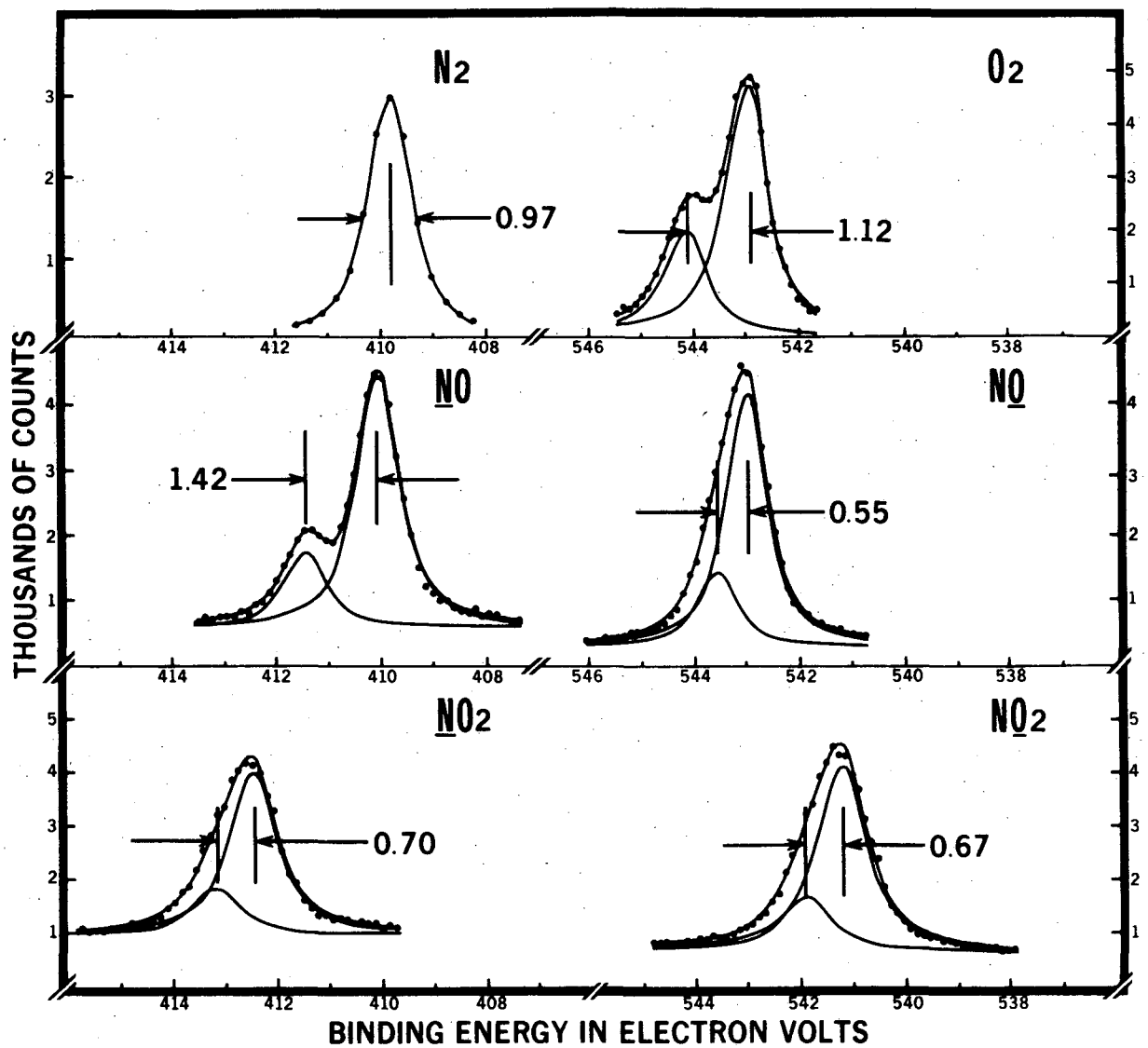
Fig. 3. Predicted vs experimental splittings; the MHT "frozen orbital" estimates are denoted by filled circles while the UHF "frozen orbital" estimates are represented by the open circles; the diagonal line has a slope of unity.

Fig. 4. Splittings predicted by the MHT "hole state" approach vs the experimental splittings. The diagonal line has unit slope.

