from the nitronyl nitroxide ring to the aromatic ring. This equation predicts that the spin density, at a given atom in the aromatic ring, should be proportional to the spin density at the bridging carbon atom in the nitronyl nitroxide ring. It is also proportional to the square of the resonance integral $(\gamma\beta)^2$ which should show the normal $\cos^2\theta$ dependence for rotation about the bridging bond's axis. The other terms in eq 24 involve bond orders and polarizabilities. One can estimate the relative contribution of these terms by considering various types of classifications which might arise.

(1) If the spin density at bridging atom s of system I is positive and atom ν of system II belongs to a different class than the bridging atom ξ of system II, then $(D_{\xi\nu})^2$ will be greater than zero and the contribution of the first term to ρ_ν will be positive. If ν and ξ belong to the same class, then $(D_{\xi\nu})$ will be either zero or small and positive, and the contribution of the first term will be unimportant and the second term will dominate ρ_ν. When ξ and ν are in the same class $\pi_{\xi\nu}$ is negative in AH.[8] The McLachlan spin density correction $\rho_s{}^1$ is normally positive when the Hückel density $\rho_s{}^0$ is positive, so ρ_ν will be small and negative.

(2) If the Hückel spin density at bridging atom s is zero, then the first term in eq 23 is zero. The McLachlan correction term $(\rho_s{}^1)$ is normally negative in this case. The polarizability is negative and small for an atom in the same class (except for $\xi = \nu$ where $\pi_{\xi\nu}$ is large). When the atoms are in different classes, the polarizability is large and positive.[8] The spin density for a given atom ν will therefore be large and negative when ν is in a different class from ξ and small and positive when ν is in the same class as ξ. Our qualitative predictions for ρ_ν are summarized as follows

spin density at bridging atom of I	different class for ξ and ν (ortho and para position)	same class for ξ and ν (meta position)
$\rho_s > 0$	large and positive	small and negative
$\rho_s < 0$	large and negative	small and positive

We used eq 24 to examine our model nitroxides (Chart II). Since $\rho_s{}^0 = 0$, only the second term contributed with $\rho_s{}^1 < 0$. In this case, the spin densities in the aromatic rings should be proportional to the polarizability. Column 10 of Table II lists the Hückel polarizabilities. These values are found to parallel the results from the variational calculation (column 6) and the perturbation calculation (column 9). The failure to predict the correct sign for the meta position of the *o*- and *p*-pyridyl radicals is not a failure of eq 24 but is inherent in the McLachlan calculation.

The perturbation procedure used in this section does not apply directly to an INDO calculation where electronic interactions have to be explicitly considered. Considering the approximate nature of eq 24, however, we thought it worthwhile to calculate the "INDO π electron polarizability" $(\pi_{\xi\nu})$ by eq 16. The INDO polarizabilities (column 5 of Table II) are found to qualitatively reproduce the signs and relative magnitudes of the experimental spin densities.

The perturbation treatment which has been outlined is useful in that it yields some insight into the mode of spin propagation in these radicals. Although eq 24 is not quantitative, we think that it will allow one to predict the signs and relative magnitudes of spin densities in radicals of this type.

Acknowledgment. This work was supported in part by National Science Foundation Grant GP-25908. Numerical calculations were carried out at the Computing Center of the University of Rochester.

Lone Pair Orbitals and Their Interactions Studied by Photoelectron Spectroscopy. I. Carboxylic Acids and Their Derivatives

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Abstract: The helium I photoelectron spectra of carboxylic acid derivatives are reported. The carbonyl oxygen lone pair orbital (n_0) and the approximately nonbonding π_2 orbital are the two highest energy filled molecular orbitals and have very similar ionization potentials. Assignments are proposed based on considerations of vibrational fine structure and inductive effects. The spectra of ethylene carbonate and ethylene trithiocarbonate are also included and discussed.

The valence shell structure of atomic and molecular vapors can be so readily obtained by the use of helium I photoelectron energy analysis (molecular photoelectron spectroscopy) that it has come to provide an important test of the adequacy of quantum calculations. Together with postulates about the degree of adherence to Koopmans' theorem, all the bands in such a photoelectron spectrum can be related in principle to the eigenvalues obtained by such calculations. In the absence of accurate quantum calculations it has often proved expedient, however, to concentrate on some feature or features which relate to particularly interesting portions of the valence shell structure. This more empirical approach has proved to be especially appropriate in organic and organometallic chemistry where studying series of compounds whose structure may vary only little from compound to compound affords a ready insight into some of the concepts of molecular orbital theory important to the practicing chemist. For example, the resonance interaction between the π electrons in multiple bonds can be discussed without reference to the electrons of the σ framework. Similarly the effect of substituents upon the π orbitals of the benzene ring has been discussed without referring to the related but more difficultly decipherable effects upon the σ framework. We shall adopt this approach in the present paper which refers in the main to ionization from oxygen lone pair orbitals and to the interactions of such orbitals.

