Contribution from the Department of Chemistry,
University of Maryland, College Park, Maryland 20742

# Energies of $\pi$-Acceptor Orbitals in $SiH_4$, $PH_3$, $H_2S$, and HCl and Their Permethylated Derivatives

J. A. TOSSELL,* J. H. MOORE, and J. C. GIORDAN[†]

*Received June 28, 1984*

Energies of unstable negative ions formed by the addition of electrons to $SiX_4$, $PX_3$, $X_2S$, and XCl (X = H, $CH_3$) have been determined by electron transmission spectroscopy (ETS). The orbitals occupied in these unstable anions are found to be of $\sigma^*$ type. For the Si, P, and S compounds these orbitals have the proper symmetry to act as acceptors of $\pi$-electron density from transition metals or aromatic systems. The electron-attachment energies determined for the Si, P, and S hydrides differ by only 0.2 eV and are lower than those found for their permethylated derivatives by 1–2 eV, consistent with the weaker $\pi$-acceptor ability of methylated compounds. Differences observed in X-ray absorption and UV spectra between these hydrides and their methyl derivatives are consistent with the ETS results. Multiple-scattering–X$\alpha$ calculations for $SiH_4$ and HCl accurately reproduce both electron transmission and UV spectra.

## Introduction

In many transition-metal organometallic compounds in which the metal is in a low oxidation state, back-donation of electron density from a metal d orbital to an unoccupied ligand orbital of $\pi$ symmetry (with respect to the metal–ligand bond) is thought to make a significant contribution to the bond strength.[1] For example, a $\sigma^*$ orbital of $PH_3$ interacts with the filled metal 3d $t_{2g}$ orbitals in $Cr(CO)_5PH_3$. Analogously, a $\sigma^*$ orbital of a $-PH_2$ group interacts with benzene $\pi^*$ orbitals in phenylalkylphosphines. The $\pi$-acceptor strength of the ligands has been assessed by analysis of bond distances,[2] vibrational frequencies,[3] and electron-binding energies.[4] According to qualitative MO theory describing metal-to-ligand back-bonding,[5] the energy of the unoccupied ligand orbital is paramount in determining the bond strength. However, there has thus far been no comprehensive discussion of the energies of such orbitals within this context. In this paper we will illustrate the utility of electron transmission spectroscopy[6] in conjunction with quantum-mechanical calculations as a means of assessing the energy and orbital character of low-lying, empty ligand orbitals. Our subject in particular is the $\sigma^*$ orbitals of a series of saturated, main-group, perhydro and permethylated compounds that commonly serve as ligands and models of ligands in organometallic chemistry.

Electron transmission spectroscopy (ETS) measures the energies of temporary negative ion states arising from electron capture by an atom or molecule. These attachment energies are often found to correlate with the atomic or molecular orbital energies, calculated or inferred from other experimental observation. Although orbitals are only artifacts arising from an independent electron model, many trends in molecular properties and many similarities between electronically related molecules can be simply interpreted by such an orbital model. Throughout this paper we often (incorrectly) treat orbitals as physical entities and thus use language such as "the orbital becomes more stable" to mean "the energy of the anion state decreases" or "an electron is captured into an unoccupied molecular orbital" to mean "an anion is produced in a state which is described in terms of molecular orbital theory as electron occupation of a previously unfilled orbital". The language used here is, however, sufficiently widespread that we assume the reader is familiar with our terminology.

Thus, we can measure an attachment energy for the lowest unoccupied orbital of $PH_3$ and identify a similar feature in the electron transmission spectra of $Cr(CO)_5PH_3$ and of phenylalkylphosphines. The attachment energy for the $PH_3$ "parent molecule" correlates with a $\sigma^*$ orbital that can interact with a metal d orbital in the transition-metal compound or a $\pi$ orbital in the substituted benzene. We can assess the extent of such an interaction in the phenylalkylphosphine where we observe a perturbation of the benzene $\pi^*$-orbital energies. Additional information on the nature of these $\sigma^*$ orbitals can be obtained by comparing the electron transmission measurements to energies from X-ray absorption, core electron energy loss, and UV spectroscopies. Further information on the $\sigma^*$-orbital character is garnered from electron-scattering calculations on the parent molecule using Hartree–Fock or continuum multiple-scattering (MS)–X$\alpha$ MO methods.

## Experimental Section

The electron transmission experiment involves the measurement of the transparency of a gas to an electron beam as a function of energy. The transparency depends in an inverse fashion upon the electron-scattering cross section. Temporary negative ion formation occurs with large cross section only over a narrow energy range. Since the negative ion promptly decays by giving up the trapped electron, the formation and decay process appears as a sharp fluctuation in the electron-scattering cross section. The process, as well as the corresponding feature in the transmission vs. electron energy spectrum, is referred to as a "resonance".

The electron spectrometer consists of an electron source followed by an electron monochromator, a gas cell, and an electron collector.[7] In practice, the first derivative of the transmitted current as a function of energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance.[8] The energy associated with a resonance is known as an "attachment energy" (AE) and, with respect to the derivative spectrum, is defined as the point vertically midway between the minimum and maximum that characterize the resonance. For the present purposes an attachment energy may be identified with the negative of the corresponding electron affinity.[9] The chief limitation is that ETS gives only the energy associated with unstable negative ions. That is, only negative electron affinities can be obtained with ETS.

## Results

We have obtained electron transmission spectra of the second-row hydrides, $SiH_4$, $PH_3$, $H_2S$, and HCl, as well as their permethylated derivatives, $SiMe_4$, $PMe_3$, $Me_2S$, and MeCl. The energies of the first negative ion resonance of each of these compounds are arranged in a correlation diagram in Figure 1. In fact, for all except the phosphorus compounds, only one resonance was observed in the energy range 0–8 eV. In both $PH_3$ and $PMe_3$, a second resonance appeared near 5.5 eV. Previous measurements on $H_2S$,[10] MeCl,[11] and $SiH_4$[12] are similar to the present ones.

---

[†] Present address: Polaroid Corp., Waltham, MA.

(1) Sherwood, D. E., Jr.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 93.
(2) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 314.
(3) Graham, W. A. *Inorg. Chem.* **1968**, *7*, 315.
(4) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.
(5) Burdett, J. K. "Molecular Shapes"; Wiley-Interscience: New York, 1980; p 205.
(6) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 344.
(7) Stamatovic, A.; Schulz, G. J. *Rev. Sci. Instrum.* **1970**, *41*, 423. McMillan, M. R.; Moore, J. H. *Rev. Sci. Instrum.* **1980**, *51*, 944.
(8) Sanche, L.; Schulz, G. J. *Phys. Rev.* **1972**, *45*, 1672.
(9) For a discussion of AE's vs. EA's as well as calibration of the ETS spectrum see: Giordan, J. C.; McMillan, M. R.; Moore, J. H.; Staley, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 4870.
(10) Sanche, L.; Schulz, G. J. *J. Chem. Phys.* **1973**, *58*, 479.
(11) Burrow, P. D.; Modelli, A.; Chiu, N. S.; Jordan, K. D. *J. Chem. Phys.* **1982**, *77*, 2699.
(12) Giordan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6544.

0020-1669/85/1324-1100$01.50/0

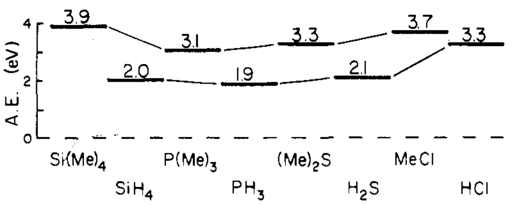


**Figure 1.** Correlation diagram giving measured attachment energies for Si–Cl hydrides and permethylated derivatives.

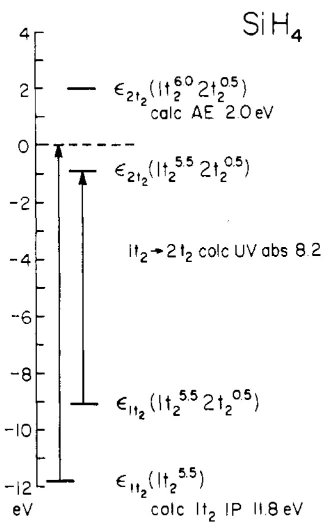


**Figure 2.** Relationship between valence $t_2$ orbital IP and values of valence $t_2 \rightarrow$ empty $t_2$ excitation energy and empty $t_2$ AE from MS–X$\alpha$ calculations on $SiH_4$.

On the basis of the experimental data alone, some preliminary observations can be made. The similarity of the resonance energies of $SiH_4$, $PH_3$, and $H_2S$ suggests a similarity of the orbital giving rise to the resonance in each of these compounds. The orbital energies in these compounds are quite sensitive to substitution, implying that the orbital is molecular as opposed to being atomic 3d in character.

To assist in assigning features observed in the spectra, we have carried out both bound-state[13] and continuum multiple-scattering-X$\alpha$ MO calculations[14] of valence spectra and elastic electron-scattering cross sections for $SiH_4$[15] and HCl. Numerous other X$\alpha$, ab initio Hartree–Fock, and ab initio CI stabilization calculations have also been consulted.[16-21] In addition UV and X-ray spectral data have been employed.[22-26]

**$SiH_4$ and $SiMe_4$.** The continuum MS–X$\alpha$ calculations for $SiH_4$[15] predict a scattering cross section maximum at 2.4 eV with the dominant contribution from the $t_2$ channel. Comparison of the Si 2p → $t_2$ XAS main-peak energy with this $t_2$ scattering resonance energy using the transition state[27] approach indicates that it is the lowest unoccupied $t_2$ orbital that is responsible for both the Si 2p XAS peak and the elastic scattering cross-section maximum. This orbital is reasonably well localized on the Si, as suggested by Schwarz,[22a] and has a significant Si d function contribution to its XAS and scattering cross sections.[15] Schwarz has given a contour diagram for this orbital (using the isoelectronic $PH_4^+$ model; ref 22b, Figure 3b) which also has the qualitative appearance of a $\sigma^*$ orbital with predominant H 1s and P 3p character but some P 3d contribution.

Table I. Experimental IP's and Excitation Energies for Si 2p Core and $t_2$ Valence Orbitals of $SiH_4$ and $Si(Me)_4$

| | $SiH_4$ | $Si(Me)_4$ |
|---|---|---|
| Si 2p IP[a] | 107.1 | 105.8 |
| Si 2p → $t_2$ XAS[b] | 103.2 | 104.1 |
| $t_2$ term energy[c] (from X-ray spectra) | 3.9 | 1.7 |
| valence $t_2$ (HOMO) IP | 12.8[d] | 10.5[e] |
| valence $t_2$ → empty $t_2$ $\Delta E$ | 8.3–8.9[f] | ~8.9[g] |
| $t_2$ term energy (from UV spectra) | 4.5–3.9 | 1.6 |

[a] Reference 28. [b] Reference 22c ($SiH_4$) and ref 23 ($Si(Me)_4$). The energy given is the absorption maximum; see ref 15 from a discussion of the assignment in $SiH_4$. [c] The term energy is defined as the IP of initial orbital minus excitation energy from this orbital; e.g., Si 2p IP − Si 2p → $t_2$ XAS energy is the term energy of empty the $t_2$ orbital. [d] Reference 29. [e] Reference 30. [f] Reference 31; Hartree-Fock CI assignment. [g] Second band, assigned as $t_2$ → 3d in ref 25.

Correlations may be drawn between the AE for occupation of this localized orbital and its energies as observed in XAS and UV spectra. The relationship of XAS energy and AE has been shown in Figure 8 of ref 15. A similar diagram showing the relationship of valence IP, UV excitation energy, and AE of $SiH_4$ appears in Figure 2. The IP for the $1t_2$ orbital of $SiH_4$ is obtained as the negative of the $1t_2$ orbital energy in a photoionization transition state with 5.5 electrons in the $1t_2$. The 1t → $2t_2$ UV absorption energy is obtained as a difference of $1t_2$ and $2t_2$ orbital energies in a transition state with 5.5 electrons in $1t_2$ and 0.5 electron in $2t_2$ orbitals. The calculated $1t_2$ IP and $1t_2 \rightarrow 2t_2$ UV excitation energies agree well with experiment. To relate the $1t_2$ IP, the $1t_2 \rightarrow 2t_2$ excitation energy, and the $2t_2$ electron-attachment energies, it is also necessary to calculate the destabilization of the $1t_2$ orbital when 0.5 electron is added to the $2t_2$ (2.7 eV) and the destabilization of the $2t_2$ orbital when 0.5 electron is added to the $1t_2$ (2.9 eV). These quantities are not necessarily equal since they are calculated for different self-consistent electron distributions and they are not directly accessible experimentally. The result of such an analysis is the estimated $2t_2$-orbital energy in the electron-attachment transition state (6.0 electrons in $1t_2$ and 0.5 electron in $2t_2$), which is in good agreement with the calculated position of the cross-section maximum (2.4 eV). The analysis of ref 15 based on the Si 2p IP and the Si 2p → $2t_2$ XAS energy is quite similar.

A similar procedure allows us to relate the spectral properties of $SiH_4$ and $SiMe_4$ to their difference of AE's using experimental Si 2p[28] and valence $t_2$ IP's[29,30] and Si 2p → empty $t_2$ XAS and valence $t_2$ → empty $t_2$ UV[31] energies for $SiH_4$ and $SiMe_4$. As shown in Table I we can establish that the empty $t_2$ orbital of $SiMe_4$ is closer to the ionization threshold (that is, it has a lower term energy) than that for $SiH_4$. For the X-ray case this difference is about 2.2 eV. If the transition-state eigenvalue destabilizations calculated in ref 15 for $SiH_4$ are added to these X-ray term energies, we obtain AE's of 2.0 and 4.2 for $SiH_4$ and $SiMe_4$, respectively, in good agreement with experiment. DVM–X$\alpha$ calculations[21] on $SiH_4$ and $SiMe_4$ (at the X(SCC) level of ap-

---

(13) Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 143.
(14) (a) Dill, D.; Dehmer, J. L. *J. Chem. Phys.* **1974**, *61*, 692. (b) Davenport, J. W.; Ho, W.; Schrieffer, J. R. *Phys. Rev. B: Condens. Matter* **1978**, *B17*, 3115.
(15) Tossell, J. A.; Davenport, J. W. *J. Chem. Phys.* **1984**, *80*, 813.
(16) Jain, A.; Thompson, D. G. *J. Phys. B* **1983**, *17*, 443.
(17) Taylor, H. S.; Goldstein, E.; Segal, G. A. *J. Phys. B* **1977**, *11*, 2253.
(18) Norman, J. G., Jr. *J. Chem. Phys.* **1974**, *61*, 4630.
(19) Xiao, S.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033.
(20) Roberge, R.; Salahub, D. R. *J. Chem. Phys.* **1979**, *70*, 1177.
(21) Berkovitch-Yellin, Z.; Ellis, D. E.; Rafner, M. A. *Chem. Phys.* **1981**, *62*, 21.
(22) (a) Schwarz, W. H. E. *Chem. Phys.* **1975**, *9*, 157. (b) Schwarz, W. H. E. *Chem. Phys.* **1975**, *11*, 217. (c) Friedrich, H.; Sonntag, B.; Rabe, P.; Butscher, W.; Schwarz, W. H. E. *Chem. Phys. Lett.* **1979**, *64*, 360.
(23) Fomichev, V. A.; Zimkina, T. M.; Vinogradov, A. S.; Evdokimov, A. M. *J. Struct. Chem.* **1970**, *11*, 626.
(24) Hitchcock, A. P.; Brion, C. E. *J. Electron Spectrosc.* **1978**, *13*, 193.
(25) Roberge, R.; Sandorfy, C.; Matthews, J. I.; Strausz, O. P. *J. Chem. Phys.* **1978**, *69*, 5105.
(26) McDiarmid, R. *J. Chem. Phys.* **1978**, *68*, 945.
(27) Slater, J. C. *Adv. Quantum Chem.* **1972**, *6*, 1.
(28) Perry, W. P.; Jolly, W. L. *Inorg. