Perfluoro Effect in Photoelectron Spectroscopy. I. Nonaromatic Molecules

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Abstract: Comparison of the successive ionization potentials in planar, nonaromatic hydrides with those in the corresponding perfluoro compounds demonstrates that σ MO's are stabilized 2.5–4 eV by the substitution, whereas the stabilization can be an order of magnitude smaller for π MO's. This preferential stabilization of σ MO's is termed "the perfluoro effect." The generality of the perfluoro effect was demonstrated experimentally and theoretically using the ethylene–tetrafluoroethylene, water–oxygen difluoride, formaldehyde–carbonyl fluoride, and diimide–difluorodiazine pairs. He(I) and He(II) photoelectron spectra of all of these molecules except diimide are presented, together with those on the acetone–hexafluoroacetone, azomethane–hexafluoroazomethane, and butadiene–1,1,4,4-tetrafluorobutadiene pairs. In the pairs containing the methyl and trifluoromethyl groups, σ and π MO's are approximately equally stabilized by the fluorine atoms, showing that the trifluoromethyl group effectively destroys the π–σ distinction in these molecules. Gaussian orbital calculations of double-ζ quality were performed for the smaller molecular pairs; the Koopmans' theorem values are in good agreement with experiment. Analysis of the wave functions shows that in the perfluoro compounds, the σ MO's are appreciably delocalized over the fluorine atoms, and are strongly stabilized by the high effective nuclear charge of that atom. In the π MO's, the delocalization onto the fluorine atoms is much less, and its stabilizing effect is counteracted by a strong π antibond between the fluorine atom and the atom to which it is σ bonded.

The technique of photoelectron spectroscopy gained immediate popularity as soon as it was shown to confirm directly many of the ideas of electronic structure which were already known to be true. However, gathering useful interpretations from the photoelectron spectra of molecules, the electronic structures of which are not known beforehand, is more difficult and uncertain. In this regard, two occasional aids invoked in assigning photoelectron transitions to ionizations from particular MO's are the study of the vibronic structure of a band and the relative differential or total cross sections of different bands in the same spectrum. For example, if a transition in an ether is a very vertical one, with only a few vibrations excited and a very strong origin, then on this basis it is safe to assign it as originating with the lone-pair electrons on the oxygen atom.[2] However, since the second and higher bands in many spectra do not show any resolvable vibrational structure, and since it may also happen that the ionization of a formally nonbonding electron can result in a broad band, this criterion is of limited use. As a second aid to assignment in highly symmetrical molecules, the photoionization cross sections are often taken as proportional to the orbital degeneracies of the MO's;[3a] however, comparison of relative intensities of bands when excited by He(I) and He(II) radiation shows how unreliable this technique can be.[2,3b]

In addition to the above, assignments can often be made by applying Koopmans' theorem to the results of semiempirical or *ab initio* molecular orbital calculations. As the present state of the art does not allow one theoretically to "resolve" bands which are any closer than, say, 1 eV, excitations which are closer than this can be very difficult to assign. The number of atoms in the molecule also imposes a limit on the utility of *ab initio* calculations, but apparently not for the semiempirical ones.

One other possible aid to the assignment of photoelectron transitions has been briefly mentioned in the literature in the past, and our present effort has been directed toward a more systematic study of this aspect of photoelectron spectroscopy. *In several instances it has been shown that the substitution of fluorine for hydrogen in a planar molecular has a much larger stabilizing effect on the σ MO's than on the π MO's; this we call the perfluoro effect.*[2,4–7] With the hope of using this as a possible diagnostic for the MO symmetry type in planar organic molecules and defining its limitations, the photoelectron spectra of several perhydro- and perfluoro-substituted pairs of molecules were investigated, and *ab initio* Gaussian type orbital (GTO) calculations were performed on certain of the molecules and their ions. In this paper, we discuss the perfluoro effect as it is found in planar nonaromatic molecules, deferring a discussion of the effect in aromatic compounds to part II.[8] Additionally, since the trifluoromethyl group often acts much like a fluorine atom, the perfluoro effect was also studied in various methyl–trifluoromethyl pairs, which are nonplanar systems in general.

The prime advantage of using the fluorine atom as a perturbation in planar molecules is that the effect is such a large one for σ MO's (typically a stabilization of 2–4 eV) but often an order of magnitude smaller for π MO's. Of course, the substitution of a simple atom such as hydrogen by a more complex one such as fluo-

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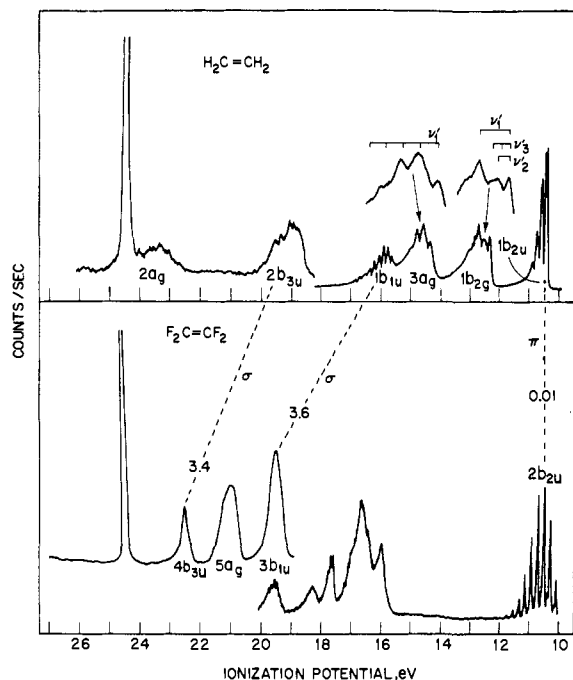(8) C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Amer. Chem. Soc.*, 94, 1466 (1972).

Figure 1. The photoelectron spectra of ethylene and tetrafluoroethylene. The spectra below 19 eV were determined using He(I) excitation, whereas those above 19 eV were determined using He(II) excitation. The strong line at 24.5 eV is due to the ionization of helium atoms by the He(II) radiation.

rine will necessarily lead to a more complex photoelectron spectrum and thereby complicate the task of correlating the MO's in the two molecules.

Experimental and Theoretical Techniques

Of the compounds used here, butadiene (Phillips Petroleum Co., research grade, 99.89%), hexafluorobutadiene, carbonyl fluoride, and tetrafluoroethylene (all from Peninsular Chemical Products), azomethane, hexafluoroazomethane, and acetone-d_6 (all from Merck Sharp and Dohme of Canada, Ltd.), and difluorodiazine (Air Products Industries) were obtained from commercial sources and subjected to several cycles of freeze–pump–thaw cycling. Samples of 1,1,4,4-tetrafluorobutadiene and oxygen difluoride were kindly prepared by Drs. S. L. Mannatt and Gordon R. Jones, respectively, and were used without further manipulation. Photoelectron spectra up to 21 eV were recorded using the He(I) resonance line generated in a dc capillary discharge, and a 127° sector electron-energy analyzer.[9] With this spectrometer, the resolution varied between 0.015 and 0.030 eV (full width at half-height) for a 5-eV electron. As about 2% of the lamp output under certain conditions is in the He(II) line (40.8 eV), we are able to obtain ionization potentials out to be about 28 eV using it, albeit with poorer resolution.[10]

With regard to the GTO calculations, the H, C, N, O, and F atomic orbital basis sets described earlier[11] were used, together with the experimentally determined ground-state geometries,[12] except for *trans*-difluorodiazine, which was presumed to have r(N–F) = 1.396 Å, r(N–N) = 1.230 Å, and $\angle$FNN = 105° 30'. The basis sets used here are equivalent to a double-ζ Slater AO basis,[11] and as such, are probably close to the Hartree–Fock sp limit. In the past, the double-ζ calculations have yielded especially good Koopmans' theorem ionization potentials after an empirical decrease of 8%.[13–15] The total energies (au) computed for each of

the molecules are as follows: ethylene, −78.0052; tetrafluoroethylene, −473.3331; water, −76.0037; oxygen difluoride, −273.-4494; diimide, −109.9418; difluorodiazine, −307.5104; formaldehyde, −113.8209; and carbonyl fluoride, −311.5244. In each case, the x direction is perpendicular to the plane of the molecule, y is in plane and along the double bond [the F–F (H–H) line in F_2O (H_2O)], and the z direction is in plane and perpendicular to the other two.

It is conceptually convenient to analyze the MO's into component AO's which can be serially labeled 1s, 2s, 2p_x, etc. However, since the basis AO's carry no such labels in a Gaussian orbital set, one must label them intuitively. For example, the lowest s-type function on carbon (consisting of four components) is called 1s, the second lowest is called 2s, etc. In the population analysis, a population is calculated for each component of an "AO," and these are then added together to give an "atomic" population. Overlap populations were similarly computed.

Description of the Spectra and Theoretical Results

The relative band intensities within the photoelectron spectra excited by He(I) and He(II) radiation may differ greatly, and though this information is interesting, it is of little value to us at present. Consequently, only a few qualitative remarks will be made as regards the intensity changes in the He(II) spectra, and in general only the He(II) spectra above 19 eV are shown in the figures. As an aid to spectral comparison, several spectra which have already been published are shown here again.

Besides the "corrected" Koopmans' theorem ionization potentials, the GTO calculations are readily analyzed to yield atomic and bond populations for each MO, which can be qualitatively correlated with the corresponding vibronic band envelope in many cases.[14] Since the calculations were performed in the ground-state geometries, the calculated ionization potentials will be compared with the experimental vertical values throughout. Adiabatic ionization potentials are also reported; the values correspond to the peaks of the (0, 0) bands where these can be determined, otherwise to the onset of ionization in the band wings.

Our plan is to identify the various photoelectron bands using the calculated ionization potentials, to then correlate the MO's of the perhydro and perfluoro partners using the atomic and overlap populations, and from this, where possible, to gauge the extent of the energy shifts on going from the perhydro to the perfluoro compound.

Ethylene–Tetrafluoroethylene. Though the high-resolution photoelectron spectrum of ethylene has been investigated repeatedly in the last few years,[16–19] it is reported again in Figure 1, for comparison with the spectrum of tetrafluoroethylene, which was also recently reported by Lake and Thompson.[20] Detailed views of the vibronic structure of the ethylene spectrum are given in Figure 1, and similar figures for tetrafluoroethylene are presented here in Figure 2. The He(I)

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Table I. Ionization Potentials Observed and Calculated for Ethylene and Tetrafluoroethylene

Orbital	0.92K.T.[a]	Adiabatic IP	Vertical IP	Orbital	0.92K.T.	Adiabatic IP	Vertical IP
$1b_{2u}$	9.45	10.51 (4)	10.51 (4)	$2b_{2u}$	10.86	10.10 (8)	10.52 (0)
$1b_{2g}$	12.72	12.45 (3)	12.85	$6a_g$	17.15	ca. 15.6	15.95 (5)
$3a_g$	14.72	14.43	14.66	$4b_{2g}$	17.40		16.4 (0)
$1b_{1u}$	16.25	15.74	15.87	$4b_{1u}$	17.77		16.6 (3)
$2b_{3u}$	19.90	ca. 18.8 (5)	ca. 19.1	$1a_u$	18.15		16.9 (5)
$2a_g$	26.10	ca. 22.8	ca. 23.5	$1b_{3g}$	18.32	17.50 (9)	17.60 (0)
$1b_{1u}$	282		290.7[b]	$5b_{3u}$	18.82	18.0	18.21
$1a_g$	282			$1b_{1g}$	19.60		
				$3b_{2g}$	19.90		
				$1b_{2u}$	20.83		
				$3b_{1u}$	21.50	19.19 (1)	19.46
				$5a_g$	22.15	ca. 20.6	21.0
				$4b_{3u}$	23.26	ca. 22.3	22.5
				$4a_g$	28.66		

[a] Taken from the BADZ + 3s, 3p calculation of M. B. Robin, H. Basch, N. A. Kuebler, E. B. Kaplan, and J. Meinwald, *J. Chem. Phys.*, 48, 5037 (1968). [b] T. D. Thomas, private communication.

and He(II) spectra of ethylene were compared in ref 17; in tetrafluoroethylene, the only qualitative difference in the He(I) and He(II) spectra below 21.2 eV is that the 10.51-eV transition is approximately 50% weaker in the He(II) spectrum, relative to the other bands.

Overall, the corrected Koopmans' theorem values calculated for ethylene, Table I, do an adequate job of explaining the spectrum, with the 10.51-eV transition securely assigned as an ionization from the $1b_{2u}$ π MO, even though the calculated value is over 1 eV too low. While there is no doubt that the 10.51-eV band is to be assigned to ionization from the $1b_{2u}$ π MO, the discrepancy between the Koopmans' theorem and observed values is larger than one usually meets with in GTO calculations; consequently, we have gone on to perform the SCF calculation on the $^2B_{2u}$ positive ion and then made the appropriate correlation energy corrections.[13,14] By this scheme, the first ionization potential of ethylene is calculated to be 10.68 eV, in much better agreement with the experimental value. The 8% empirically reduced Koopmans' theorem values are in excellent agreement with the remaining vertical ionization potentials, except in the case of the $2a_g$ MO, where the predicted value is about 2.5 eV too high. Still, there can be no doubt as to the assignments of the ethylene bands.

Vibrational analysis of the 10.51-eV band of ethylene shows a strong excitation of ν_2' (totally symmetric C-C stretch), with attendant double quanta of ν_4' (H_2C-CH_2 torsion) and possible excitation of ν_3' (totally symmetric H_2C scissors). That ν_2' is excited in the first photoelectron band of ethylene, but ν_1', the totally symmetric C-H stretch, is not, is reasonable, since the $1b_{2u}$ MO is strongly C-C bonding, but has a zero C-H overlap population according to Table II. However, excitation of the torsional motion, ν_4', cannot be explained by consideration of overlap populations. Of the remaining bands in ethylene, ionization from $3a_g$ (14.66 eV) is largely out of the C-C σ bond formed by the $2p\sigma$ AO's, whereas the others involve C-H σ-bonding orbitals intermixed with bonding and antibonding C-C σ combinations, as described in Table II. In several of the corresponding photoelectron bands, excitation of ν_1' and ν_2' can be identified.

The general agreement between theory and experiment is less obvious for tetrafluoroethylene, thanks to

the 12 transitions predicted to fall within the 17-23-eV interval. On comparing the spectrum with the Koopmans' theorem predictions, Table I, it seems likely that the transition at 10.52 eV in tetrafluoroethylene can be assigned
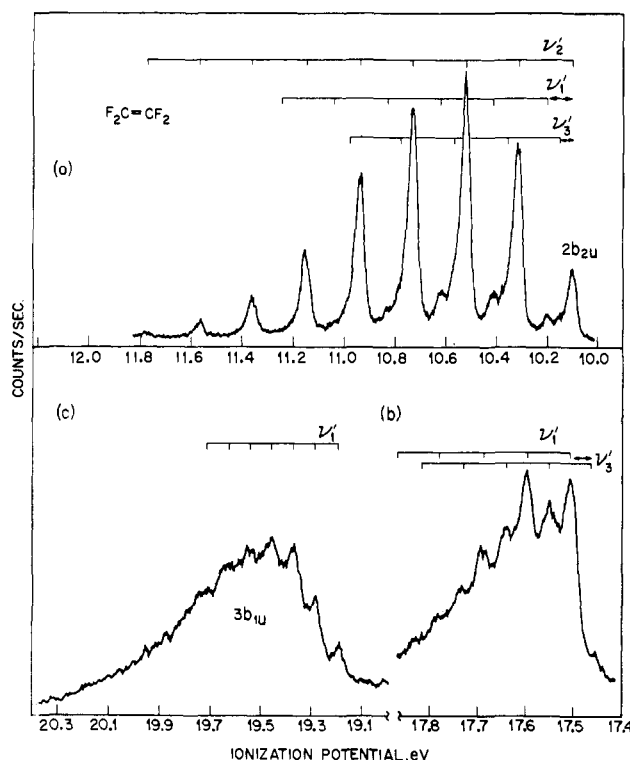

Figure 2. Details of the vibronic structure of the 10.52- (a), 17.60- (b), and 19.46-eV (c) bands of tetrafluoroethylene.

to ionization from the $2b_{2u}$ MO and that the last three bands observed at 19.46, 21.0, and 22.5 eV are associated with the $3b_{1u}$, $5a_g$, and $4b_{3u}$ MO's, respectively, but little else can be said about the intermediate transitions in the 16.0-18.5-eV region.

Though the first bands in ethylene and tetrafluoroethylene have very nearly the same energy and correspond to ionization from the corresponding uppermost π MO in each case, the vibronic structures are in strong contrast. As seen in Figure 2, ionization from the $2b_{2u}$ π MO of tetrafluoroethylene is accompanied

Table II. Atomic and Overlap Population Analysis for Ethylene

MO	H 1s	2s	2p$_x$	C 2p$_y$	2p$_z$	C-C	C-H	H-H^a
1b$_{2u}$	0.000	0.000	0.980	0.000	0.000	0.562	0.000	0.000
1b$_{2g}$	0.268	0.000	0.000	0.000	0.437	−0.186	0.249	−0.072
3a$_g$	0.140	0.004	0.000	0.706	0.000	0.326	0.110	0.033
1b$_{1u}$	0.212	0.000	0.000	0.000	0.569	0.153	0.167	−0.041
2b$_{3u}$	0.201	0.439	0.000	0.150	0.000	−0.167	0.234	0.025
2a$_g$	0.068	0.780	0.000	0.069	0.000	0.543	0.075	0.004

^{a} Calculated for geminal hydrogens.

Table III. Atomic and Overlap Population Analysis for Tetrafluoroethylene

MO	2s	2p$_x$	C 2p$_y$	2p$_z$	2s	2p$_x$	F 2p$_y$	2p$_z$	C-C	C-F	F-F^a
2b$_{2u}$	0.000	0.733	0.000	0.000	0.000	0.132	0.000	0.000	0.480	−0.210	0.014
6a$_g$	0.030	0.000	0.169	0.000	0.001	0.000	0.397	0.002	0.229	−0.049	0.018
4b$_{2g}$	0.000	0.000	0.000	0.008	0.000	0.000	0.188	0.307	−0.001	0.009	−0.064
4b$_{1u}$	0.000	0.000	0.000	0.028	0.001	0.000	0.141	0.344	0.002	0.013	−0.067
1a$_u$	0.000	0.000	0.000	0.000	0.000	0.500	0.000	0.000	0.000	0.000	−0.020
1b$_{3g}$	0.000	0.000	0.000	0.000	0.000	0.500	0.000	0.000	0.000	0.000	−0.020
5b$_{3u}$	0.006	0.000	0.016	0.000	0.000	0.000	0.427	0.058	−0.075	0.044	0.025
1b$_{1g}$	0.000	0.093	0.000	0.000	0.000	0.453	0.000	0.000	−0.033	0.062	0.014
3b$_{2g}$	0.000	0.000	0.000	0.188	0.023	0.000	0.255	0.127	−0.029	0.085	−0.012
1b$_{2u}$	0.000	0.285	0.000	0.000	0.000	0.357	0.000	0.000	0.080	0.080	0.010
3b$_{1u}$	0.000	0.000	0.000	0.252	0.035	0.000	0.265	0.073	0.057	0.053	−0.006
5a$_g$	0.013	0.000	0.251	0.000	0.027	0.000	0.017	0.324	0.061	0.065	0.018
4b$_{3u}$	0.166	0.000	0.084	0.000	0.059	0.000	0.028	0.288	0.060	0.058	0.008
4a$_g$	0.474	0.000	0.270	0.000	0.051	0.000	0.051	0.025	0.585	0.009	0.000

^{a} Calculated for geminal fluorine atoms.

by a long progression in the totally symmetric vibration ν_2' (C-C stretch, 1660 cm^{-1} in the ion, 1872 cm^{-1} in the neutral molecule ground state), together with single quanta of ν_1' (C-F stretch, 790 cm^{-1} in the ion, 778 cm^{-1} in the neutral molecule) and ν_3' (F$_2$C scissors, 370 cm^{-1} in the ion, 394 cm^{-1} in the neutral molecule)[21] attached to each quantum of ν_2'. That ν_1 is excited at all in tetrafluoroethylene, that ν_2 forms the prominent progression, and that $\nu_1' > \nu_1''$, but $\nu_2' < \nu_2''$ and $\nu_3' < \nu_3''$ all can be rationalized using the overlap populations of Table III, for there it is seen that the 2b$_{2u}$ MO is rather strongly C-F antibonding while being strongly C-C bonding and weakly F-F bonding. Thus, those vibrations are excited for which the internuclear distances are expected to change, with ionization from bonding regions leading to lowered frequencies and ionization from antibonding regions leading to increased frequencies. Similar effects are reported for the $\pi \rightarrow$ 3p Rydberg optical transitions and photoelectron bands of the chloroethylenes.[20,22,23] Interestingly, unless the 370-cm^{-1} interval in tetrafluoroethylene is really $2\nu_4'$ ($\nu_4'' = 190$ cm^{-1}) rather than ν_3', the torsional vibration does not appear in the first band, showing that the C$_2$F$_4^+$ ion is effectively planar in its ground state, whereas C$_2$H$_4^+$ is twisted about the C-C axis by 27°.[24] Since the C-C stretching progression in the 1b$_{2u}$ band of ethylene is strongest at the origin and is rather short, whereas that in the 2b$_{2u}$ band of tetrafluoroethylene is maximal at $v_2 = 3$ and is twice as long, it is clear that the increase in C-C

bond length is much larger in the tetrafluoroethylene ion than in the ethylene ion.

As there are 14 separate transitions predicted in the 10–28-eV range of tetrafluoroethylene and only 10 are obvious, any assignments beyond the first few levels that we make on the basis of the calculations will be somewhat arbitrary. Also, several of the bands are predicted to be so close together that their predicted ordering could easily be in error. Not only is the identification of many of the bands of tetrafluoroethylene in question, but according to the atomic population analysis, Table III, the mixing of fluorine AO's in the MO's of ethylene is quite large, and so the correlations between ethylene and tetrafluoroethylene MO's also are tentative. Nonetheless, on the basis of the atomic and overlap populations it seems that the 1b$_{2g}$, 3a$_g$, 1b$_{1u}$, 2b$_{3u}$, and 2a$_g$ MO's of ethylene can be correlated with the 3b$_{2g}$, 6a$_g$, 3b$_{1u}$, 4b$_{3u}$, and 4a$_g$ MO's of tetrafluoroethylene, respectively, Tables II and III. Experimentally, 6a$_g$ in tetrafluoroethylene could be any of the four transitions in the 15–17-eV region, and 3b$_{2g}$ is similarly difficult to place with any confidence. Consequently, for the 1b$_{2g}$–3b$_{2g}$ and 3a$_g$–6a$_g$ perfluoro shifts we will use the theoretical values rather than trying to guess the experimental ones. In the case of the 1b$_{1u}$–3b$_{1u}$ and 2b$_{3u}$–4b$_{3u}$ pairs, the situation is a little clearer, and the experimental assignments will be used. According to this scheme, the 1b$_{2g}$–3b$_{2g}$ σ-MO perfluoro shift is at least +5–6 eV, depending upon the exact location of 3b$_{2g}$ in tetrafluoroethylene, and the 3a$_g$–6a$_g$ σ-MO shift is about 2 eV. For the 1b$_{1u}$–3b$_{1u}$ and 2b$_{3u}$–4b$_{3u}$ pairs, the experimental perfluoro shifts are 3.6 and 3.4 eV, respectively, while the 2a$_g$–4a$_g$ perfluoro shift is calculated to be 2.6 eV.