The lone pair concept in photoelectron spectroscopy arose naturally out of the identification in the photoelectron (pe) spectra of certain compounds of strong, sharp peaks lacking an extensive vibrational progression which marked them as due to ionization from orbitals localized mainly upon one atom. The earliest clear example of this in a complex molecule is chlorobenzene where the only sharp peaks in the spectrum are assigned to the $3p_x$ and $3p_y$ chlorine lone pairs. More strictly, such absence of vibrational structure points to a similarity of geometry between the molecule and ion, a condition which may not necessarily be fulfilled by ionization from a formal lone pair. Nevertheless, this conceptual simplification is a useful one even though ionization of what a chemist would regard as a lone pair may in fact involve extensive geometrical changes which prevent its easy recognition in a pe spectrum. Thus the nitrogen lone pair in amines as well as some oxygen and sulfur lone pairs affords evidence of marked geometrical changes upon ionization which make their identification in pe spectra less obvious.

In simple monocarbonyl compounds (*e.g.*, formaldehyde) and in ethers only one molecular orbital (O 2p) is describable easily as an oxygen lone pair. Sometimes this corresponds, as here, to the highest energy electrons but in other cases (*e.g.*, anisole) a deeper lying orbital has been so designated. In the carboxylic acid derivatives, however, there are two molecular orbitals which can be approximately so described though one has the appropriate symmetry to be involved with the σ framework, while the other has the appropriate symmetry to be involved with a π orbital. In the present paper we report and discuss the photoelectron spectra of a range of carboxylic acid derivatives on this basis.

Experimental Section

Most of the compounds were purchased from standard sources. The 2,2,2-trifluoroethyl esters were synthesized by standard methods. The He I photoelectron spectra were recorded on a Perkin-Elmer PS 15 instrument equipped with a heated inlet system. Only two compounds, acetamide and ethylene trithiocarbonate, required heating to obtain sufficient vapor pressure. The sample vapor pressure was usually maintained at about 0.1 Torr.

Results and Discussion

Derivatives of Formic Acid and Acetic Acid. Calculations predict the two highest filled orbitals in the esters and amides of simple carboxylic acids to be the carbonyl oxygen lone pair (n_O) and the approximately nonbonding antisymmetric π_2 orbital. The latter orbital arises from the p orbitals on C, O, and X (mainly O and X) in the R′COX molecule where X is OH, OR,

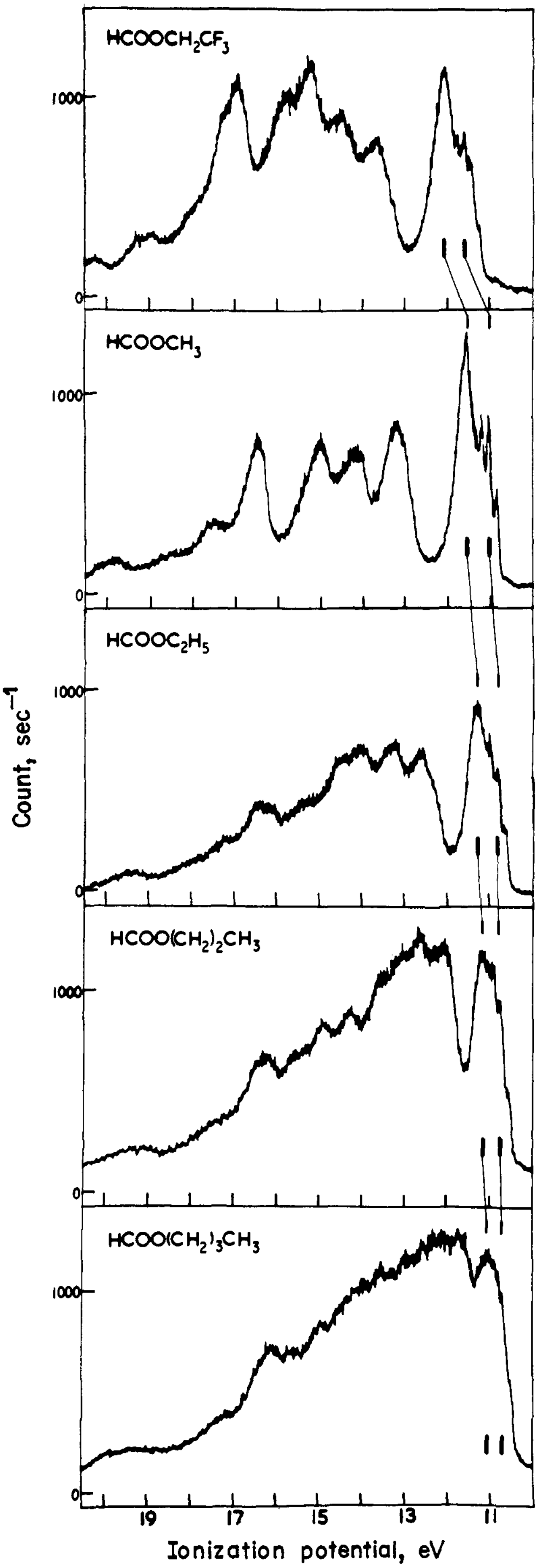

Figure 1. The He I photoelectron spectra of some esters of formic acid. The n_0 and π_2 photoelectron bands are indicated by vertical bars.

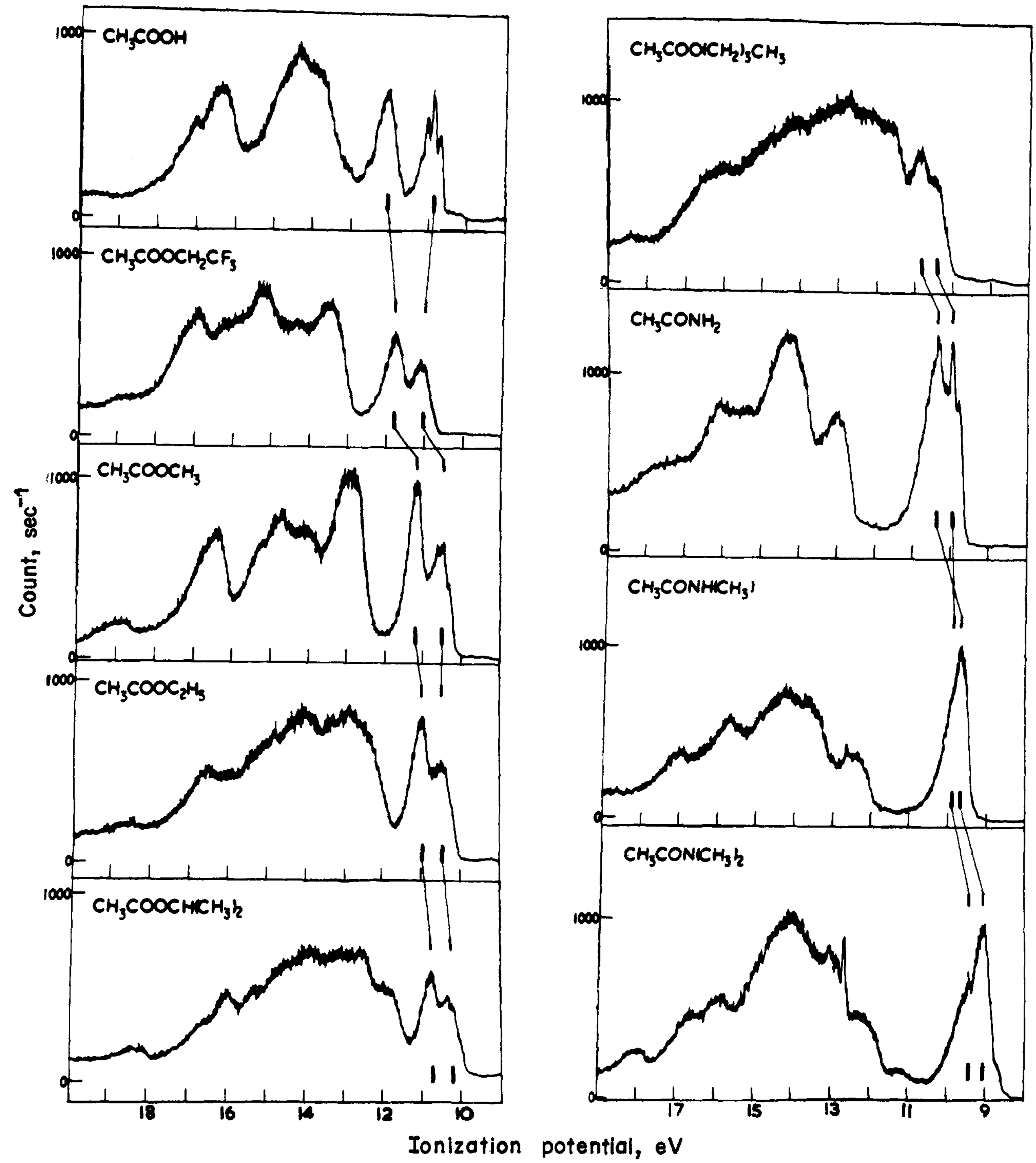

Figure 2. The He I photoelectron spectra of some derivatives of acetic acid. The n_0 and π_2 photoelectron bands are indicated by vertical bars.

or NR_2. If the conjugation between X and the carbonyl group were removed, the π_2 orbital would correspond to the lone pair p orbital on the X group.

According to Hunt and Simpson[1] and n_0 and π_2 orbitals in carboxylic acids, amides and esters should be accidentally degenerate. Brundle, *et al.*,[2] previously reported the photoelectron spectra of formic acid and certain of its amides. Armed with SCF calculations they concluded that the IP (ionization potential) of the electrons in the n_0 orbital was lower than the IP of the π_2 electrons in formic acid and formamide, the reverse being true in *N*-methylformamide and *N*,*N*-dimethylformamide. In addition, it was found that the n_0 ionization excited the C=O stretching vibrations, the frequency range in the ions being 1450–1600 cm^{-1}. Ionization from π_2 excited a low frequency vibration, 600–700 cm^{-1} for the amides and 1120 cm^{-1} for formic acid.

We felt that a study of a series of carboxylic acids, esters, and amides would be of interest particularly

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(1) H. D. Hunt and W. T. Simpson, *J. Amer. Chem. Soc.*, 75, 4540 (1953).

(2) C. R. Brundle, D. W. Turner, M. B. Robin, and H. Basch, *Chem. Phys. Lett.*, 3, 292 (1969).

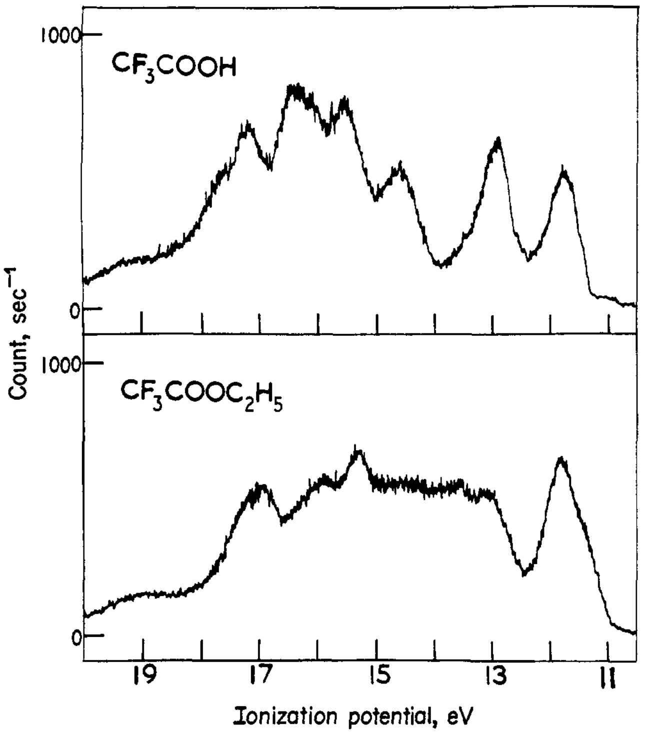

Figure 3. The He I photoelectron spectra of trifluoroacetic acid and its ethyl ester.

with respect to the question of the n_0, π_2 separation. A possible correlation with inductive effects would also be useful. A recent calculation[3] suggests that in the formic acid derivatives, HCOX, the order of increasing stability (*i.e.*, increasing IP) of the n_0 orbital *relative* to the π_2 is $X = F < OH < NH_2 < O^-$. This would lead one to expect the esters to lie between the acids and amides insofar as the n_0 and π_2 orbital IP's are concerned. The results to follow show this to be the case.

The photoelectron spectra of the formic acid and acetic acid derivatives are given in Figures 1-3. The first two highest energy (lowest IP) bands are almost certainly due to ionization from the n_0 and π_2 orbitals. Figure 4 shows the n_0 and π_2 bands on an expanded scale for some of the compounds. Table I lists the ionization potentials and vibrational spacings present in the n_0 and π_2 photoelectron bands.

It is well known that carboxylic acids are associated in condensed phases and frequently in the gas phase also. Using known equilibrium constants for dimer formation in the gas phase[4] we calculate, at the pressure ($\leqslant$0.1 Torr) and temperature (room temperature) used, that formic acid and trifluoroacetic acid were at least 97% dissociated to the monomer while acetic acid was at least 90% dissociated. Actually the temperature of the sample vapor in the target area generally exceeded room temperature meaning that even a smaller percentage of the molecules were in the associated form. Accordingly we feel that the main, intense bands in the photoelectron spectra of the acids are to be ascribed simply to the monomeric species.

As Figures 1-4 show, there is a band structure suggestive of n_0, π_2 overlap in many of the compounds

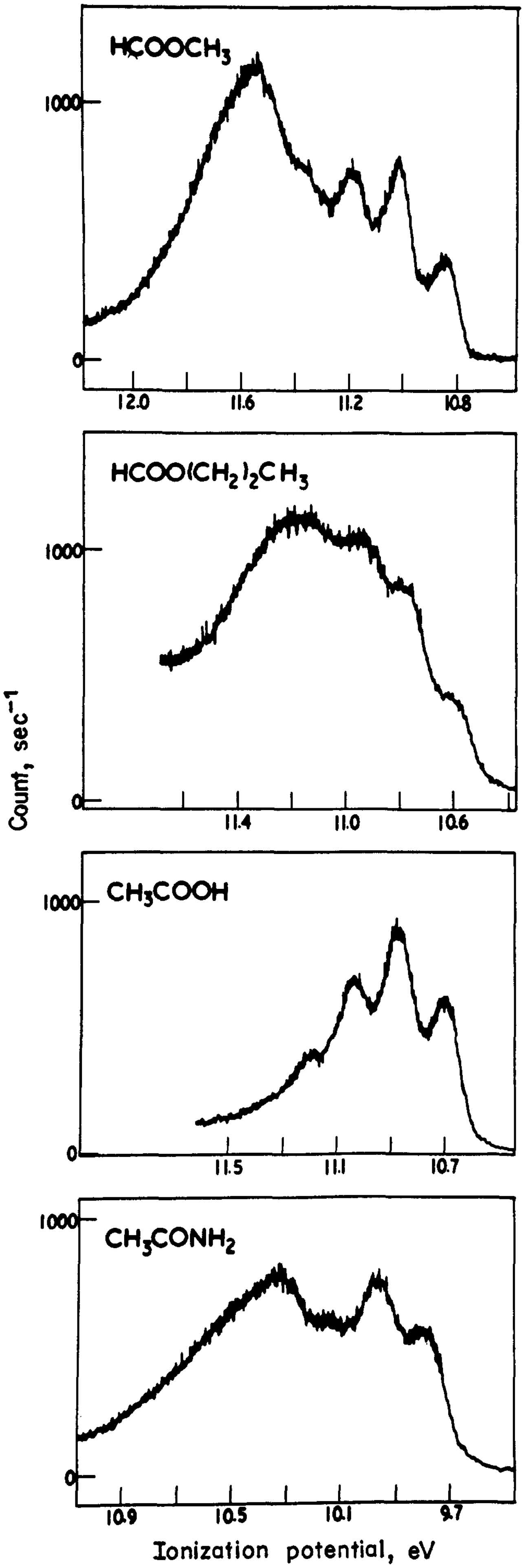

Figure 4. Details of the n_0 and/or π_2 photoelectron bands for some simple carboxylic acid derivatives.

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(3) H. Basch, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **49**, 5007 (1968).

(4) F. H. MacDougall, *J. Amer. Chem. Soc.*, **58**, 2585 (1936); J. Karle and L. O. Brockway, *ibid.*, **66**, 574 (1944); E. W. Johnson and L. K. Nash, *ibid.*, **72**, 547 (1950); M. D. Taylor, *ibid.*, **73**, 315 (1951); R. E. Lundin, F. E. Harris, and L. K. Nash, *ibid.*, **74**, 4654 (1952); M. D. Taylor and M. B. Templeman, *ibid.*, **78**, 2950 (1956).

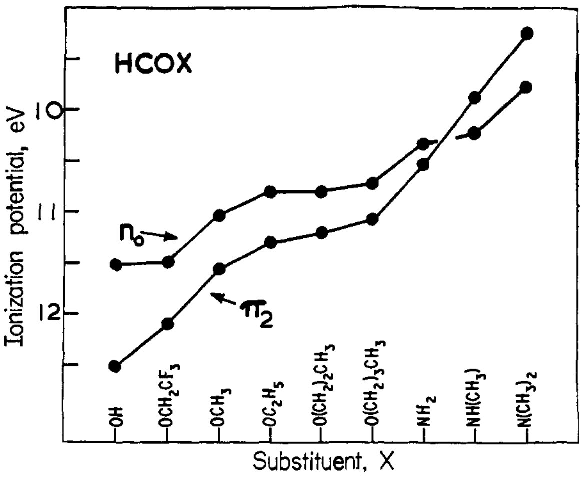

Figure 5. Comparison of n_0 and π_2 orbital IP's for formic acid derivatives. The amide IP's are from ref 2.

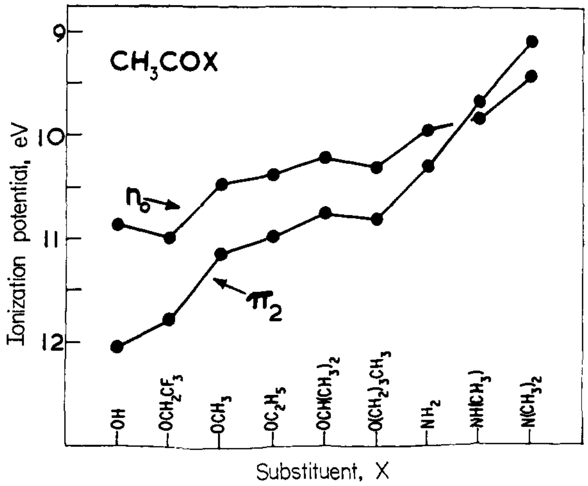

Figure 6. Comparison of n_0 and π_2 orbital IP's for acetic acid derivatives.

Table I. IP's of the n_0 and π_2 Orbitals of Carboxylic Acid Derivatives

	IP(n_0), eV				IP(π_2), eV
Compound	Adiabatic	1 ← 0	Vertical	ν, cm^{-1} [b]	Vertical
HCOOH[a]	11.33	11.51	11.51	1460	12.51
$HCOOCH_2CF_3$	11.31	11.48	11.65	1370	12.09
$HCOOCH_3$	10.85	11.02	11.02	1370	11.55
$HCOOCH_2CH_3$	10.62	10.79	10.96	1370	11.28
HCOO(n-C_3H_7)	10.62	10.79	10.95	1370	11.19
HCOO(n-C_4H_9)	10.54	10.71	10.88	1370	11.06
$HCONH_2$[a]	10.13	10.32	10.32	1600	10.52
$HCONHCH_3$[a]	10.05	10.24	10.05	1500	9.87
$HCON(CH_3)_2$[a]	⩾9.40		9.77	1600	9.25
CF_3COOH	11.46	11.62	11.77	~1250[d]	12.92
$CF_3COOC_2H_5$			~11.6		11.81
CH_3COOH	10.70	10.87	10.87	1310	12.05[c]
$CH_3COOCH_2CF_3$	10.84	11.00	11.15	~1250[d]	11.79
CH_3COOCH_3	10.33	10.48	10.48	1200	11.16
$CH_3COOC_2H_5$	10.24	10.39	10.39	1200	10.99
CH_3COO(i-C_3H_7)	10.08	10.23	10.38	1200	10.77
CH_3COO(n-C_4H_9)	10.17	10.32	~10.5	~1200[d]	10.83
CH_3CONH_2	9.80	9.96	9.96	~1350[d]	10.32
$CH_3CONHCH_3$			~9.85		9.68
$CH_3CON(CH_3)_2$			9.43	~1400[d]	9.09

[a] From ref 2. [b] Estimated uncertainty ±50 cm^{-1} except for cases d. [c] Vibrational progression present (~1050 cm^{-1}). [d] Estimated uncertainty ±100 cm^{-1}.

studied. The suggestion[1] that they would be degenerate is seen to be approximately true for most of the esters and amides.

The assignment of the first two highest energy bands to n_0 or π_2 is based on the following considerations. The assignments for formic acid and the formamides are taken from the work of Brundle, *et al.*,[2] in which the n_0, π_2 ordering in formic acid is strongly supported by SCF calculations. One expects a similar ordering in acetic acid and trifluoroacetic acid. As mentioned above a recent calculation[3] suggests that n_0 is above π_2 in orbital energy for the formates. Our assignments (Table I) agree with this. The band assigned to ionization from n_0 almost always displayed vibrational fine structure while the π_2 band generally displayed no fine structure. Using the approximate relationship[5] between the breadth of a photoelectron band and the reduction in vibrational frequency occurring upon ionization, it can be estimated that the vibrational spacings in the n_0 bands (Table I) are reduced about 25% from the molecules. Hence it seems likely that the vibrational fine structure in the n_0 bands corresponds to excitation of a mode consisting mainly of C=O stretching. The vapor-phase infrared spectra of, for example, formic acid[6] and acetic acid[7] show that we must assign the vibrational progression here to the C=O stretching mode. Excitation of the C=O stretch is of course expected on the basis that the mode excited should mainly involve motion of the atoms on which the orbital is localized, the n_0 orbital being mainly localized on the carbonyl oxygen. Brundle, *et al.*,[2] also reported excitation of the C=O stretching mode in the n_0 (but not π_2) ionization of formic acid and its amides. It will be shown that consideration of inductive effects and orbital populations lends strong support to the assignments in Table I. The n_0, π_2 ordering in N-methylacetamide was assigned so as to agree with the formamide results and considerations of inductive effects to be discussed.

Figures 5 and 6 correlate the n_0 and π_2 ionizations for the formic acid and acetic acid derivatives, respectively. The vertical IP is used for ionization from π_2. The IP used for ionization from n_0 is the $v' = 1 \leftarrow 0 = v''$ transition except for some of the methylamides, for which the vertical IP was used because the 1 ← 0 value could not be clearly identified. Usually the 1 ← 0 transition is the vertical IP but in some cases the overlapping of n_0 and π_2 causes ionization to a higher vibrational member appear to be the vertical IP. Instead of using the apparent vertical IP for the n_0 ionization we chose to always use the 1 ← 0 band whenever making correlations. We also measured the IP of n_0 relative to π_2 by superimposing the spectra on a reference spectrum (the methyl ester) and measuring the lateral translation needed to first superimpose the n_0 bands and then the π_2 bands. This method utilizes the full symmetry of the photoelectron bands and is probably the better method in terms of internal consistency. We found that the two methods gave es-

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(5) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, London, 1970, Chapter 1.

(6) L. G. Bonner and R. Hofstadter, *J. Chem. Phys.*, 6, 531 (1938).

(7) R. C. Herman and R. Hofstadter, *ibid.*, 6, 534 (1938).

sentially identical results. It is seen in Figures 5 and 6 that there is a steady decrease in both the n_0 and π_2 IP as the X group in RCOX becomes more electron releasing. This is as expected.

Figure 7 shows how the separation between n_0 and π_2 varies with the X group. The π_2 orbital is largely localized on O and X in proportions which vary with the nature of X. In formamide π_2 is localized about 46% on oxygen and 52% on nitrogen.[8] In the esters π_2 should be even more localized on the X group (the ester oxygen) and so be more like a pure p lone pair orbital. This means that π_2 should be particularly sensitive to changes in the R group in R'COOR and $R'CONR_2$. The n_0 orbital is largely localized on the carbonyl oxygen, being only 6% localized on nitrogen in formamide.[8] Hence we expect n_0 to be less sensitive than π_2 to substituent changes. As the X group in R'COX becomes more electron releasing, both n_0 and π_2 should have lower IP's but the π_2 IP should be lowered more. Therefore, as X becomes more electron releasing, the magnitude of the separation between the n_0 and π_2 IP's should decrease if n_0 is at a lower IP and increase if n_0 has a higher IP than π_2. This is in agreement with Figures 5–7 and the assignments in Table I.[9]

Figure 7 shows that the n_0, π_2 separation is greater in the acetic acid derivatives except for the methylamides. This can be readily explained by noting that calculations on formamide[8,10] show that the n_0 orbital has a greater localization on the carbon and the hydrogen bonded to carbon than does π_2. One would expect this to also be the case for the compounds reported here. This means that n_0 should be more sensitive to changes in substituent at the carbonyl carbon. One would expect n_0 to be destabilized relative to π_2 as CH_3 is substituted for H, as is observed.

As noted before, the vibrational progressions in the n_0 bands (Table I) most likely correspond to the C=O stretching mode. Comparison of the C=O stretching frequencies in the neutral molecules[11] and the ions shows that the reduction in frequency in the ion decreases in the order ester > acid > amide. This suggests that the "nonbonding character" of the carbonyl oxygen lone pair may follow the reverse order. The frequency reductions (in cm^{-1}) are approximately as follows. HCOX: ester (390) > acid (340) > amide (100–150). CH_3COX: ester (560) > acid (470) > amide (150–300). An attempt to correlate the n_0 and π_2 IP's with Hammett or Taft substituent constants was not successful.

Ethylene Carbonate and Ethylene Trithiocarbonate. Figures 8 and 9 give the photoelectron spectra of ethylene carbonate and ethylene trithiocarbonate. An X-ray analysis[12] shows that ethylene carbonate is nonplanar in the solid state; however, an ir and Raman study[13] suggests that it is planar in solution and in the gas phase. On the other hand, the trithiocarbonate is suggested[14] to be nonplanar in solution as well as in the solid state. Presumably the trithiocarbonate would also be nonplanar in the gas phase. The general features of the two photoelectron spectra (Figure 8) are quite dissimilar. This suggests that the two compounds may indeed have different structures in the gas phase. Ethylene carbonate yields the simpler spectrum. This may be due to its higher symmetry (C_{2v} if it is planar).

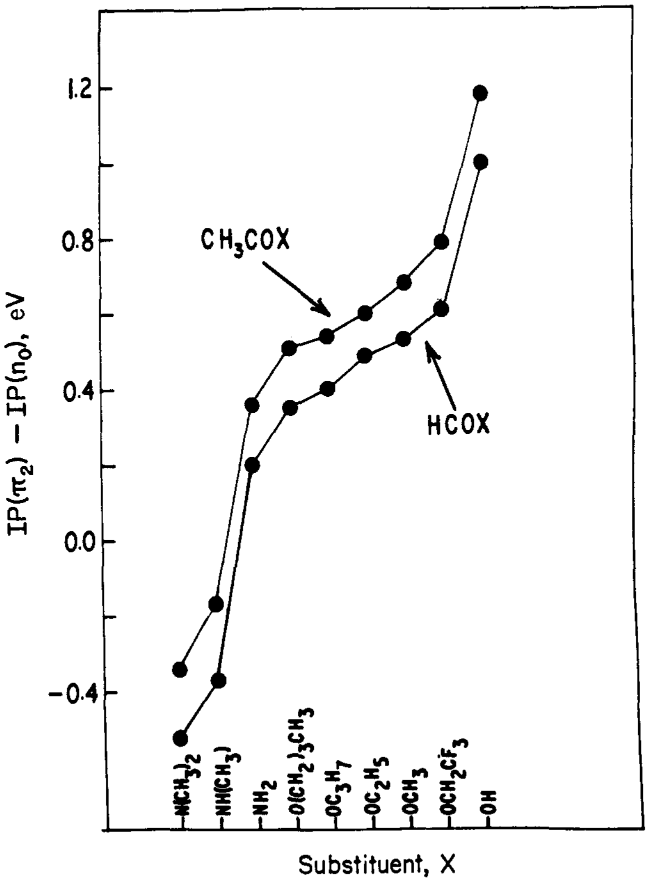

Figure 7. Separation of π_2 and n_0 orbital IP's for derivatives of formic acid and acetic acid. The propyl ester is isopropyl as the acetate and *n*-propyl as the formate.

If we assume that ethylene carbonate is planar in the gas phase, the three oxygen atoms and the carbonyl carbon form a conjugated π system in which the two highest filled orbitals would be approximately nonbonding. Without conjugation these two π orbitals correspond to lone pair p orbitals on the two equivalent oxygen atoms. One would expect the carbonyl oxygen lone pair orbital to have an IP close to the IP's of the two approximately nonbonding π orbitals. Figures 8 and 9 show that the highest energy band indeed must be ascribed to several ionization processes. Fine structure is present on the low IP side, with the vibrational spacing being about 1500 cm^{-1}. This is probably the C=O stretch reduced from 1870 cm^{-1} in the molecule.[13] The adiabatic IP is 10.70 eV. In view of this vibrational spacing and the discussion above on the carboxylic acid derivatives it seems likely that the carbonyl oxygen lone pair has the lowest IP with the nonbonding π orbitals very close, being almost unsplit.

Ethylene trithiocarbonate has three high energy (low IP) bands. If, as suggested above, this compound

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(8) H. Basch, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **47**, 1201 (1967).

(9) We assume Koopmans' theorem to be valid here.

(10) D. H. Christensen and R. N. Kortzeborn, *J. Chem. Phys.*, **53**, 3912 (1970).

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1958; E. J. Hartwell, R. E. Richards, and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948).

(12) C. J. Brown, *Acta Crystallogr.*, 7, 92 (1954).

(13) C. L. Angell, *Trans. Faraday Soc.*, **52**, 1178 (1956).

(14) P. Klaeboe, *Acta Chem. Scand.*, **22**, 1532 (1968).

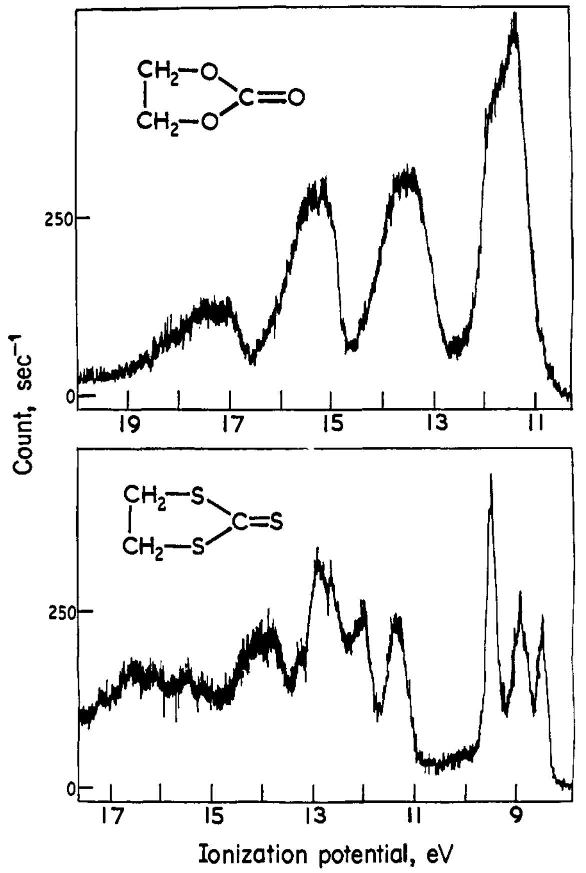

Figure 8. The He I photoelectron spectra of ethylene carbonate and ethylene trithiocarbonate.

is nonplanar in the gas phase, the conjugation of the p orbitals on carbon and the three sulfur atoms is reduced and the two nonbonding π orbitals in the carbonate approximate sulfur 3p lone pair orbitals in the trithiocarbonate. The highest energy (lowest IP) band has fine structure (Figure 9): 8.47, 8.57 eV. This corresponds to a frequency of 810 cm^{-1} and is probably the C=S stretch which in the molecule occurs[15] at 1099 cm^{-1}.

In analogy with the analysis of the acetate and formate spectra, we assign this band to the thiocarbonyl sulfur lone pair orbital. The second band in the trithiocarbonate spectrum (vertical IP = 8.92 eV) shows some feeble fine structure. An average of five spectra yields a vibrational spacing of ~800 ± 100 cm^{-1}. This may be the C=S stretch. The third band (vertical IP = 9.46 eV) shows no fine structure. We assign the 8.92- and 9.46-eV bands to the lone pairs on the two equivalent sulfur atoms.

The splitting of the sulfur 3p lone pair orbitals can arise from several sources. One expects the molecule to have C_s or C_2 symmetry[16] in the gas phase if it is in fact nonplanar. If the symmetry is C_s the p orbitals on the two equivalent sulfur atoms are inclined toward each other. This means that direct overlap becomes possible, especially in view of the large size of the sulfur 3p orbitals. This overlap could account for the 0.54-eV separation of the lone pair IP's.[17] If the molecule has C_2 symmetry direct overlap is much less likely to account for the splitting which probably now arises from through-bond interaction with the σ network[17] or interaction with the thiocarbonyl carbon p-π orbital. In as much as ethylene carbonate possesses C_2 symmetry in the solid state,[12] we favor a C_2 conformation for ethylene trithiocarbonate with little of the lone pair splitting arising from direct overlap. A similar situation may occur in 1,3-dioxolane.[17]

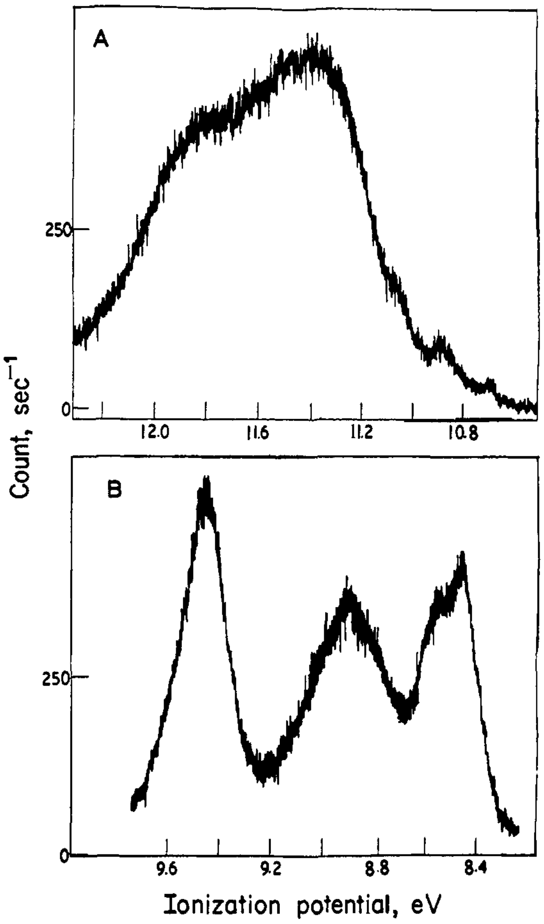

Figure 9. Details of the lone pair photoelectron bands in (A) ethylene carbonate and (B) ethylene trithiocarbonate.

Group theory shows that the lone pair orbitals transform as a + b in C_2 symmetry. The plus combination ($p_1 + p_2$) has b symmetry while ($p_1 - p_2$) has a symmetry. Simple overlap considerations suggest that the highest filled MO localized on the C–H bonds is of a symmetry. This means that if the lone pair splitting occurred *via* the C–H σ orbitals (through bond), the lone pair a orbital should be the first one ionized. However, the C=S π orbital is of b symmetry and this would split the lone pair orbitals putting b above a.

As mentioned above, the spectrum (Figure 9) shows that the first lone pair band (8.92 eV) has fine structure. It is difficult to assign this to any particular vibration. However, since π orbitals frequently display more pronounced fine structure than σ-bonding orbitals, one could assign the 8.92-eV band to an orbital with some localization in the C=S region. The lone pair orbital of b symmetry could acquire such localization by interacting with the C=S π orbital. The lone pair orbital of a symmetry cannot do this and should not ionize

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(15) L. J. Bellamy and P. E. Rogasch, *J. Chem. Soc.*, 2218 (1960).

(16) K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81**, 3213 (1959).

(17) D. A. Sweigart and D. W. Turner, unpublished work.