Fig. 5. Total valence electron density and (spin density) illustrating migration accompanying photoionization; the hole states are those used in the "equivalent cores" approximation.

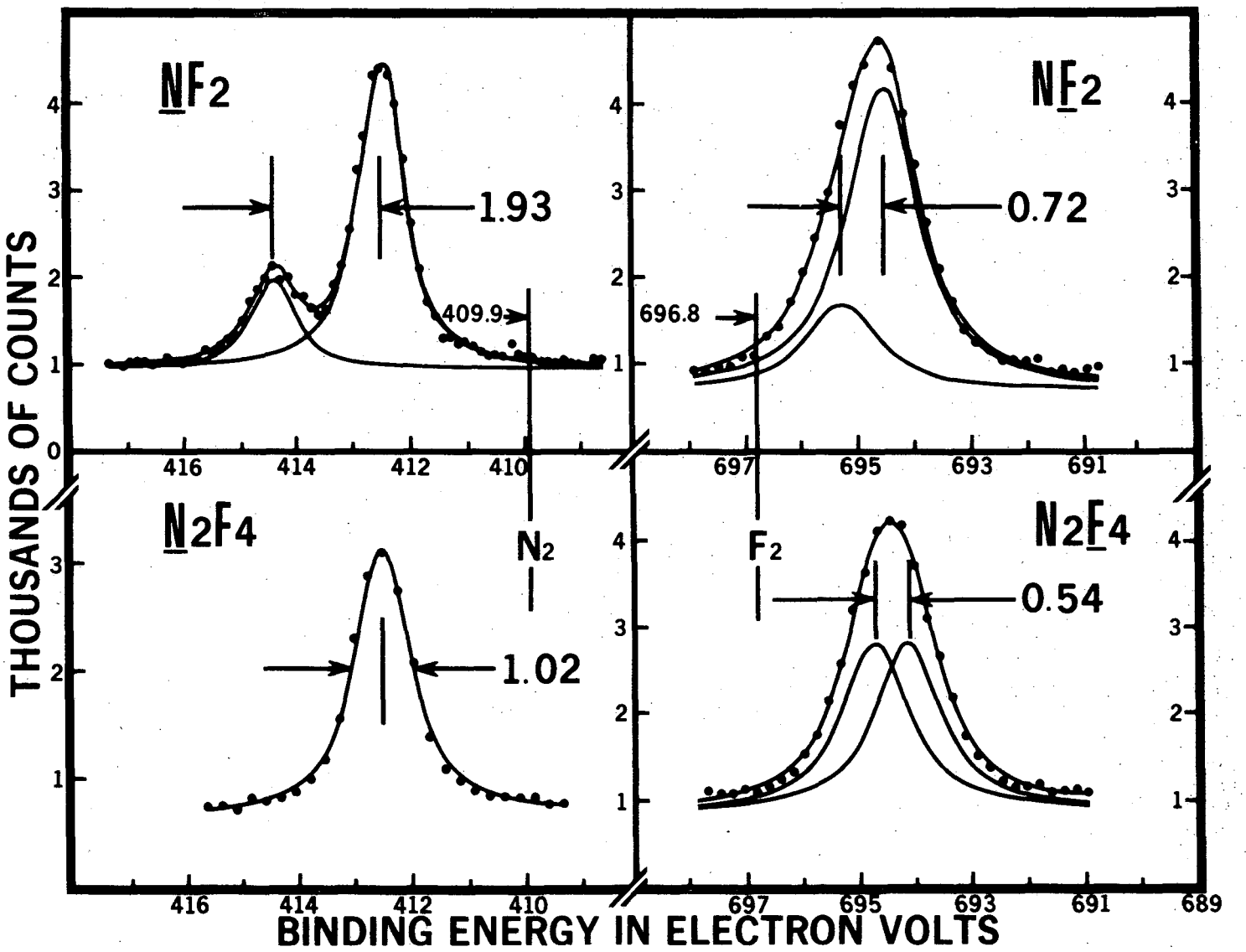
Fig. 6. The two center exchange integral $\langle \chi_a(1)\ \chi_b(2) | \frac{1}{r_{12}} | \chi_b(1)\ \chi_a(2) \rangle$ vs the internuclear separation. The X(1s)--Y($2p_\pi$) integrals are approximately 0.000 - 0.003 eV and are not shown.

Fig. 7. The two center exchange integral $\langle \chi_a(1)\ \chi_b(2) | \frac{1}{r_{12}} | \chi_b(1)\ \chi_a(2) \rangle$ vs the square of the overlap integral $\langle \chi_a | \chi_b \rangle$. The data were obtained in the internuclear separation region 1.15 - 1.40 Å. Integrals between F(1s) and N(2s) Slater type orbitals, as well as N($2p_\sigma$) orbitals, are denoted by filled circles; F(1s)--O(2s,$2p_\sigma$) data denoted by triangles; O(1s)--O(2s,$2p_\sigma$) integrals shown by open circles; O(1s)--F(2s,$2p_\sigma$) data represented by squares.



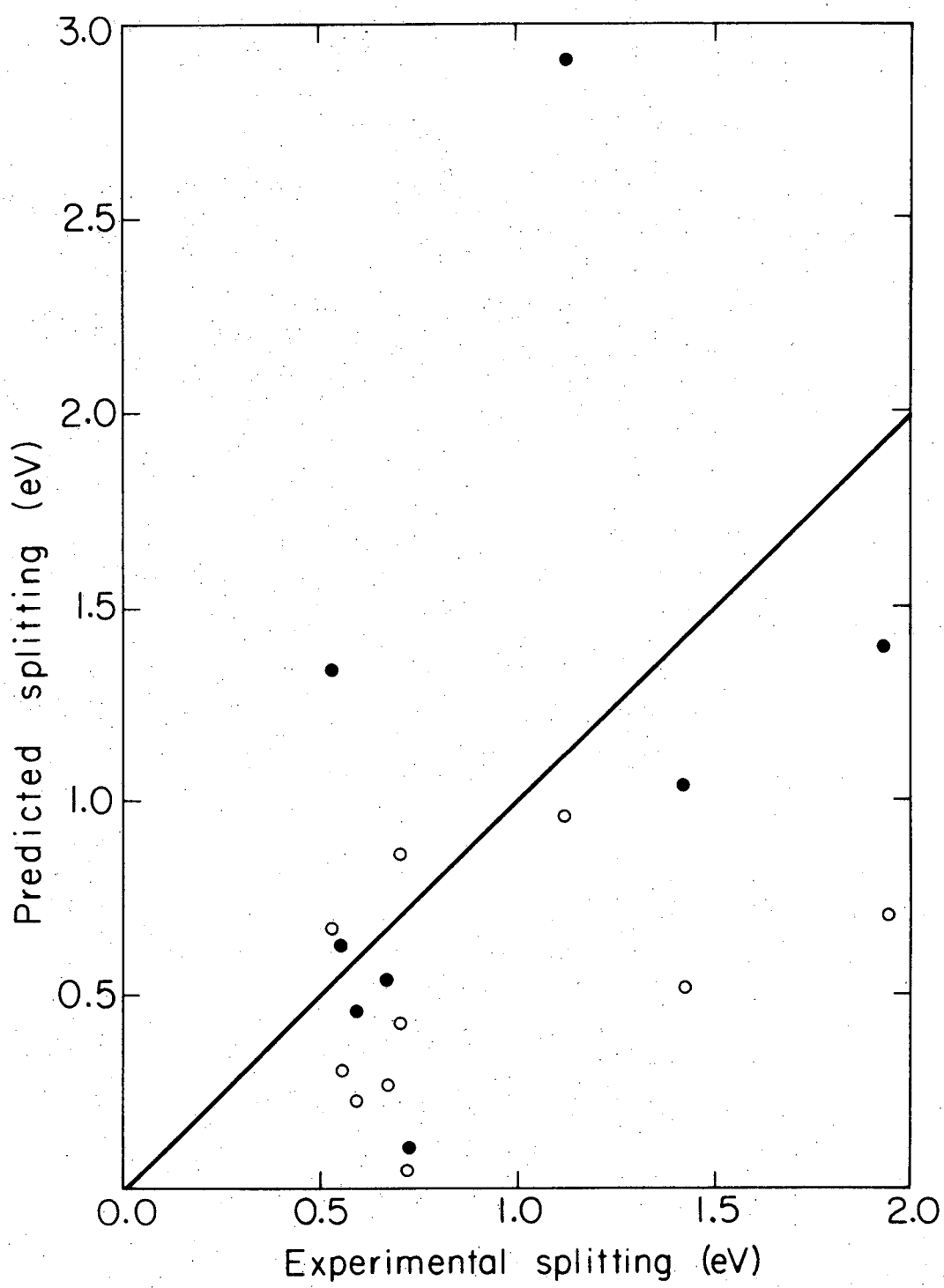
XBL 736-752

Fig. 1



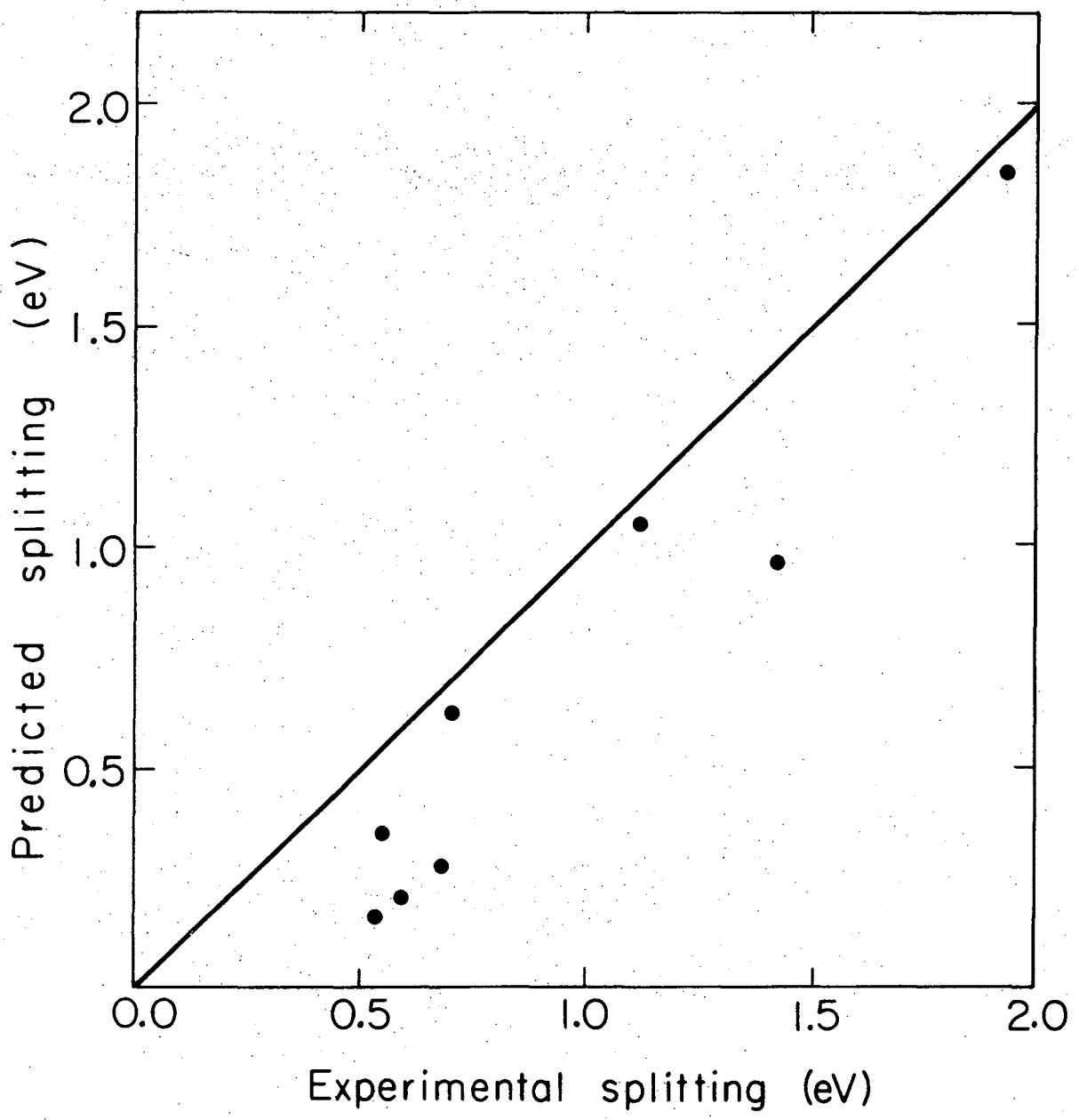
XBL 736-753

Fig. 2



XBL735 - 3003

Fig. 3



XBL 735-3004

Fig. 4

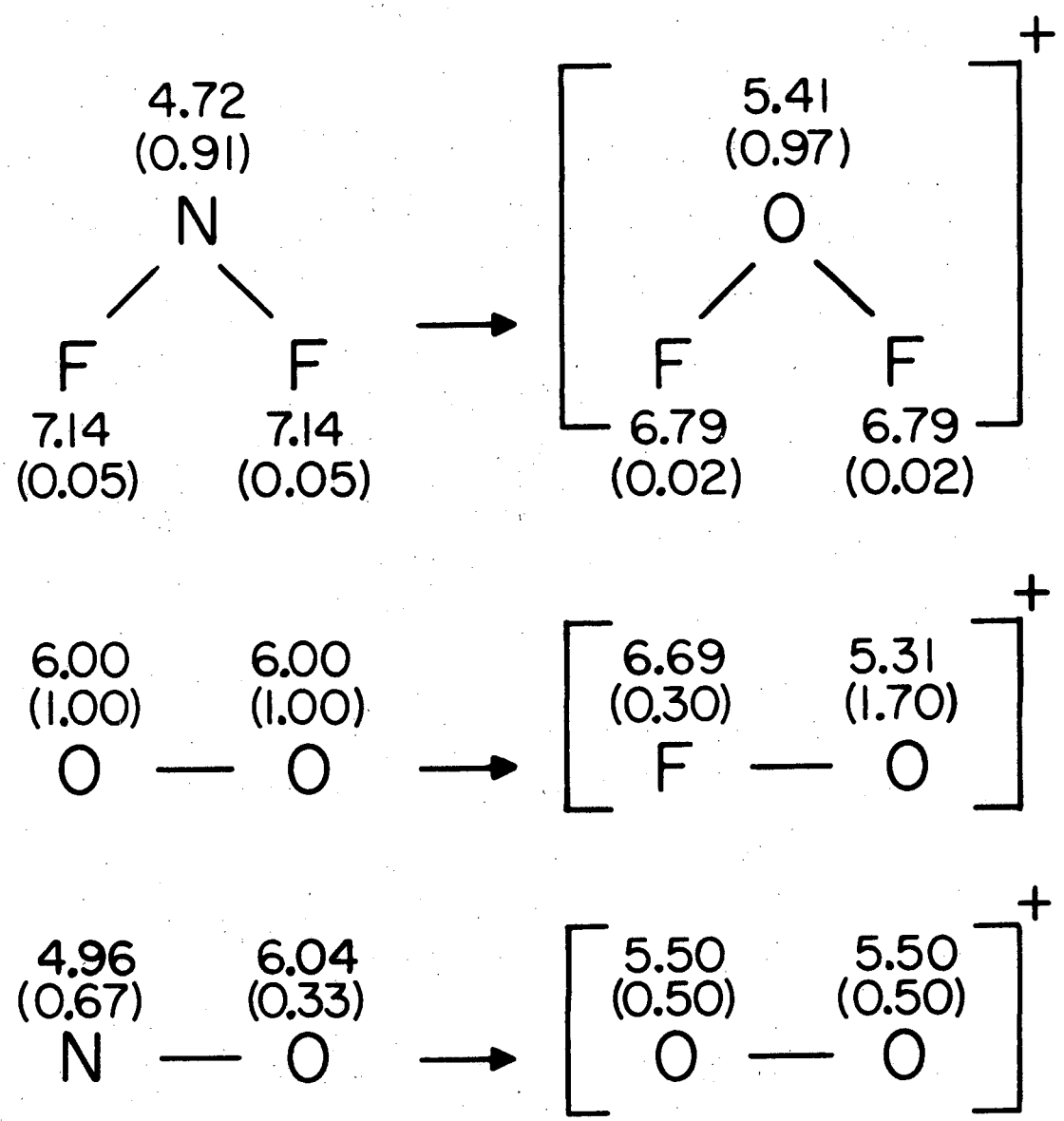


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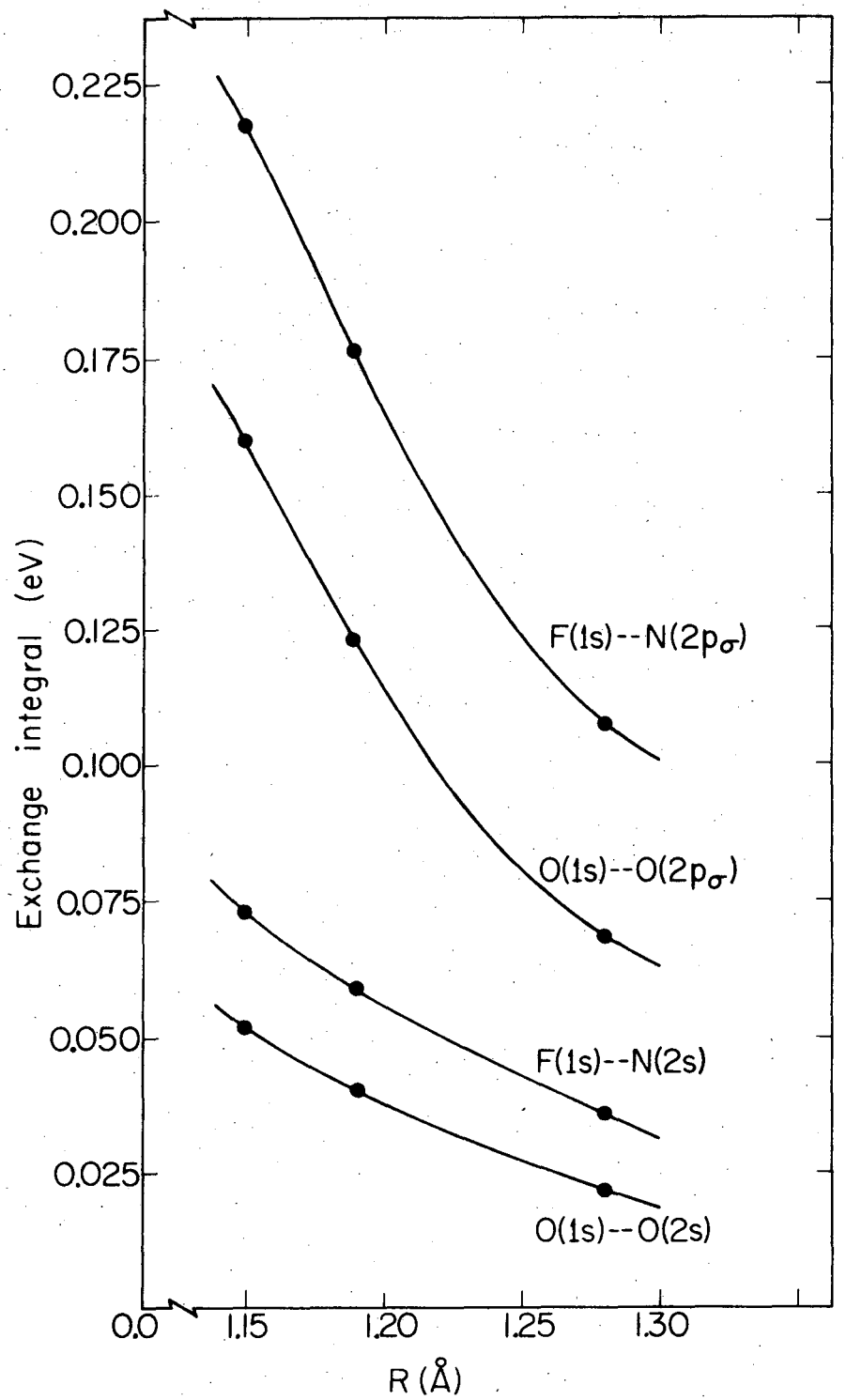
Fig. 5



XBL735-2862

Fig. 6

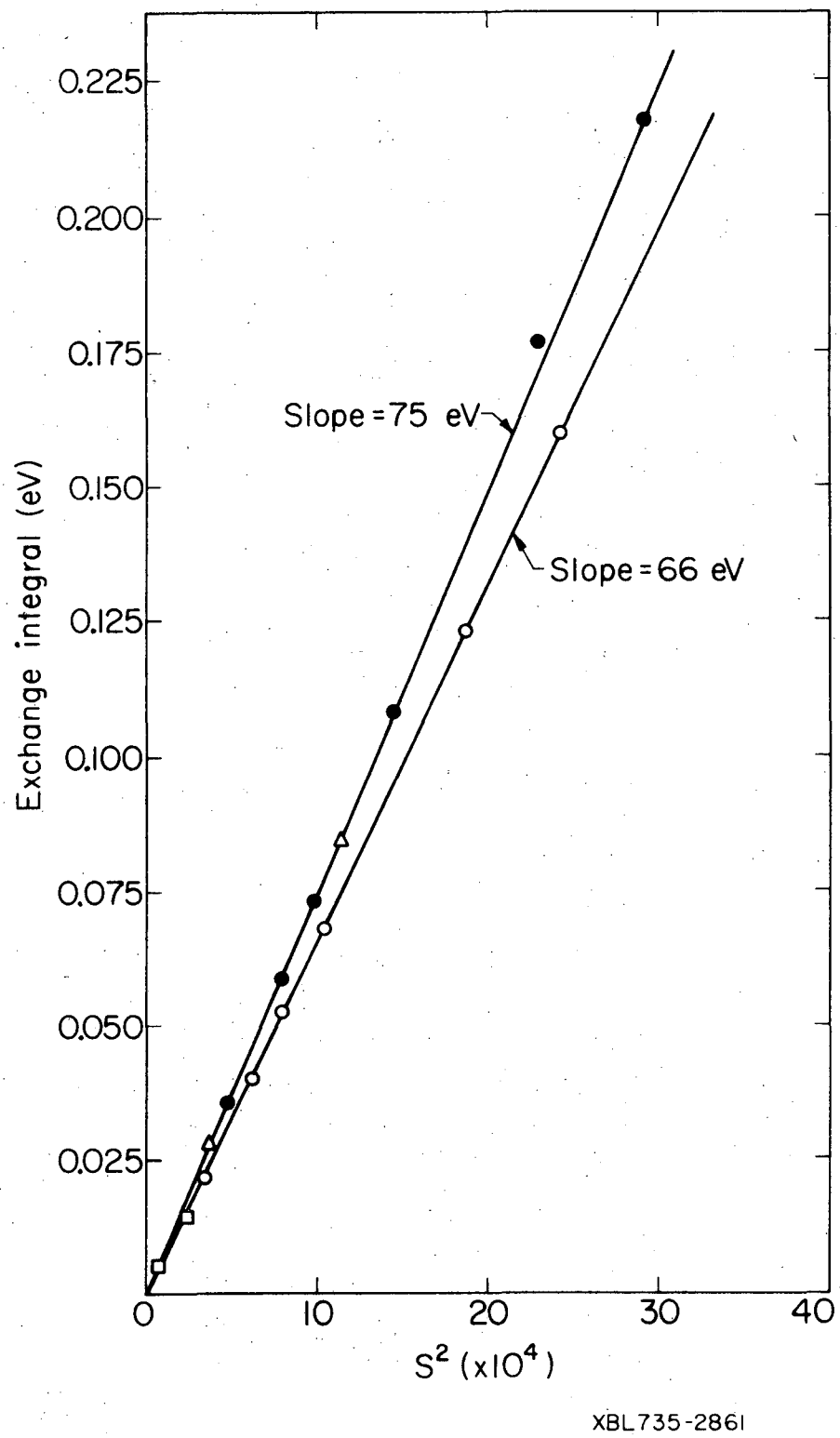

0.225
0.200
0.175
0.150
0.125
0.100
0.075
0.050
0.025
Exchange integral (eV)
Slope = 75 eV
Slope = 66 eV
0
10
20
30
40
S² (x10⁴)
XBL735-2861

Fig. 7

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