with excitation of the C=S stretch. Hence it is tempting to assign the 8.92-eV IP to the b orbital and the 9.46-eV band to the lone pair a orbital.

Acknowledgment. D. A. S. is grateful to the U. S. Air Force Office of Scientific Research and the National Research Council for a postdoctoral fellowship.

Lone Pair Orbitals and Their Interactions Studied by Photoelectron Spectroscopy. II. Equivalent Orbitals in Saturated Oxygen and Sulfur Heterocycles

D. A. Sweigart and D. W. Turner*

Contribution from the Physical Chemistry Laboratory, Oxford University, Oxford, England. *Received November 9, 1971*

Abstract: The helium I photoelectron spectra of some oxygen and sulfur heterocycles are reported. Lone pair interactions are interpreted in terms of through-space and through-bond mechanisms. Lone pair interaction in six-membered heterocycles having the heteroatoms para seems to occur predominantly through bond and is greater for oxygen; with the heteroatoms meta the interaction is mainly through space and is greater in the sulfur compounds. Evidence of the Jahn–Teller effect operating in 1,3,5-trioxane is presented.

In an earlier paper[1] we described the He I molecular photoelectron spectra (pe spectra in the text) of a number of carboxylic acid derivatives concentrating upon those bands ascribable to lone pairs on the oxygen and (in the amides) nitrogen atoms. We considered the different interactions that these might experience with other molecular orbitals of appropriate symmetry. Generally, these interactions were between nonequivalent orbitals of rather different energy.

There has been considerable interest of late in the interactions of equivalent orbitals.[2] Heilbronner[3] especially has used the photoelectron spectroscopic technique to investigate equivalent orbital interactions in various systems. We have studied the photoelectron spectra of oxygen and sulfur heterocycles with the hope of ascertaining the mechanisms by which equivalent lone pair orbitals interact in these systems. Qualitative overlap notions and group theory have been used to try to establish whether the lone pair orbital splitting is due primarily to through-space or through-bond interaction. In addition, an attempt has been made to identify the orbitals responsible for any through-bond interactions.

Experimental Section

Most of the compounds were purchased from standard sources. The He I photoelectron spectra were recorded on a Perkin-Elmer PS 15 instrument equipped with a heated inlet system. Only 1,3,5-trithiane required heating to obtain sufficient vapor pressure. The sample vapor pressure was usually maintained at about 0.1 Torr.

Results and Discussion

The He I photoelectron spectra of the compounds studied are given in Figures 1–5. Table I lists the lone pair orbital ionization potentials (IP's) together with any observed splitting.

Table I. Lone Pair IP's in Some Oxygen and Sulfur Heterocycles

Compound	IP(n),[a] eV	ΔIP(n)
1,3-Dioxolane	10.1, 10.65	0.55
2,2-Dimethyl-1,3-dioxolane	9.71, 10.20	0.49
Tetrahydropyran	9.50	
1,3-Dioxane	10.1, 10.35	0.25
1,4-Dioxane	9.43, 10.65	1.22
1,3,5-Trioxane	~10.8, 11.15	≤0.3[b]
Pentamethylene sulfide	8.45	
1,3-Dithiane	8.54, 8.95	0.41
1,4-Dithiane	8.58, 9.03	0.45
1,3,5-Trithiane	8.76, 9.27	0.51
1,4-Thioxane	8.67 (S), 10.00 (O)	

[a] Vertical IP's of lone pair orbitals. [b] See discussion in text.

The lone pair orbitals (n) are expected to be the highest energy filled molecular orbitals and the bands at low IP in Figures 1–5 are due to ionization from these orbitals. Because of symmetry restrictions the oxygen and sulfur lone pairs are primarily p-type orbitals and are essentially nonbonding. This is the reason that the corresponding photoelectron bands are often rather sharp. One should note that the situation with nitrogen compounds is very different. Nitrogen "lone pair" photoelectron bands tend to be broad, meaning that nitrogen lone pairs are, in fact, bonding to a significant degree. The clearest examples of these effects are water and ammonia.[4,5] The oxygen lone pair in water is of pure p type (b_1 in C_{2v}) and cannot interact with the O–H σ orbitals since they are of $a_1 + b_2$ symmetry. In ammonia the nitrogen lone pair transforms as a_1 in C_{3v} and hence can mix with the N–H σ orbitals which transform as $a_1 + e$. Indeed, the lone pair band in the photoelectron spectrum of water is sharp while in ammonia it is broad. We shall have occasion to refer to this difference between nitrogen and oxygen (sulfur) below.

---

(1) D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5592 (1972).

(2) R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971).

(3) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 1033 (1970).

(4) D. W. Turner, A. D. Baker, C. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, London, 1970.

(5) D. A. Sweigart and J. Daintith, *Sci. Progr.* (*London*), **59**, 325 (1971).

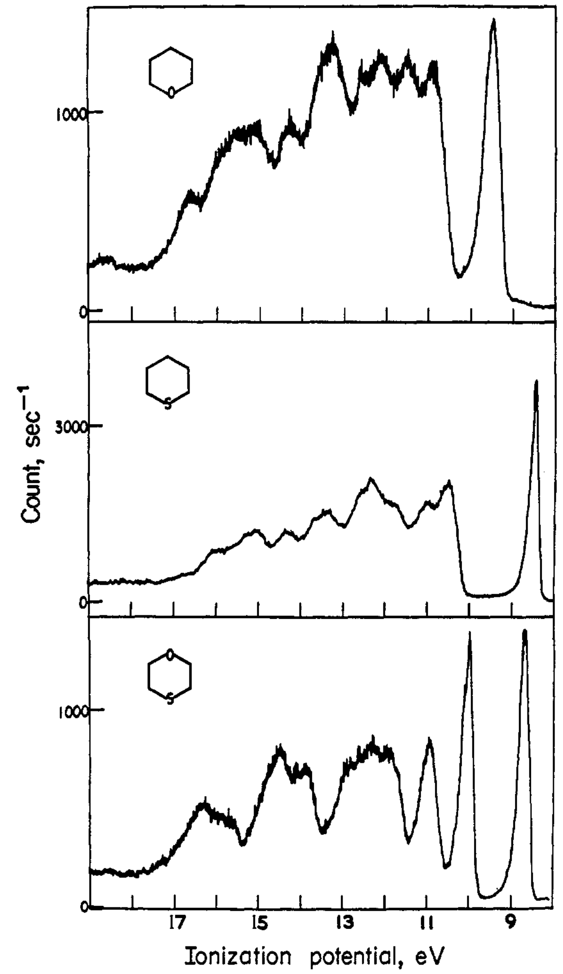

Figure 1. The He I photoelectron spectra of some oxygen and sulfur heterocycles.

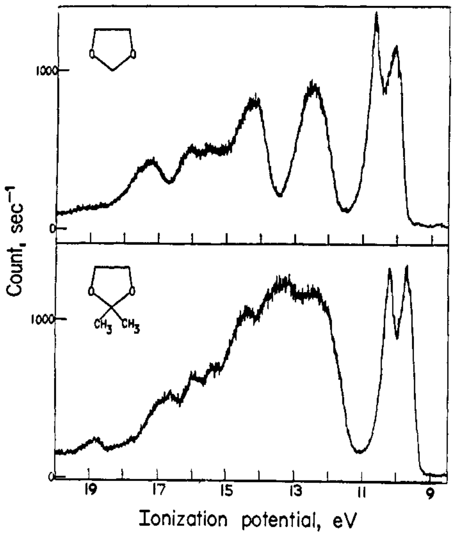

Figure 2. The He I photoelectron spectra of 1,3-dioxolane and its 2,2-dimethyl derivative.

Figure 1 illustrates the relative energy[6] of oxygen and sulfur lone pairs in heterocyclic systems. The sulfur lone pair IP in pentamethylene sulfide is 1.05 eV lower than the oxygen lone pair IP in tetrahydropyran. In 1,4-thioxane this difference increases to 1.33 eV.

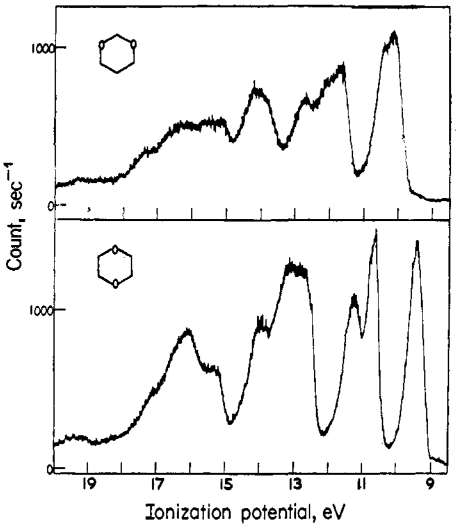

Figure 3. The He I photoelectron spectra of 1,3-dioxane and 1,4-dioxane.

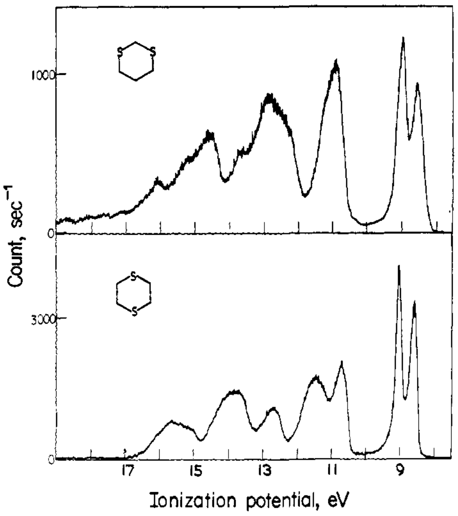

Figure 4. The He I photoelectron spectra of 1,3-dithiane and 1,4-dithiane.

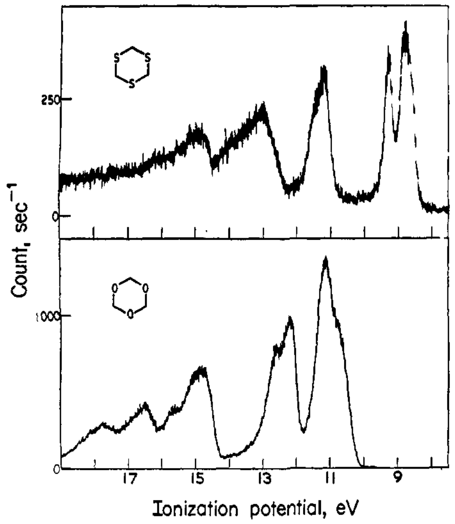

Figure 5. The He I photoelectron spectra of 1,3,5-trithiane and 1,3,5-trioxane.

---

(6) Assuming Koopmans' theorem to be valid.

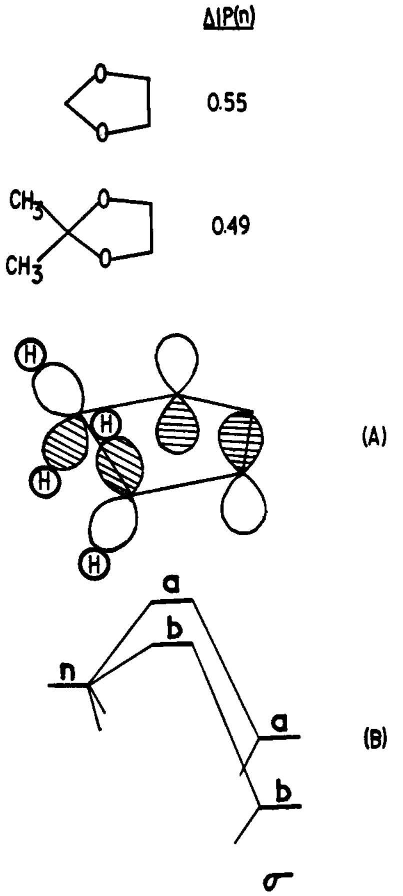

Figure 6. Splitting of lone pair orbital IP's in dioxolane: (A) interaction of the lone pair orbital of a symmetry (C_2) with the C–H σ orbitals of a symmetry; (B) a qualitative MO scheme.

The He I photoelectron spectra of 1,3-dioxolane and its 2,2-dimethyl derivative are given in Figure 2. Infrared and Raman studies[7,8] as well as nmr work[9,10] suggest that the ring in the dioxolanes is puckered so that the molecule possesses C_2 symmetry. The degree of puckering is not known, but the infrared and Raman spectra of 1,3-dioxolane have been assigned[7] assuming near C_{2v} symmetry, *i.e.*, near planarity of the ring. In C_2 symmetry the lone pair orbitals transform as a + b. The plus combination ($n_1 + n_2$) has b symmetry and the minus combination ($n_1 - n_2$) has a symmetry. The photoelectron spectra show that a and b are separated by 0.55 eV in 1,3-dioxolane and 0.49 eV in the 2,2-dimethyl derivative (Table I). Molecular models show that direct overlap of the lone pair orbitals is not likely to be large. Hence we cannot ascribe the 0.5-eV splitting to through-space interaction. We must look for a through-bond mechanism. To investigate this we divide the σ orbital network into orbitals localized between the ring C and O atoms and into orbitals localized along the C–H bonds. Such a separation is permissible for qualitative arguments and is commonly used.[2,11]

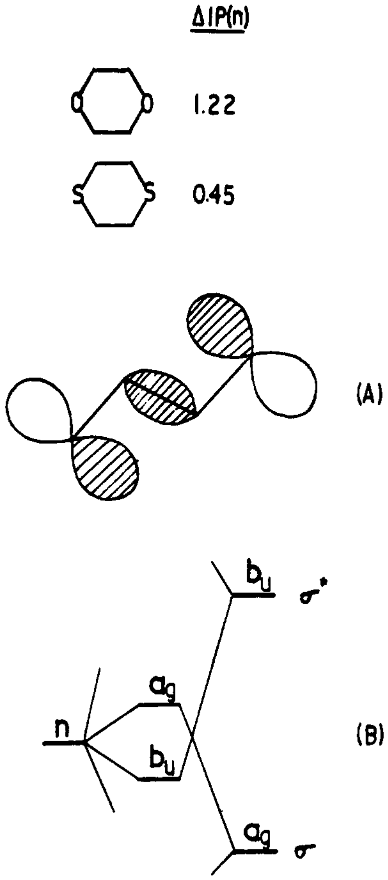

Figure 7. Splitting of lone pair orbital IP's in para systems: (A) interaction of lone pair orbitals of a_g symmetry with C–C bonds of a_g symmetry; (B) a qualitative MO scheme.

In 1,3-dioxolane the orbitals centered on the C–H bonds of carbon C_2 transform as a + b. The other C–H σ orbitals (C_4 and C_5) transform as 2a + 2b. Simple overlap and electronegativity considerations suggest that the highest energy bonding C–H σ orbital should be of a symmetry. This orbital and the C–C σ orbital may be responsible for the photoelectron band centered at 12.5 eV in 1,3-dioxolane. A similar situation occurs in ethane.[4] Figure 6 illustrates how this a orbital interacts with the lone pair a orbital to produce the splitting shown. Any through-space interaction would also lead to the order a above b and would increase the splitting expected. If the lone pair splitting were to be ascribed largely to interaction with the C–H σ orbitals on C_2 one might expect methyl substitution at C_2 to have a pronounced effect on the lone pair splitting. That this does not occur (Table I) supports the suggestion that the principal interaction is *via* the C–H σ orbitals of C_4 and C_5. We infer that the dominant effect of C_4 and C_5 compared with C_2 group orbitals reflects tighter binding for the latter and a higher electronegativity for C_2.