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Now the most striking feature of the comparisons in Figure 1 and Table I is that though the σ ionizations are shifted upward in tetrafluoroethylene by at least 2–3 eV, the vertical ionization potentials of the $1b_{2u}$ π MO of ethylene and the $2b_{2u}$ π MO of tetrafluoroethylene differ by less than 0.1 eV. This behavior results in a gap of almost 6 eV between the first and second ionization potentials of tetrafluoroethylene, Figure 1. Though the GTO calculation is really of very little help in assigning the photoelectron spectrum of tetrafluoroethylene in the region above 16 eV, it is indisputable that the σ MO's of tetrafluoroethylene have been greatly stabilized relative to the π MO, and that this stabilization effect is predicted by the GTO calculation, which correctly places the π ionization at 10.86 eV, with the first σ ionization coming at 17.15 eV. This contrasting behavior of the π and σ MO's upon the fluorination of ethylene is our first example of the perfluoro effect in action.

Ethylene also allows one to investigate the π and σ energy shifts as a function of the degree of fluorination. Of the various combinations, Lake and Thompson[20] report the photoelectron spectra of vinyl fluoride and 1,1-difluoroethylene, and we have determined the spectra of cis- and trans-difluoroethylene and of trifluoroethylene in order to complete the series.[25] The vertical values of the first two ionization potentials (from the uppermost π and uppermost σ MO's) are reported in Table IV. As might be expected, there is only a

Figure 3. The photoelectron spectra of water and oxygen difluoride. In the latter, the spectrum above 18 eV was determined using He(II) excitation.

Table IV. Vertical Ionization Potentials of Ethylene and the Fluoroethylenes

	First ionization potential (π)	Second ionization potential (σ)
$H_2C=CH_2$	10.6	12.85
$H_2C=CHF^a$	10.58	13.79
$H_2C=CF_2{}^a$	10.72	14.79
cis-FHC=CHF	10.43	13.97
trans-FHC=CHF	10.38	13.90
$F_2C=CHF$	10.53 (6)	14.64 (8)
$F_2C=CF_2$	10.52 (0)	15.95 (5)
trans-$H_3CHC=CHCH_3$	9.11	11.90
trans-$F_3CFC=CFCF_3$	11.55	14.16

^{a} Taken from ref 20.

slight variation of the vertical π ionization potential (± 0.20 eV) throughout the fluoroethylene series, whereas the σ ionization potential is progressively shifted upward from its value in ethylene, the shift being less than 1 eV in vinyl fluoride but over 3 eV in tetrafluoroethylene. The data suggest that the perfluoro effect can be observed even when the fluorinated component is less than fully fluorinated, but that the effect will be smaller than when all of the hydrogens are replaced by fluorine.

In contrast to the pattern in the fluoroethylene series, the perfluorination of trans-butene-2 shifts the π ionization potential from 9.11 to 11.55 eV and the uppermost σ ionization potential from 11.90 to 14.16 eV, Table IV.[25] In this case, there is no specificity as regards the perfluoro shift, this being approximately 2.3 eV for both types of MO's. As illustrated by sev-

eral other examples quoted below, this is the general result of the perfluoro effect in methyl-containing molecules.

Water–Oxygen Difluoride. The photoelectron spectra of water and its perfluoro analog, oxygen difluoride, are shown in Figure 3. That of water is taken from

Table V. Observed and Predicted Ionization Potentials for Water and Oxygen Difluoride

Orbital	0.92K.T.	SCF diff	Adiabatic IP	Vertical IP
		H_2O^a		
$1b_2$	12.7		12.61 (6)	12.61 (6)
$3a_1$	14.1		13.7	14.73 (6)
$1b_1$	17.9		17.22	18.55
$2a_1$	34.1			32.2^b
$1a_1$	513			539.7^b
		F_2O		
$2b_2$	15.4	13.5	13.11 (5)	13.25 (2)
$6a_1$	16.4	16.3	15.74	16.10
$4b_1$	17.2	16.9		16.44
$1a_2$	18.4	18.3	ca. 17.9	18.50
$3b_1$	20.0			19.55
$5a_1$	20.2			
$1b_2$	20.8			20.7
$4a_1$	32.6			
$2b_1$	41.5			
$3a_1$	44.3			
$2a_1$	522			
$1a_1$	662			
$1b_1$	662			

^{a} Three lowest ionization potentials determined by Brundle and Turner.[26] ^{b} Experimental values from the ESCA work of K. Siegbahn, et al., "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969, p 82.

(25) N. A. Kuebler, C. R. Brundle, and M. B. Robin, unpublished work.

Table VI. Atomic and Overlap Population Analysis Calculated for Water and Oxygen Difluoride

MO	H 1s	O 2s	2p$_x$	2p$_y$	2p$_z$	F 2s	2p$_x$	2p$_y$	2p$_z$		
					H$_2$O					O–H	H–H
1b$_2$	0.000	0.000	2.000	0.000	0.000					0.000	0.000
3a$_1$	0.099	0.209	0.000	0.000	1.592					0.202	0.005
1b$_1$	0.370	0.000	0.000	1.250	0.000					0.331	−0.103
2a$_1$	0.142	1.641	0.000	0.000	0.065					0.034	0.025
1a$_1$	0.000	0.003	0.000	0.000	0.000					0.000	0.000
					F$_2$O					O–F	F–F
2b$_2$		0.000	1.210	0.000	0.000	0.000	0.394	0.000	0.000	−0.234	0.020
6a$_1$		0.125	0.000	0.000	0.632	0.006	0.000	0.010	0.604	−0.130	0.025
4b$_1$		0.000	0.000	0.106	0.000	0.003	0.000	0.788	0.266	0.015	−0.151
1a$_2$		0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	−0.004
3b$_1$		0.000	0.000	0.545	0.000	0.031	0.000	0.044	0.650	0.128	−0.019
5a$_1$		0.032	0.000	0.000	0.410	0.009	0.000	0.543	0.226	0.084	0.061
1b$_2$		0.000	0.793	0.000	0.000	0.000	0.603	0.000	0.000	0.139	0.016
4a$_1$		1.244	0.000	0.000	0.000	0.296	0.000	0.043	0.035	−0.205	0.007
2b$_1$		0.000	0.000	0.065	0.000	0.961	0.000	0.001	0.004	0.037	−0.044
3a$_1$		0.526	0.000	0.000	0.054	0.674	0.000	0.023	0.009	0.202	0.026

ref 26, but that of oxygen difluoride is new; the He(II) spectrum of oxygen difluoride below 21.2 eV is much like that obtained using He(I) excitation. One sees from Table V that the corrected Koopmans' theorem values for the ionization potentials of water compare quite nicely with the experimental values and that the agreement is similarly quite good for oxygen difluoride, except for the 2b$_2$ value, which is over 2 eV too high. In this particular molecule, an error of 2 eV on the first ionization potential does not change the ordering of the levels; still, the magnitude of the disagreement is quite large for this type of calculation. Consequently, the energies of the first four ionic states of oxygen difluoride were calculated and subtracted from the neutral molecule energy, yielding ionization potentials corrected for electronic reorganization. In this way, the error in the 2b$_2$ ionization potential is reduced to 0.25 eV, while the good agreement with the other higher ionization potentials remains undisturbed, Table V. The good agreement with experiment suggests either that the correlation energy corrections are very small in this molecule or that the wave functions are better for the ionic states than for the ground state. In the region above 19 eV, ionizations from the 3b$_1$, 5a$_1$, and 1b$_2$ MO's of oxygen difluoride are expected between 20 and 21 eV, whereas only two bands are observed, at 19.55 and 20.7 eV. Most likely, the 19.55-eV band is a composite of the 3b$_1$ and 5a$_1$ ionizations, and the 20.7-eV band corresponds to ionization from the 1b$_2$ MO. Only the first transition of oxygen difluoride shows vibronic structure, whereas all three of the water bands are discrete.

According to the GTO calculations, Table V, the first ionization potentials in both water and oxygen difluoride involve π MO's of b$_2$ symmetry. However, as in the ethylene–tetrafluoroethylene case, the two π orbitals are again rather different, Table VI, and this is reflected clearly in the photoelectron vibronic envelopes. In water, the 1b$_2$ π MO is wholly centered upon the oxygen atom for reasons of symmetry, and the corresponding photoelectron transition, Figure 3, is appropriately extremely vertical, with a very in-

tense origin. The totally symmetric O–H vibration is weakly excited in the ^{2}B$_2$ ionic state of water, with a frequency (3200 cm^{-1}) decidedly lower than in the neutral molecule (3652 cm^{-1}). On the other hand, the 2b$_2$ π MO of oxygen difluoride has large contributions from both oxygen and fluorine AO's and is strongly O–F π antibonding. Consequently, the 2b$_2$ photoelectron transition is an extended one, and the associated vibrational progression (1010 cm^{-1}, ν_1', the totally symmetric O–F stretch) has a *higher* frequency in the ion than in the neutral molecule ($\nu_1'' = 928$ cm^{-1}), Figure 3. Notice, however, that though the wave functions and the vibronic envelopes differ considerably, the energies of the 1b$_2$ and 2b$_2$ vertical ionizations differ by only 0.6 eV. Once again, the π ionization potential is relatively insensitive to fluorination.

Excepting the π MO's 1b$_2$ and 2b$_2$, the correlation of the water and oxygen difluoride MO's is somewhat indirect, for all of the MO's of oxygen difluoride, except for the nonbonding 1a$_2$ MO, consist of a mixture of fluorine and oxygen AO's. However, by considering the major components, a correlation can be made. Thus the 3a$_1$ MO in water is largely 2p$_z$ on oxygen (1.592), with a significant oxygen 2s component (0.209), and is O–H σ bonding. The 6a$_1$ and 5a$_1$ MO's in oxygen difluoride also have large oxygen 2p$_z$ components (0.632 and 0.410), smaller oxygen 2s components (0.125 and 0.032), and large fluorine σ AO components, Table VI. Note, however, that 6a$_1$ is O–F σ antibonding (−0.130) whereas 5a$_1$ is O–F σ bonding (+0.084), Table VI. On this basis, we correlate the 3a$_1$ MO of water with the 5a$_1$ MO of oxygen difluoride and arrive at an experimental σ perfluoro shift of 4.8 eV. Similarly, the 1b$_1$ MO of water correlates with the 3b$_1$ MO of oxygen difluoride rather than 4b$_1$, since 4b$_1$ is largely a fluorine lone-pair orbital. In this case, there is a shift of only 1.0 eV. In the water–oxygen difluoride pair, the π-MO shift is smaller than that for σ MO's, as appropriate for the perfluoro effect, but the difference is not nearly as large as observed in the ethylene–tetrafluoroethylene pair.

As regards the ionization from the 1a$_2$ MO of oxygen difluoride, alternate assignments must be mentioned. The 1a$_2$ MO in oxygen difluoride is calculated to be

(26) C. R. Brundle and D. W. Turner, *Proc. Roy. Soc., Ser. A*, 307, 27 (1968).