The photoelectron spectra of 1,4-dioxane and 1,4-dithiane (Figures 3 and 4) show lone pair splittings of 1.22 and 0.45 eV, respectively. Both of these molecules exist in the chair conformation in the gas phase.[12] Molecular models show that direct overlap of the lone pair orbitals is unlikely. So again we must look for a through-bond mechanism to explain the splitting.

---

(7) S. A. Barker, E. J. Bourne, R. M. Pinkard, and D. H. Whiffen, *J. Chem. Soc.*, 802 (1959).

(8) J. R. Durig and D. W. Wertz, *J. Chem. Phys.*, **49**, 675 (1968).

(9) R. U. Lemieux, J. D. Stevens, and R. R. Fraser, *Can. J. Chem.*, **40**, 1955 (1962).

(10) C. Altona and A. P. M. van der Veek, *Tetrahedron*, **24**, 4377 (1968).

(11) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

(12) E. L. Eliel, N. L. Albinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965.

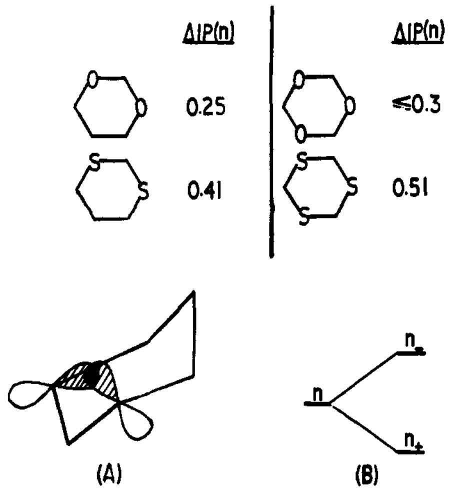

Figure 8. Splitting of lone pair orbital IP's in meta systems. Through-space interaction is shown in (A) and an orbital diagram in (B).

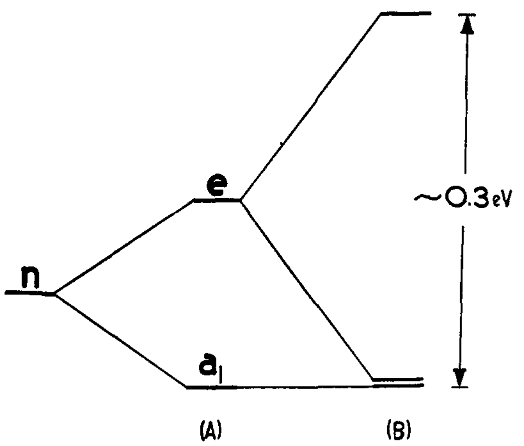

Figure 9. Lone pair orbital splitting in trioxane. Through-space and -bond splitting leads to (A); (B) represents Jahn–Teller forces operating on the ^2E state.

The molecules have C_{2h} symmetry and the lone pair orbitals transform as $a_g + b_u$. Models suggest that the major through-bond interaction is with the C–C σ orbitals which transform as $a_g + a_u$ while the C–C σ^* orbitals transform as $b_g + b_u$. Through-bond coupling *via* the C–H bonds should be small because the bonds are staggered. The situation is illustrated in Figure 7. The important thing to note about these cases is that the splitting in oxygen exceeds that in sulfur. This may be because the oxygen lone pair orbitals are a better match with the C–C σ orbitals. Thus the energy separation between the C–C σ orbital and the lone pairs is probably greater for sulfur. This would yield greater splitting in the oxygen compound. In addition, the sulfur orbitals may be too diffuse for optional overlap with the σ orbitals.

Figure 8 gives the lone pair splitting for some six-membered rings having the heteroatom meta. All these compounds exist in the chair conformation[12,13] and models suggest that direct overlap is likely. This is shown in Figure 8. We therefore ascribe most of the lone pair splitting to through space (direct overlap) in these compounds. Direct overlap would stabilize the plus combination (n_+). For the meta systems the splitting in sulfur is greater than in oxygen. This is opposite to that shown by the para systems (Figure 7). It seems that through-space coupling is greater for sulfur due, perhaps, to the greater size of the sulfur 3p orbitals.

Trioxane and trithiane represent a somewhat unusual situation. These molecules have C_{3v} symmetry and the lone pair orbitals transform as a_1 + e. Direct overlap would be expected to stabilize the a_1 orbital relative to the e orbitals. Simple overlap considerations suggest that any through-bond interaction should also place e above a_1. This is nicely confirmed in trithiane (Figure 5) where two lone pair bands are observed, the lowest IP band having approximately twice the area of the next band. In trioxane the bands overlap and their separate areas cannot be measured. If we associate the shoulder on the higher energy side with an unresolved band of lower integrated intensity, the splitting appears in the reverse sense from that in trithiane. It is difficult to understand how this could occur unless some special force is operating in trioxane. Ionization from the lone pair e level yields an ion in a ^2E electronic state which may be susceptible to Jahn–Teller forces. We suggest that in trioxane the e level is placed above the a_1 due to through-space interaction, but Jahn–Teller forces remove the degeneracy in the ^2E state as shown in Figure 9. A Jahn–Teller splitting of about 0.3 eV would be sufficient to produce the observed spectrum if the splitting by direct overlap were about 0.15 eV.

A through-space splitting of 0.15 eV in trioxane would be less than that in trithiane (0.51 eV), in agreement with the results for 1,3-dioxane and 1,3-dithiane. That a Jahn–Teller splitting is seen should not be surprising. Such splitting has been observed in numerous molecules.[4,14–18] However, it must be explained why Jahn–Teller forces operate in trioxane while apparently not operating to a noticeable degree in trithiane. Considering the nature of the Jahn–Teller effect[19] one expects the splitting to decrease as the frequency of the Jahn–Teller active vibration decreases. Vibrational frequencies usually decrease as one goes down a group in the periodic table. This is due in part to a simple mass effect. Thus the failure to observe Jahn–Teller splitting in the photoelectron spectra of CCl_4 and CBr_4, while CH_4 shows a splitting of about 0.7 eV, has been ascribed[4] to the large masses of Cl and Br. The Jahn–Teller splitting in the hydrides of group IV decreases as the atomic number increases and is approximately proportional to the M–H bond distances, where M = C, Si, and Ge.[17]

One also expects Jahn–Teller splitting to decrease as the orbital involved becomes more nonbonding.[15] The

---

(13) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967, Appendix II.

(14) H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969).

(15) C. R. Brundle, M. B. Robin, and H. Basch, *ibid.*, **53**, 2196 (1970).

(16) A. W. Potts, H. J. Lempka, D. G. Streets, and W. G. Price, *Phil. Trans. Roy. Soc. London, Ser. A*, **268**, 59 (1970).

(17) B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, *J. Chem. Phys.*, **53**, 768 (1970).

(18) P. J. Bassett and D. R. Lloyd, *J. Chem. Soc. A*, 1551 (1971).

(19) H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser. A*, **161**, 220 (1937); R. F. W. Bader, *Can. J. Chem.*, **40**, 1164 (1962).

separation between the average lone pair orbital IP and the σ orbital IP's for trioxane is less than in trithiane. For example, the separation between the lone pairs and the first σ ionization is 1.2 eV in trioxane and 2.2 eV in trithiane. On this basis one expects the trioxane lone pair orbitals to be mixed in with the σ network to a greater extent, *i.e.*, be more bonding and so, other things being equal, be more susceptible to Jahn–Teller forces.

Finally, we observe that the first σ orbital bands in trioxane and trithiane are split. From group theory and overlap arguments one expects the first σ level to be degenerate (e) and hence susceptible to Jahn–Teller forces. This may be the origin of the σ level splitting. The first σ band (Figure 5) is split by 0.40 eV in trioxane and 0.2 eV in trithiane. By the above arguments one indeed would expect a greater splitting in the trioxane σ level if Jahn–Teller forces operate.

It is of interest to note that the arguments presented above for oxygen and sulfur heterocycles cannot be applied to the analogous nitrogen systems. This is due to the different symmetry properties of the nitrogen lone pair orbitals, as is discussed above. For example, the lone pair splitting in piperazine[20] and *N,N*-dimethylpiperazine[21] is very small while, as seen above, it is substantial in the oxygen and sulfur systems.

In conclusion we emphasize that lone pair splitting in the heterocycles studied here is greater in sulfur when through space and greater in oxygen when through bond.

Acknowledgment. D. A. S. is grateful to the U. S. Air Force Office of Scientific Research and the National Research Council for a postdoctoral fellowship.

---

[20] C. R. Brundle and M. B. Robin, "Determination of Organic Structures by Physical Methods," Vol. 3, Academic Press, in press.

[21] D. A. Sweigart and D. W. Turner, unpublished work.

Ab Initio Studies of Hyperfine Coupling in Free Radicals. II. Methyl and Fluoromethyl Radicals, and α-Fluorine Spin Coupling Parameters[1]

Hideyuki Konishi and Keiji Morokuma*[2]

Contribution from the Department of Chemistry,
the University of Rochester, Rochester, New York 14627.
Received January 13, 1972

Abstract: By using an *ab initio* LCAO–SCF–MO–CI method with Slater sis basets, the isotropic H, ^{19}F, and ^{13}C coupling constants of planar CH_3 and planar and nonplanar CH_2F are calculated. The basis set DZS proposed in I improves the calculated ^{13}C and ^{19}F coupling drastically. Angular dependency of the ^{19}F coupling is very small as a result of cancellation between an increase of the spin delocalization contribution and a decrease of the spin polarization contribution. Based on models in which the half-occupied π^* orbital of CH_2F is artificially modified, new sets of values of spin coupling parameters Q which are very different from existing ones are proposed. An important feature of the new values suggests that the $a(^{19}F)$ is mainly due to the net π spin population on the C–F bond that polarizes the fluorine s spin.

Isotropic and anisotropic hyperfine coupling constants by electron spin resonance (esr) and nuclear magnetic resonance (nmr) spectroscopy provide an important insight to the electron distribution in polyatomic free radicals. Interpretation of coupling constants has been carried out mostly by semiempirical molecular orbital (MO) and valence bond methods. Semiempirical methods can often explain experimental results, but always leave an ambiguity in their conclusions due to the arbitrary parametrization.

The recent development of programs and faster computers has made it possible to carry out reliable *ab initio* calculations of electronic structures for polyatomic molecules. Nevertheless hyperfine coupling calculations by *ab initio* methods have been limited to simple hydrides such as CH, OH, NH_2, and CH_3.[3–5] One of the reasons for this is that the minimal basis set, the double ζ basis set and the double ζ set with additional p and d polarization orbitals, which predict the geometry, energy, and other expectation values reasonably well, often give coupling constants in poor agreement with experiments. More extended basis sets are often prohibitive for calculations of larger molecules.

In the preceding paper,[1] we proposed two new basis sets of Slater-type orbitals, called MZS and DZS sets, for some of the first-row atoms. They are the minimal and double ζ Slater-type basis sets, respectively, augmented by an extra 2s orbital with a large exponent. These basis sets are proposed upon our belief that the minimal or double ζ basis sets predict correctly most electronic properties of molecules and that the only main reason why they failed to predict spin densities is their inadequacy near the nucleus. The extra 2s orbital drastically improves the behavior of the spin density

---

[1] Part I of the series: H. Konishi and K. Morokuma, *Chem. Phys. Lett.*, 12, 408 (1971).

[2] Alfred P. Sloan Research Fellow.

[3] S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, 49, 529 (1968); 52, 1740, 5596 (1970); S. Y. Chang, Thesis, University of Washington, 1969.

[4] W. Meyer, *J. Chem. Phys.*, 51, 5149 (1969), and literature therein.

[5] J. Higuchi and S. Aono, *ibid.*, 28, 527 (1958); 32, 52 (1960); A. Padgett and M. Krauss, *ibid.*, 32, 189 (1960); A. L. H. Chung, *ibid.*, 46, 3144 (1967).