Table VII. Observed and Calculated Ionization Potentials of Formaldehyde and Carbonyl Fluoride

Orbital	H₂CO[a] 0.92K.T.	Adiabatic IP	Vertical IP	Orbital	F₂CO 0.92K.T.	Adiabatic IP	Vertical IP
$2b_1$	11.0	10.88	10.88	$5b_1$	14.4	13.02	13.6
$1b_2$	13.4	14.09	14.5	$2b_2$	14.8	14.09	14.6
$5a_1$	16.1	15.85	16.0	$8a_1$	17.7 ⎱	⎰16.1	16.6
$1b_1$	17.6		16.6	$4b_1$	18.0 ⎰	⎱16.91	17.2
$4a_1$	21.7		ca. 21.8[b]	$1a_2$	18.5		
$3a_1$	35.8			$7a_1$	20.4	19.15	19.15
$2a_1$	284.1			$1b_2$	21.0		19.8
$1a_1$	514.0			$3b_1$	22.0		21.1
				$6a_1$	24.1	ca. 22.7	23.4
				$5a_1$	38.3		
				$2b_1$	42.8		
				$4a_1$	44.7		
				$3a_1$	290.0		
				$2a_1$	516.5		
				$1b_1$	661.8		
				$1a_1$	661.8		

[a] Experimental values taken from ref 16. [b] From the He(II) spectrum of ref 27.

completely O–F nonbonding, and according to the general practice in molecular spectroscopy, should be expected to give an extremely vertical photoelectron transition, appearing much like an atomic line. Instead, if our assignment is correct, a broad band is observed at 18.50 eV, Figure 3. On the other hand, it is possible that the calculations are not as accurate as we suppose, and that the $1a_2$ ionization potential should be included in the 16–17-eV region, together with those from the $4b_1$ and $6a_1$ MO's. The relatively sharp peak at 16.44 eV could then be ascribed to the nonbonding $1a_2$ orbital, and the broad bands between 18 and 22 eV to the $3b_1$, $5a_1$, and $1b_2$ orbitals.

Formaldehyde–Carbonyl Fluoride. The experimental work on formaldehyde quoted here is that of ref 16 and 27. Our sample of carbonyl fluoride is slightly contaminated with carbon dioxide, and the impurity lines have been suppressed in drawing Figure 4. As is evident from Table VII, the orbital structure of formaldehyde is relatively uncomplicated, and the Koopmans' theorem values stand in rather good agreement with the experimental values. In earlier work, there was some question as to whether the $1b_2$ π ionization preceded or followed that from the second nonbonding pair on the oxygen atom, $5a_1$; the GTO calculations leave little doubt that the first ionization of formaldehyde involves the $2b_1$ MO, with ionizations from $1b_2$ and $5a_1$ following in that order. The situation is not as clear-cut in carbonyl fluoride, wherein the first few ionizations at both ends of the spectrum can be identified with confidence, but the central region of the spectrum (16–19 eV) is badly overlapped, and a band is missing. The GTO calculations, Table VII, do predict that the first two ionization potentials in carbonyl fluoride are out of the n_O and π MO's, as in formaldehyde itself.

As appropriate for ionization from the nonbonding electron pair on oxygen $2b_1$, the first photoelectron band of formaldehyde (10.88 eV) is quite vertical, resembling the first band of water in that respect. The $2b_1$ band of formaldehyde shows weak excitation of the totally symmetric vibrations ν_1', ν_2', and ν_3', with a 10–20% lowering of the frequencies in the ionic state. That the totally symmetric C–H and C–O stretching and H–C–H deformation motions are ex-

(27) D. W. Turner, private communication.

cited upon ionization follows from the overlap populations, Table IX, which show $2b_1$ to be appreciably C–H bonding (0.137) and C–O (−0.205) and H–H (−0.114) antibonding. According to the GTO calcu-
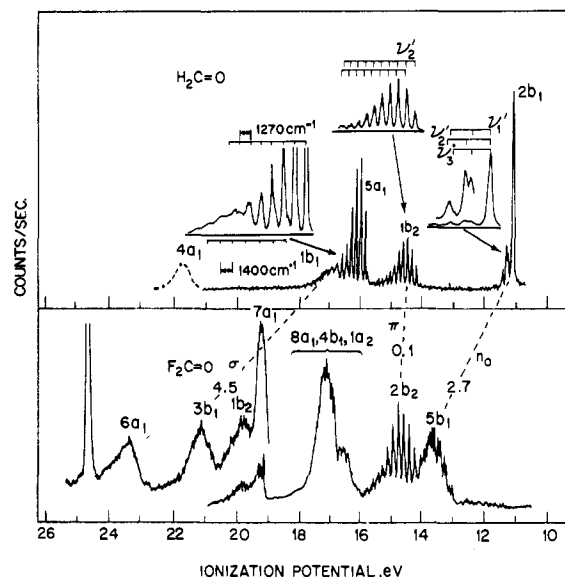

Figure 4. The photoelectron spectra of formaldehyde and carbonyl fluoride. The spectrum above 21 eV in formaldehyde (dashed line) was determined by Turner using He(II) excitation,[27] and the spectrum beyond 19 eV in carbonyl fluoride was similarly determined in this work.

lations, Table VII, the corresponding band in carbonyl fluoride comes at 13.6 eV ($5b_1$) and has a vibronic structure very different from that observed in its perhydro analog, Figure 5a. The $5b_1$ band of carbonyl fluoride is very nonvertical and displays a long vibrational progression (at least five members) of 1550 cm⁻¹ built upon the origin and upon a single quantum of 530 cm⁻¹. The 1550-cm⁻¹ interval is undoubtedly ν_1', the C–O stretch, reduced from a value of 1944 cm⁻¹ in the neutral molecule ground state, whereas the 530 cm⁻¹ interval is possibly ν_3', the F–C–F bending mode reduced from 626 cm⁻¹ in the ground state. (Note that Herzberg[12] prefers 584 cm⁻¹ for the ν_3'' frequency.) Alternatively, the 530-cm⁻¹ spacing
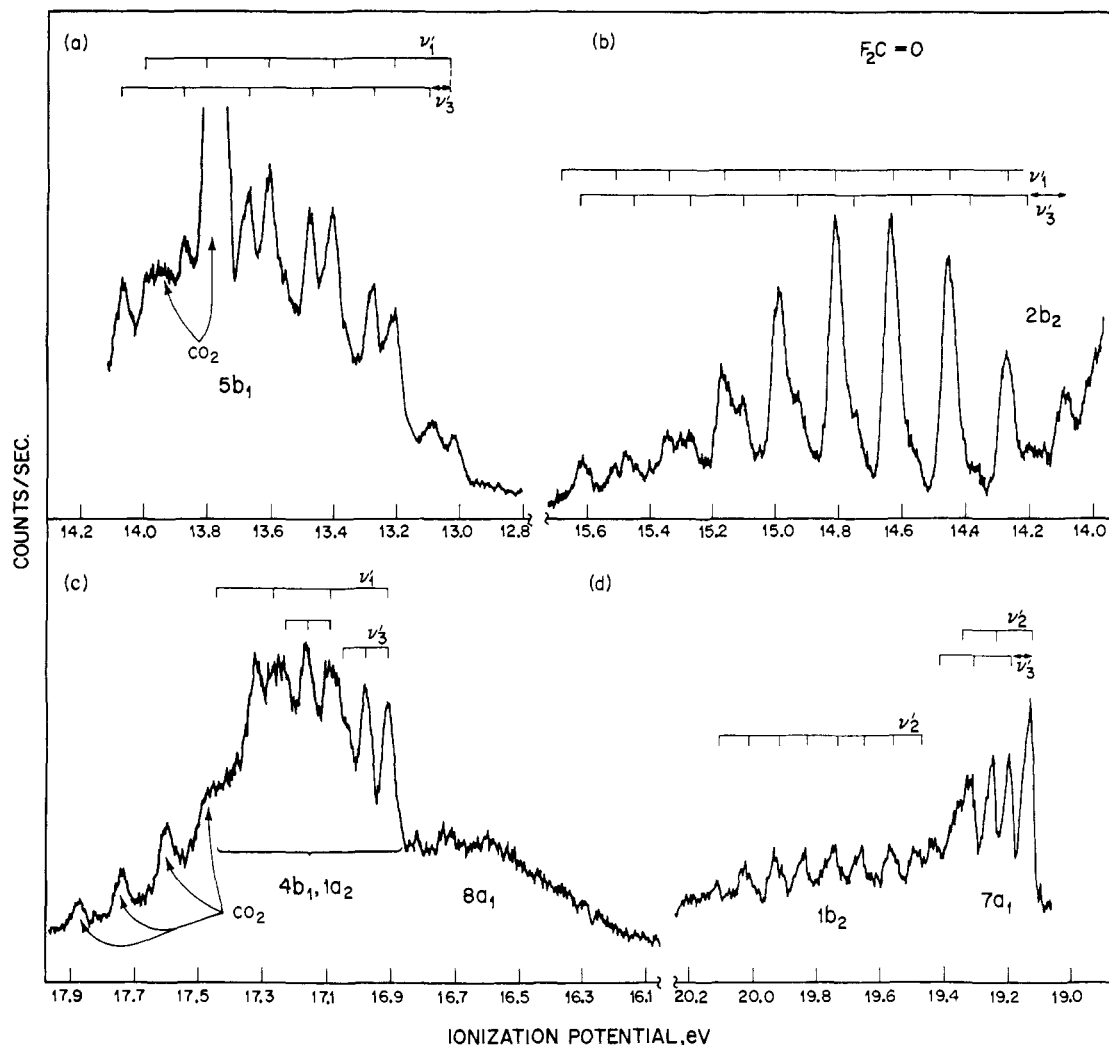
Figure 5. Details of the vibronic structure of the 13.6- (a), 14.6- (b), 17.2- (c), and 19.15–19.8-eV (d) bands of carbonyl fluoride.

might correspond instead to the excitation of ν_2', the C–F stretch (965 cm^{-1} in the ground state). Of the two assignments for the 530-cm^{-1} interval, the F–C–F bending (ν_3') one is preferred, since only 1 quantum of the motion appears in the band envelope, and a decrease of ν_2 from 965 cm^{-1} to 530 cm^{-1} implies a large change of geometric coordinate and a long vibrational progression. The weak excitation of ν_3' together with a long progression in ν_1', the C–O stretch, upon ionization from the 5b$_1$ MO of carbonyl fluoride can be rationalized using the overlap populations, Table IX, which show 5b$_1$ to be strongly C–O bonding (0.136), but weakly F–F antibonding (−0.028).

It is by now common knowledge that the 2b$_1$ lone-pair orbital of formaldehyde is somewhat delocalized over the hydrogen and carbon atoms, Tables VIII and IX. In carbonyl fluoride, the corresponding orbital 5b$_1$ contains a smaller fraction of both carbon and fluorine (as compared to hydrogen) AO's, is more localized upon the oxygen atom, and has a smaller C–O overlap population, and yet the photoelectron transition is a very nonvertical one as compared to that in formaldehyde, with a long progression of C–O stretching being excited. Perhaps this odd situation can be explained as either due to the effect of electronic reorganization upon the molecular geometry of the

carbonyl fluoride positive ion, or the C–O bonding population in the 5b$_1$ MO of carbonyl fluoride is much more effective than the C–O antibonding population in the 2b$_1$ MO of formaldehyde.

Though the changes in band shapes are much alike, the similarities in the water–oxygen difluoride and formaldehyde–carbonyl fluoride "lone-pair" ionizations are no longer evident when the energy shifts are considered, for in the latter pair the shift is +2.7 eV, whereas in the former it is only +0.6 eV. Within the framework of the perfluoro effect, this is to be expected, since the orbitals involved in the first bands of the carbonyls are σ MO's and are subject to large shifts, whereas those in the first bands of water and oxygen difluoride are π MO's and are shifted much less.

The π ionization potential of formaldehyde (1b$_2$, 14.5 eV) remains essentially unchanged in both energy and profile in carbonyl fluoride (2b$_2$, 14.6 eV), in accord with the relative insensitivity of π MO's to fluorination. However, due to the fluorine 2p$_x$ AO content, the 2b$_2$ MO of carbonyl fluoride is appreciably C–F antibonding (−0.117), whereas there is no counterpart to this in formaldehyde. The vibrational assignment of the 1b$_2$ band of formaldehyde unfortunately is uncertain, because the long vibrational series in it suggests the excitation of ν_2' (C–O stretch) with 1

Table VIII. Atomic Population Analysis of the MO's in Formaldehyde and Carbonyl Fluoride

MO	H 1s	C 2s	2p$_x$	2p$_y$	2p$_z$	O 2s	2p$_x$	2p$_y$	2p$_z$	F 2s	2p$_x$	2p$_y$	2p$_z$
					H$_2$CO								
2b$_1$	0.288	0.000	0.000	0.000	0.150	0.000	0.000	0.000	1.272				
1b$_2$	0.000	0.000	0.707	0.000	0.000	0.000	1.293	0.000	0.000				
5a$_1$	0.077	0.031	0.000	0.471	0.000	0.278	0.000	1.063	0.000				
1b$_1$	0.227	0.000	0.000	0.000	0.940	0.000	0.000	0.000	0.604				
4a$_1$	0.258	0.864	0.000	0.244	0.000	0.233	0.000	0.139	0.000				
3a$_1$	0.002	0.390	0.000	0.200	0.000	1.308	0.000	0.110	0.000				
					F$_2$CO								
5b$_1$		0.000	0.000	0.000	0.050	0.000	0.000	0.000	1.636	0.006	0.000	0.107	0.041
2b$_2$		0.000	0.327	0.000	0.000	0.000	1.246	0.000	0.000	0.000	0.213	0.000	0.000
8a$_1$		0.030	0.000	0.204	0.000	0.225	0.000	0.756	0.000	0.000	0.000	0.382	0.008
4b$_1$		0.000	0.000	0.000	0.036	0.000	0.000	0.000	0.001	0.001	0.000	0.224	0.683
1a$_2$		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000
7a$_1$		0.047	0.000	0.112	0.000	0.282	0.000	0.308	0.000	0.000	0.000	0.461	0.164
1b$_2$		0.000	0.448	0.000	0.000	0.000	0.132	0.000	0.000	0.000	0.710	0.000	0.000
3b$_1$		0.000	0.000	0.000	0.490	0.000	0.000	0.000	0.192	0.065	0.000	0.455	0.138
6a$_1$		0.327	0.000	0.166	0.000	0.071	0.000	0.047	0.000	0.123	0.000	0.065	0.507
5a$_1$		0.211	0.000	0.380	0.000	1.156	0.000	0.120	0.000	0.160	0.000	0.005	0.002

Table IX. Overlap Populations Calculated for Formaldehyde and Carbonyl Fluoride

		H$_2$CO		
MO	H–H	C–H	C–O	O–H
2b$_1$	−0.132	0.137	−0.205	−0.114
1b$_2$	0.000	0.000	0.433	0.000
5a$_1$	0.015	0.060	0.097	−0.015
1b$_1$	−0.028	0.216	0.259	0.024
4a$_1$	0.018	0.295	−0.100	0.011
3a$_1$	0.000	0.000	0.588	0.000

		F$_2$CO		
	F–F	C–F	C–O	O–F
5b$_1$	−0.028	−0.040	0.136	−0.084
2b$_2$	0.014	−0.117	0.329	−0.034
8a$_1$	0.017	−0.042	0.110	−0.009
4b$_1$	−0.134	0.017	0.000	0.001
1a$_2$	−0.040	0.000	0.000	0.000
7a$_1$	0.036	0.073	−0.150	−0.019
1b$_2$	0.021	0.147	0.075	0.009
3b$_1$	0.009	0.094	0.096	0.012
6a$_1$	0.011	0.101	0.020	0.002
5a$_1$	0.000	0.001	0.611	0.004

quantum of ν_1' (symmetric C–H stretch) added to each quantum of ν_2', whereas in formaldehyde-d_2, both vibrations seem to be insensitive to deuteration, although only ν_2' should be.[16] In the corresponding 2b$_2$ band of carbonyl fluoride, Figure 5b, we observe a long progression of 1450 cm^{-1} which would appear to be ν_1', the C–O stretch, which is the only ground-state vibration in the 2000–1300-cm^{-1} range. As in formaldehyde, each member of the main progression in carbonyl fluoride is accompanied by another vibration, which in this case may be either 970 or ca. 500 cm^{-1}, depending upon where the electronic origin is located. As both the 2b$_2$ and 5b$_1$ MO's of carbonyl fluoride are predominantly C–O bonding, ionizations from both would be expected to show long progressions of C–O stretching, as observed. Finally, we note that the vertical ionization potentials of the π MO's of formaldehyde and carbonyl fluoride remain very nearly equal, in contrast to the σ MO's, demonstrating the selective nature of the perfluoro effect.

The next MO of formaldehyde, 5a$_1$, is largely the second lone pair on the oxygen atom, aligned along

the C–O axis and somewhat C–O and C–H bonding. The transition from 5a$_1$ (16.0 eV) is somewhat less vertical than that from 2b$_1$, and consists of two nearly coincident vibration progressions of (1270 ± 50)-cm^{-1} spacings. One of these is undoubtedly ν_2' and the other is probably ν_3'.[16] It is difficult to specify the carbonyl fluoride analog of the 5a$_1$ band, since both 8a$_1$ and 7a$_1$ MO's have large amounts of the a$_1$ oxygen lone-pair component. However, 8a$_1$ has much more of this and is C–O bonding as is 5a$_1$ in formaldehyde, whereas 7a$_1$ is C–O antibonding. Thus, if one must make a choice, it seems that 5a$_1$ of formaldehyde (16.0 eV) must correlate with the 8a$_1$ MO of carbonyl fluoride. Experimentally, it is rather difficult to be sure where the 8a$_1$ ionization of carbonyl fluoride is to be found, for the GTO calculations place 8a$_1$, 4b$_1$, and 1a$_2$ very close together in the 17.7–18.5-eV region, while two and possibly three bands are observed, Figure 5c, in the 16–18-eV range. It is most probable that the 8a$_1$ vertical excitation energy lies in the range 16.6–17.2 eV, yielding a σ perfluoro shift of only 0.6–1.2 eV. As a shift of nearly 3 eV ordinarily would be expected for this σ MO, the result is at first rather surprising. We interpret this as showing that the perfluoro effect can be of little value when the perhydro transition is close to and strongly mixed with the fluorine AO's. Though the population analysis appears to discourage the correlation of the 5a$_1$ and 7a$_1$ MO's, even though they have the energy difference expected for a normal σ perfluoro shift and have similar atomic populations, it should be noted that the 2b$_1$ and 5b$_1$ MO's of formaldehyde and carbonyl fluoride are obviously correlated, yet they have overlap populations of opposite sign. Thus the 5a$_1$/7a$_1$ correlation should not be entirely ruled out.

Correlation with the fourth band of formaldehyde, 1b$_1$ (16.6 eV), suffers somewhat from ambiguity as well. The 1b$_1$ MO of formaldehyde is an in-plane π MO having strong C–H and C–O bonding contributions. In carbonyl fluoride, both 4b$_1$ and 3b$_1$ partake of this, both with large admixtures of fluorine AO's, but with 3b$_1$ being much more closely related to 1b$_1$ of formaldehyde on the basis of atomic and overlap populations, Tables VIII and IX. Now according to the GTO calculations, Table VII, the 3b$_1$ ionization is
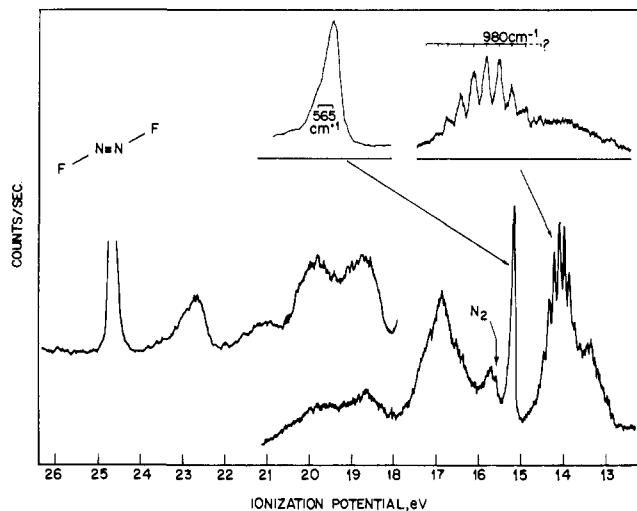
Figure 6. The photoelectron spectrum of difluorodiazine, determined above 18 eV using He(II) excitation, and below 18 eV using He(I) excitation.

associated with the band observed in carbonyl fluoride at 21.1 eV, leading to a perfluoro shift of 4.5 eV, which is a very large shift, but certainly not impossibly so. The $3b_1$ ionization of carbonyl fluoride shows no vibrational structure in the He(II) spectrum under conditions wherein splittings of 700 cm^{-1} or more could be resolved.

As there is a strong resemblance between the spectra in the 15.5–18.0-eV region of formaldehyde and in the 19–20.5-eV region of carbonyl fluoride, Figures 4 and 5, and as the shift between them is of the expected size, one might try and correlate these bands with one another empirically. However, the GTO calculations show that such a correlation is at least ambiguous if not incorrect. The formaldehyde–carbonyl fluoride pair is a particularly good example of how hopeless a study such as this would be without reliable calculations to serve as a guide.

We turn now to the further end of the carbonyl fluoride spectrum; as there are no transitions observed between 23.4 and 28 eV, it is probable from the GTO calculations that the final band of carbonyl fluoride at 23.4 eV corresponds to ionization from the final MO in this region, $6a_1$. Its counterpart, $4a_1$, is found at ca. 21.8 eV in formaldehyde.[27] Being more removed from the fluorine atom transitions, the $4a_1$–$6a_1$ σ MO pair shows a more normal perfluoro shift of +1.6 eV. The 23.4-eV band of carbonyl fluoride exhibits a vibrational fine structure of 730-cm^{-1} spacing. This is most reasonably assigned as ν_2', the totally symmetric C–F stretch, reduced from its ground-state value of 965 cm^{-1}. In accord with this, the overlap population, Table IX, predicts that the $6a_1$ MO of carbonyl fluoride is strongly C–F σ bonding (0.101). If there later proves to be another band in the 24–28-eV region of carbonyl fluoride (which we strongly doubt), then it would have to be assigned to the $6a_1$ ionization, thereby making the $4a_1$–$6a_1$ σ shift larger than 1.6 eV. In either event, it does appear that the perfluoro effect is once again operative in the formaldehyde–carbonyl fluoride molecular pair.

Four ionizations remain in carbonyl fluoride which have no analogs in formaldehyde. According to the

GTO atomic population analysis, $4b_1$ and $1a_2$ are very well described as fluorine lone-pair MO's, and are expected in the 17–18-eV region, where one or more unassigned bands are observed. The remaining two MO's of carbonyl fluoride, $7a_1$ and $1b_2$, are assigned respectively to the transitions observed at 19.15 and 19.8 eV, Figure 5d. These MO's are largely fluorine lone pairs, but $7a_1$ is strongly mixed with oxygen σ AO's, and $1b_2$ with carbon σ AO's. The 900-cm^{-1} vibration in the 19.15-eV band is most likely ν_2', the C–F stretch, as is the 730-cm^{-1} interval in the $1b_2$ ionization. Since the $7a_1$ MO is somewhat C–F bonding and $1b_2$ is strongly C–F bonding, it is reasonable that the $7a_1$ ionization is rather vertical with the C–F stretch appearing at near its ground-state frequency, while the $1b_2$ ionization has an extended Franck–Condon display, Figure 5d, with a greatly reduced ν_2' frequency.

Diimide–Difluorodiazine. The study of the energy levels of these two compounds contributes minimally to our knowledge of the perfluoro effect, since there are no photoelectron data for trans-diimide, HN=NH, and the photoelectron spectrum of trans-difluorodiazine, FN=NF, may contain bands due to an isomeric impurity. The GTO calculations on this pair are not too revealing either. The spectrum of difluorodiazine is displayed in Figure 6, and the computational results on diimide and difluorodiazine are summarized in Table X. The electronic structure of

Table X. Observed and Calculated Ionization Potentials for Diimide and trans-Difluorodiazine

Orbital	N$_2$H$_2$ 0.92K.T.	Orbital	N$_2$F$_2$ 0.92K.T.	Adiabatic IP	Vertical IP
$4a_g$	9.84	$7a_g$	13.92	12.8	13.4
$1a_u$	13.07	$2a_u$	14.24	13.65	14.1
$3b_u$	15.97	$6b_u$	16.60		
$3a_g$	17.42	$6a_g$	17.50		
$2b_u$	23.93	$1b_g$	18.57		
$2a_g$	34.80	$1a_u$	19.80	18.0	18.70
$1b_u$	391.4	$5b_u$	20.20		19.80
$1a_g$	391.5	$5a_g$	20.39		21.0
		$4b_u$	24.06	22.3	22.7
		$4a_g$	35.8		
		$3b_u$	42.4		
		$3a_g$	43.5		
		$2b_u$	396		
		$2a_g$	396		
		$1b_u$	661		
		$1a_g$	661		

diimide was calculated earlier in a smaller GTO basis,[28] with results very similar to those obtained here.

The highest MO in diimide, $4a_g$, is the antibonding combination of the lone-pair orbitals on the nitrogen atoms,[28] and, according to the calculation, should appear at 9.84 eV in the photoelectron spectrum. Experimentally, an electron impact measurement on the transient species N$_2$H$_2$ of unknown geometry gave a first ionization potential of 9.85 ± 0.1 eV.[29] As expected, the corresponding MO in difluorodiazine, $7a_g$, contains a significant amount of N–F σ-antibonding character (−0.151), in addition to the N–N-antibond-

(28) M. B. Robin, R. R. Hart, and N. A. Kuebler, J. Amer. Chem. Soc., 89, 1564 (1967).
(29) S. N. Foner and R. L. Hudson, J. Chem. Phys., 28, 719 (1958).

ing lone-pair component (−0.169). The GTO calculations place the 7a$_g$ MO at 13.92 eV, in good agreement with the first band of the difluorodiazine spectrum observed at 13.4 eV. The transition is very nonvertical and is without vibrational structure. The perfluoro shift for the 4a$_g$–7a$_g$ orbital pair is +3.6 eV, at the higher end of the range spanned by σ MO's.

As there are no higher ionization potentials reported for diimide, we must rely upon the calculations, which place the ionization from the 1a$_u$ π MO at 13.07 eV. This level of diimide correlates with the 2a$_u$ level of difluorodiazine, predicted to come at 14.24 eV and found at 14.1 eV, with a vibrational pattern of 980 cm^{-1}. As both the N–N and N–F bonds are deeply involved in the 2a$_u$ MO, the 980-cm^{-1} vibration could be interpreted as either the N–N stretch (1522 cm^{-1} in the ground state) or, less likely, the N–F stretch (1010 cm^{-1} in the ground state), or a mixture of the two.[30] In this case, the 1a$_u$(predicted)/2a$_u$(observed) perfluoro shift is +1.0 eV, which is rather large for π MO's, but not nearly as large as observed for the σ MO's in this molecular pair.

The third and deeper MO's in the azo compounds are very close to the region of fluorine atom transitions, and consequently those of difluorodiazine are so strongly mixed with fluorine AO's that a meaningful comparison is difficult to make with the MO's of diimide. The GTO calculations also assign seven more bands in the 15–25-eV region of difluorodiazine, whereas eight or possibly nine are observed. The characteristic bands of the contaminants N$_2$, NF$_3$, SF$_6$, CO$_2$, and N$_2$O, which were demonstrated to be at a low level mass spectrometrically, did not appear in the photoelectron spectrum, but it is quite possible that the sample is isomerized and contains a significant amount of the cis isomer. Once beyond the 15–18-eV span, the MO correlations can be taken up again. Thus, the 2b$_u$ MO of diimide (23.93 eV, predicted) and the 4b$_u$ MO of difluorodiazine (24.06 eV, predicted; 22.7 eV, observed) are both describable as the N–N antibonding MO's formed largely of 2s$_N$ AO's, which explains the seemingly anomalously small σ shift for these MO's.

Butadiene–1,1,4,4-Tetrafluorobutadiene. The photoelectron spectra of butadiene, 1,1,4,4-tetrafluorobutadiene, and hexafluorobutadiene have been published earlier[31] in a study focusing upon the molecular structure of the hexafluoride. Because it was shown that hexafluorobutadiene deviates significantly from planarity, but that the tetrafluoride is trans planar, as is butadiene itself, we must use these latter two molecules for the perfluoro test rather than butadiene and its hexafluoro derivative. As was already demonstrated in the case of the partially fluorinated ethylenes (*vide supra*), a significant perfluoro shift is to be expected in 1,1,4,4-tetrafluorobutadiene, even though it is not totally fluorinated. The pertinent He(I) spectra are shown in Figure 1 of ref 31, and the observed transition energies are tabulated in that paper. The He(I) butadiene spectrum has also been studied under high resolution by Eland.[32] In the He(II) spectrum of butadiene, the bands at 11.8 and 15.5 eV increase some-

what in intensity with respect to the other bands in the spectrum.

The fluorinated butadienes are too large for high-quality GTO calculations, but the calculation of Buenker and Whitten[33] on *trans*-butadiene is of interest to us. The highest MO in butadiene is undoubtedly the 1b$_g$ π MO and is the origin of the photoelectron band at 9.06 eV. The corresponding 2b$_g$ band in the tetrafluoro compound appears at 9.38 eV, the near-zero perfluoro shift being in accord with our expectations for π-electron excitations. Note also that the band in butadiene is rather vertical, but that mixing with the fluorine AO's in the tetrafluoro derivative leads to a much less vertical excitation, as always seems to be the case in the perfluoro derivatives. Now the interesting point is that the next two ionizations in butadiene at 11.47 and 12.23 eV are assigned as 1a$_u$(π) and 7a$_g$(σ) by the GTO computation, but semiempirical calculations reverse this ordering.[34] As one of the two bands is from a σ MO and one is from a π MO, this is obviously an excellent opportunity for the perfluoro effect to prove its worth, and it is rather disappointing that the result is still largely ambiguous. It is abundantly clear that the perfluoro effect is operative in tetrafluorobutadiene, for there is only one transition in the 10–13-eV region of this molecule, whereas there are two in the same region in butadiene. However, the 12.04-eV 2a$_u$ π ionization potential of tetrafluorobutadiene could be reasonably correlated with either the 11.47- or 12.23-eV band of butadiene, the band not so correlated having been shifted above 14 eV. As the 12.23-eV band is closer to the 12.04 band of the tetrafluoro compound, it had been assigned as originating with the 1a$_u$ π MO, and the 11.47-eV band with the 7a$_g$ σ MO. However, our experience has been that the perfluoro shifts for π MO's may be as large as 1 eV, but are always upward (with one exception). In this case, one must argue that the 11.47-eV band of butadiene is the π MO and shifts 0.57 eV upward to 12.04 eV in tetrafluorobutadiene, rather than 0.19 eV downward, as required by the previous assignment. Whereas we now prefer the π, π, σ ordering predicted by the GTO calculations, it must be admitted that the second and third bands in butadiene are just too close for the perfluoro effect to give a definitive answer. In the twisted diene, hexafluorobutadiene, the two π MO ionizations are found at 10.4 and 11.4 eV, whereas the lowest σ MO ionization comes at 14.45 eV, indicating that the strong preferential stabilization of the σ MO's is operating as well in this twisted molecule.[31]

Acetone–Hexafluoroacetone. In this and the following section, we explore briefly the effect of perfluorination on the methyl derivatives of formaldehyde and diimide. Because of the size of these molecules, we cannot perform GTO calculations of reliable accuracy, and so will be guided in the spectral assignments more by intuition and experience than by theory. The first transition in acetone is a vertical one, Figure 7 and Table XI, with an origin at 9.72 (3) eV and 2 quanta of 1210 cm^{-1} and 1 of 360 cm^{-1} excited. In the optical spectrum of acetone,[35,36] the n$_0$ → 3s Rydberg ex-

(30) R. H. Sanborn, *J. Chem. Phys.*, **33**, 1855 (1960).
(31) C. R. Brundle and M. B. Robin, *J. Amer. Chem. Soc.*, **92**, 5550 (1970).
(32) J. H. D. Eland, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 471 (1969).
(33) R. J. Buenker and J. L. Whitten, *J. Chem. Phys.*, **49**, 5381 (1968).
(34) See, for example, N. C. Baird and M. J. S. Dewar, *Theor. Chim. Acta*, **9**, 1 (1967).
(35) M. Lawson and A. B. F. Duncan, *J. Chem. Phys.*, **12**, 329 (1944).
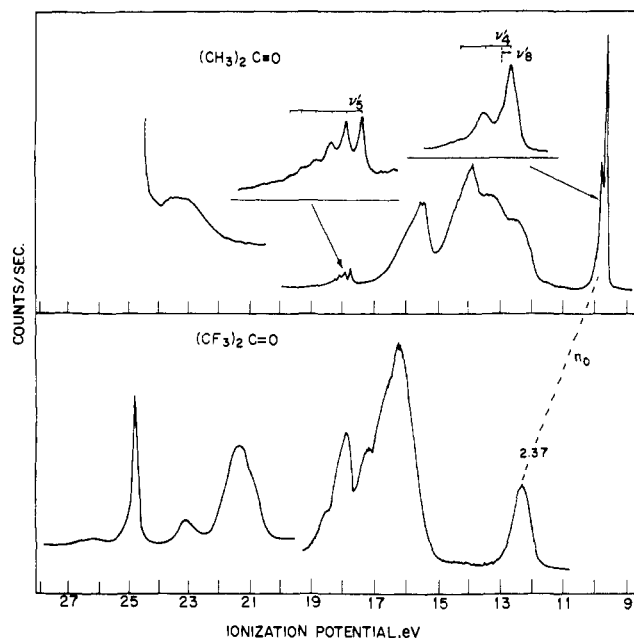
Figure 7. The He(I) and He(II) photoelectron spectra of acetone and hexafluoroacetone.

citation shows an almost identical profile, the vibrational frequencies there being 1195 and 325 cm^{-1} (among others). The 1195-cm^{-1} vibration in the optical spectrum was first thought to be ν_3', the C–O stretch (1710 cm^{-1} in the ground state), but Lawson and Dun-

Table XI. Ionization Potentials Observed in Acetone, Acetone-d_6, and Hexafluoroacetone

Adiabatic IP	Vertical IP	Vibrations[a]
	(CH$_3$)$_2$CO	
9.72 (3)	9.72 (3)	1210, 360 (?)
ca. 11.8	12.6	
	13.4	
	13.9	
	14.5	
	15.55	
17.73 (3)	17.73 (3)	1370
ca. 21	23.2	
	(CD$_3$)$_2$CO[b]	
9.68 (8)	9.68 (8)	880
17.77 (7)	17.90 (5)	1050
	(CF$_3$)$_2$CO	
11.44	12.09	
	16.0	
	16.5	
	17.1	
	17.75	
	18.4	
ca. 20.3	21.2	
ca. 22.5	22.9	
	26.0	

[a] Vibrational intervals (cm^{-1}) listed in decreasing order of prominence in the band envelope. [b] The ionization potentials of acetone and acetone-d_6 appear identical in the 10–17-eV region.

can[35] and Ito, et al.,[36] find this frequency reduced to 906 cm^{-1} in the n$_0$ → 3s band of acetone-d_6. On this basis, they assign the vibration instead to ν_4', the methyl group symmetric deformation mode (1435 cm^{-1}

(36) H. Ito, Y. Nogata, S. Matsuzaki, and A. Kuboyama, Bull. Chem. Soc. Jap., 42, 2453 (1969).

in the acetone ground state). Our photoelectron spectrum of acetone-d_6 shows the 1210-cm^{-1} mode reduced in frequency to 880 cm^{-1} in the ionic ground state, thereby confirming the ν_4' assignment in the photoelectron spectrum as well. Undoubtedly, the electron being ionized is an n$_0$ lone-pair electron on the oxygen atom. Watanabe[37] has found the limit of the the n$_0$ → ns Rydberg series in acetone to be 9.705 eV and the onset of photoionization to come at 9.69 ± 0.01 eV.

As in the other perfluoro compounds studied here, perfluorination of acetone has two large effects on the lone pair ionization; i.e., the vertical excitation of acetone becomes appreciably less vertical in hexafluoroacetone (the half-width increases by a factor of 3) and the ionization potential moves 2.37 eV to higher energy. This behavior parallels very closely that found for the n$_0$ orbitals in the formaldehyde–carbonyl fluoride pair and indirectly suggests that the n$_O$ MO of hexafluoroacetone is partially delocalized over the fluorine atoms of the trifluoromethyl groups.

With a substantial perfluoro effect established for the σ MO's of the acetone–hexafluoroacetone pair, we now turn to the π MO's (loosely called) under the same perturbation. Though the second band in formaldehyde clearly involves the 1b$_1$ π MO (14.5 eV), the second band in acetone (12.6 eV) could be this or, just as likely, a methyl group excitation derived from the 1t$_2$ MO set of methane. Looking at the ethylene–isobutylene pair, two methyl groups on the same carbon atom are seen to reduce the π ionization potential by 1.2 eV.[25] The same reduction applied to the 14.5-eV band of formaldehyde (1b$_2$ π) places the π MO of acetone at 13.3 eV. On this basis, we tentatively assign the 13.4-eV band of acetone as originating at the C–O π MO and the 12.6-eV band as originating with methyl group MO's. Actually, for our purpose, it makes no difference if the above assignment is correct, inverted, or if both the 12.6- and 13.4-eV bands of acetone are methyl group ionizations, with the π band coming at 14.0 eV, because the second ionization potential of hexafluoroacetone is 16.0 eV. Thus, on perfluorination of acetone, the π level must be shifted upward by at least 2 eV, and more likely by 2.6 eV. One must conclude from the size of this shift that the trifluoromethyl group orbitals are strongly mixed with those of the carbonyl group, so that π and σ are poor symmetry descriptions electronically, and that the specific effect of perfluorination on σ electrons in planar molecules operates indiscriminately in nonplanar compounds. (Recall, however, the specific effect uncovered in the nonplanar molecule hexafluorobutadiene.) The indiscriminate upward shift of both π and σ MO's in the butene-2–octafluorobutene-2 pair mentioned earlier (Table IV) parallels that found for the acetone–hexafluoroacetone pair.

Azomethane–Hexafluoroazomethane. In our preliminary work, it was thought that the azomethane–hexafluoroazomethane pair would be a useful one in the study of the effects of perfluorination on molecules containing the methyl group. While this study was in progress, the electron diffraction work of Chang, et al.,[38] appeared, showing that azomethane has the planar trans configuration but that hexafluoroazo-

(37) K. Watanabe, J. Chem. Phys., 22, 1564 (1954).
(38) C. H. Chang, R. F. Porter, and S. H. Bauer, J. Amer. Chem. Soc., 92, 4313 (1970).

methane, as obtained from Merck Sharp and Dohme of Canada, has the planar cis configuration. Consequently, the comparison between the photoelectron spectra of these two molecules is not strictly valid as regards the perfluoro effect. The He(I) spectra of these two molecules are shown in Figure 8 and the He(I) and He(II) results tabulated in Table XII.

Table XII. Observed Ionization Potentials of Azomethane and Hexafluoroazomethane

| Azomethane | | Hexafluoroazomethane | |
Adiabatic IP	Vertical IP	Adiabatic IP	Vertical IP
ca. 8.20	8.98	ca. 10.5	11.35
11.35	11.81	ca. 14.6	15.3
	12.3		15.9
ca. 13.1	13.6		16.8
	14.5		17.7
ca. 15.3	15.8	20.3	21.4
ca. 17.8	18.6	22.7	23.1
ca. 21.6	22.4	ca. 26.2	27.1

The He(I) spectrum of azomethane reported here is in agreement with that of Haselbach, et al.,[39,40] except that we find an obvious transition at 18.6 eV which is absent on their record. In the He(II) spectrum of azomethane, the relative intensities of the 8.98- and 15.8-eV bands have increased with respect to the others, whereas the intensity ratios in the He(II) spectrum of hexafluoroazomethane are the same as those in the He(I) spectrum. There is an unexplained extra band in the He(I) spectrum of hexafluoroazomethane obscuring the origin of the first ionization potential. That this is not a genuine part of the spectrum is clear from the He(II) spectrum, Figure 8, in which the spurious peak is absent.

In both molecules, the first band is due to ionization from the antobonding combination of nitrogen lone-pair AO's,[28,39,40] these being analogous to the $4a_g$ MO of diimide and the $7a_g$ MO of difluorodiazine (vide supra). Ignoring geometrical effects, the fluorination of azomethane shifts the first ionization potential upward by 2.37 eV, a shift which is smaller than that experienced by the equivalent MO's on going from diimide to difluorodiazine (+3.56 eV). This parallels the behavior in the ketone series, where the fluorination of acetone shifts the first ionization potential upward by 2.37 eV. Thus, ignoring the different geometry of hexafluoroazomethane, the data on the azo series would seem to indicate a large perfluoro shift for the uppermost σ MO. The second band in azomethane (11.81 eV) is assigned by Haselbach, et al., as originating with the π MO, and we agree. While we have no hint as to which band this corresponds to in hexafluoroazomethane, it is sufficient for our purpose to note that the second band of this compound is at 15.35 eV. Thus the perfluoro shift of the π level must be at least 3.5 eV upward, in sharp distinction to the behavior of the related MO in the diimide–difluorodiazine pair, for which the shift is estimated to be 1.0 eV. And so we find the azo series to parallel closely the results of the keto and olefin series; the trifluoromethyl group

(39) E. Haselbach, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem., Int. Ed. Engl.,* **8**, 878 (1969).

(40) E. Haselbach and E. Heilbronner, *Helv. Chim. Acta,* **53**, 684 (1970).
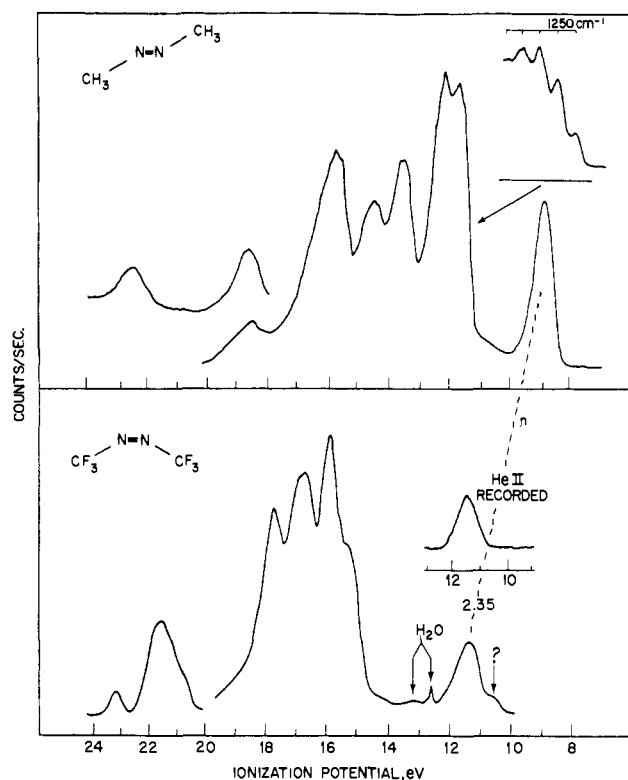
Figure 8. The He(I) and He(II) photoelectron spectra of *trans*-azomethane and *cis*-hexafluoroazomethane.

destroys the π–σ distinction electronically and the perfluoro effect is therefore of no value in compounds containing this group.

The magnitude of the splitting between the two "lone-pair" MO's in *trans*-diimide and *trans*-azomethane is of some interest. According to Haselbach, et al.,[38,40] the first and third ionizations in azomethane are assigned to the n_+ and n_- MO's, the splitting being 3.3 ± 0.2 eV. In the case of diimide, the corresponding ionization potentials have not been observed, but a splitting of 6.13 eV is calculated. That this number is so much larger in diimide than in azomethane is surprising, but we have faith in the GTO calculations and feel that the difference must be a real one. In the cis azo compound diazirine

$$\underset{\underset{CH_2}{\diagdown\diagup}}{N=N}$$

the n_+/n_- split is calculated to be 4.0 eV.[41]

Acetylene–Fluoroacetylene. Baker and Turner[42] report the π ionization potential of acetylene as 11.40 eV, and this is followed by two σ ionizations at 16.44 and 18.42 eV. Haink, et al.,[43] report the π ionization potential of fluoroacetylene to be 11.26 eV. The small difference between this value and that of acetylene is comparable with the perfluoro effect on π electrons. In the higher energy region of fluoroacetylene, only a single band at 17.8 eV is reported, which is most likely the fluorine "lone-pair" ionization, the σ MO's of the $C\equiv C$-H group being shifted into the 20-eV region.

(41) M. B. Robin, H. Basch, N. A. Kuebler, K. B. Wiberg, and G. B. Ellison, *J. Chem. Phys.,* **51**, 45 (1969).

(42) C. Baker and D. W. Turner, *Chem. Commun.,* 797 (1967).

(43) H. J. Haink, E. Heilbronner, V. Hornung, and E. Kloster-Jensen, *Helv. Chim. Acta,* **53**, 1073 (1970).

This is a tentative explanation designed to support the perfluoro effect.

Methane–Difluoromethane. In the difluoromethane molecule, consider the CF_2 plane to be the one which defines σ and π MO's. With this definition, the two C–H bond orbitals form a π MO ($2b_2$, analogous to the $2b_2$ π MO of oxygen difluoride) having an ionization potential of 13.27 eV and a σ MO ($4a_1$) with an ionization potential of 23.9 eV.[15] Within the context of our discussion, this is the perfluoro partner of the perhydrocompound, methane. The corresponding ionizations in methane are found at 13.2 and 23.0 eV, respectively, leading to a π perfluoro shift of less than $+0.1$ eV and a σ perfluoro shift of $+0.9$ eV. On a relative basis, it would appear that the perfluoro effect is operating in this pair of molecules, but the σ shift is only one-half to one-third that expected, when compared to ethylene and butadiene.

Discussion

The data presented above strongly support the existence of the perfluoro effect, while pointing out at the same time the difficulties of using it unaided for symmetry assignments. The effect seems to be at its most definitive in the nonaromatic hydrocarbons, in which fluorination shifts the π MO's by 0–0.5 eV and the σ MO's by 2–3 eV. With atoms other than carbon in the system, the difference in shifts is not necessarily as distinct, and one must instead quote a range of 0–1.5 eV for the π-electron shift and 1.5–4 eV for the σ electrons. Though these ranges tend to overlap, in every case so far the σ shift is larger than the π shift. Fluorination of the methyl derivatives of the same molecules results in an indiscriminate upward shift of all ionization potentials. It also seems that perfluorination makes all nonbonding electrons much less so, irrespective of whether they are σ, as in formaldehyde, or π, as in water.

That the first ionization potential of ethylene should be very nearly the same as those of its variously fluorinated derivatives is at first sight peculiar, since many examples can be quoted of large upward shifts of the first ionization potential upon fluorination. For example, the first ionization potential of ethane (12.1 eV) is strongly shifted upward in hexafluoroethane (14.488 eV),[25] the first ionization potential of methane (14 eV) shifts to 16.2 eV in carbon tetrafluoride,[15] and a similarly large effect is noted in the silane (12.36 eV)[44]– silicon tetrafluoride (16.46 eV),[3a] phosphine (9.9 eV)[45]– phosphorus trifluoride (12.3 eV),[46] and ammonia (10.85 eV)[47]–nitrogen trifluoride (13.73 eV)[48] pairs. In contrast, the lowest ionization potential of ethylene (10.51 eV) is virtually equal to that of tetrafluoroethylene (10.52 eV), Table I. In order to gain insight into the radically different behavior of the ethylene–fluoroethylene ionization potentials, let us first focus on ethylene and the methylethylenes. In the methylethylenes, the π ionization potential decreases in a

regular manner from 10.51 to 8.30 eV on going from ethylene to tetramethylethylene. Price, *et al.*,[49] considered the heats of formation of the methylethylenes and found that the ground states were stabilized by about 3 kcal/mol per methyl group, presumably through hyperconjugation. On the other hand, the π ionization potentials show that each methyl group is stabilizing the ionic state by about 15 kcal/mol. This is accomplished by the delocalization of the positive charge of the ion onto the methyl group. In their photoionization threshold work on olefins, Bralsford, *et al.*,[50] found the (0, 0) band of the tetrafluoroethylene π ionization to be lower in energy than that of ethylene and argued that in this case, the ionic state again was stabilized by delocalization of the positive charge over the fluorine atoms, but that the ground state was stabilized by the inductive effect of the strongly electronegative fluorine atoms. The net result of the inductive stabilization of the ground state and the mesomeric stabilization of the upper state is an essentially unaltered ionization potential on substituting hydrogens by fluorines. Comparison with other nonplanar and supposedly nonmesomeric systems such as ammonia–nitrogen trifluoride places the magnitude of the inductive effect at about 2–3 eV.

In the GTO calculations of the neutral molecule's total energy and wave function, one cannot extract an estimate of the stabilization of the π MO due to the inductive effect alone; however, the suggested stabilization due to delocalization in the ionic state can be readily estimated. In the Koopmans' theorem approximation, the total energy of the $C_2F_4^+$ ion ($^2B_{2u}$) is equal to the total energy computed for C_2F_4 (^1A_g) diminished by the $2b_{2u}$ orbital energy. This result, -472.89855 au, presumes that the occupied MO's of the ion are identical with those of the neutral molecule. If, instead, the MO's in the ion are allowed to reorganize by repeating the SCF calculation for the ion, the total energy is then -472.93159 au. The difference between these two calculated total energies, -0.89 eV, is the total stabilization accrued by *all* MO's upon reorganization. Clearly, the stabilization of the $2b_{2u}$ MO by reorganization (delocalization) cannot be very large. Atomic population analyses of the $2b_{2u}$ MO's of tetrafluoroethylene and its positive ion show that upon ionization, only 0.035 of a π electron is shifted from each of the fluorine atoms to carbon, again demonstrating that the concept of significantly increased π-electron delocalization and stabilization in the positive ion is incorrect.

An important clue to the source of the perfluoro effect in planar, nonaromatic molecules is that in the single most important valence-bond structure describing the ground states of the neutral molecules, the σ electrons of the central group are formally bonded to the fluorine atoms but the π electrons are not. In the MO theory, this is usually expressed as a heavy mixing of fluorine and carbon σ AO's, accompanied by a large change of orbital energies for these MO's. Table III shows that this is the case for tetrafluoroethylene: the $2b_{2u}$ π MO is predominantly on the carbon atoms, whereas in each of the next 13 σ MO's, the population on a fluorine atom is larger than on a carbon atom! Thus, the qualitative statement seems warranted that σ levels will

(44) 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).

(45) G. R. Branton, D. C. Frost, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, **5**, 1 (1970).

(46) P. J. Bassett, D. R. Lloyd, I. H. Hillier, and V. R. Saunders, *ibid.*, **6**, 253 (1970).

(47) G. R. Branton, D. C. Frost, T. Makita, C. A. McDowell, and I. A. Stenhouse, *Phil. Trans. Roy. Soc. London, Ser. A*, **268**, 77 (1970).

(48) A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *ibid.*, *Ser. A*, **268**, 59 (1970).

(49) W. C. Price, R. Bralsford, P. V. Harris, and R. G. Ridley, *Spectrochim. Acta*, **14**, 45 (1959).

(50) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc.*, **258**, 459 (1960).

be more delocalized onto the fluorine atoms than π levels, and through the very high ionization potential of the fluorine atom (17.42 eV), the σ MO's will be much more strongly stabilized. The second significant factor is that all of the σ MO's (except $6a_g$) have a small C–F bonding overlap population, whereas that in the $2b_{2u}$ π MO is strongly C–F antibonding and therefore destabilizing. Thus we arrive at a very simple picture of the perfluoro effect in tetrafluoroethylene; the σ MO's are strongly stabilized by the extensive mixing of the ethylene group orbitals with the σ AO's of the highly electronegative fluorine atoms, whereas this mixing and stabilization is much smaller for the π MO and is countered by a strong C–F antibonding overlap. The reality of the strong C–F π antibonding effect in tetrafluoroethylene is quite clear in the $2b_{2u}$ photoelectron band envelope discussed above.

Obviously, the extent of the net shift of the π-MO energies will differ from molecule to molecule, depending upon their opposing delocalization and antibonding characters, but should remain smaller than the σ shift, as observed. The story is much the same in the water–oxygen difluoride pair, Table VI. As the $2b_2$ π MO of oxygen difluoride remains overwhelmingly centered on the oxygen atom and has significant O–F antibonding overlap, the opposing effects of delocalization onto the highly electronegative fluorine atoms and the O–F antibonding lead to an ionization potential close to that of the $1b_2$ π MO of water. Now in the ethylene–tetrafluoroethylene pair, mixing of the carbon and fluorine AO's shifts σ electrons from an atom of low ionization potential (carbon) to one of high ionization potential (fluorine) and thus a considerable stabilization results. In oxygen difluoride this effect will not be as large, since the ionization potentials of oxygen and fluorine are more alike, and since the oxygen competes more successfully with fluorine in the atomic populations. Consequently, it is reasonable that the σ shifts are smaller here than in the ethylene–tetrafluoroethylene pair.

The situation in the formaldehyde–carbonyl fluoride pair is less clear-cut, for the $5b_1$ σ MO of carbonyl fluoride remains overwhelmingly centered on the oxygen atom, yet the perfluoro shift is again very large ($+2.7$ eV). The atomic populations do show that a sizable amount of hydrogen atom density in formaldehyde becomes fluorine atom density in carbonyl fluoride, and that $2b_1$ is C–O antibonding, whereas $5b_1$ is C–O bonding. Thus the delocalization and bonding–antibonding characters act in unison to increase the n_O ionization potential in carbonyl fluoride. Considering the π MO's, that of carbonyl fluoride has a component on the fluorine atoms, but is strongly C–F antibonding, such that these opposing factors lead to a very small net shift of the ionization potential compared with the $1b_2$ MO of formaldehyde. A similar remark applies to the π-MO ionizations in diimide and difluorodiazine.

In the case of nonplanar systems, such as those containing the trifluoromethyl group, the ammonia–nitrogen trifluoride pair, etc., the σ–π distinction is no longer valid and the ionization potentials of all MO's of the perhydro compound suffer a large shift upward in the

perfluoro analog. In these cases, there is no doubt a heavy and indiscriminate mixing of fluorine AO's into all MO's, with a concomitant stabilization of 2–3 eV.

We conclude from this study that there is a selective stabilization of σ MO's in planar perfluorinated compounds which can be traced back to high percentages of fluorine atom AO's mixed into the σ MO's of the central grouping, and that the π MO's show a much smaller fluorine AO content and are strongly antibonding between the fluorines and the central-group π orbitals. However, the utility of the effect in assigning π and σ MO's has yet to be demonstrated in planar, nonaromatic systems, since a priori knowledge of the MO symmetries, energies, and AO compositions is required before one can make a confident comparison of various experimental ionization potentials. This is most true for the higher ionization potentials; the situation for first or second ionization potentials and for aromatic compounds[8] is a little brighter. Another possibility for an effect of the sort discussed here is offered by substitution of the protons in planar, nonaromatic molecules by the trimethylsilyl group, $(CH_3)_3Si$–, which is known to have a very strong stabilizing effect on π MO's.[51,52] However, the trimethylsilyl group will add even more complications to the spectrum, thus making it potentially less useful than the fluorine perturbation. A discussion of the perfluoro effect in planar aromatic systems is given in the following paper.[8]

Another interesting aspect of the GTO calculations are the $1s_C$ binding energies which are predicted. In an earlier study of fluorine-containing molecules,[53] it was concluded that Koopmans' theorem as applied to $1s_C$ energies required multiplication by the empirical factor 0.952. Application of this rule to ethylene and tetrafluoroethylene yields $1s_C$ binding energies of 292.2 and 298.1 eV, respectively, whereas Thomas reports 290.7 eV for gaseous ethylene.[54] The difference of 5.9 eV predicted between $1s_C$ in ethylene and tetrafluoroethylene is very nearly equal to the differences calculated between methane and difluoromethane (5.7 eV),[53] and between formaldehyde and carbonyl fluoride (6.1 eV, this work). All of this leads to the peculiar situation wherein the change of ionization potential on fluorination is largest for the carbon 1s electrons, even though these are surely the most nonbonding in the molecule. The $1s_O$ binding energies in the water–oxygen difluoride pair behave in the manner mentioned for the ethylene–tetrafluoroethylene pair. Thus the predicted stabilization of the $1s_O$ orbital on going from water to oxygen difluoride is 9.3 eV, which is much larger than the stabilization of any of the MO's in the valence shell.

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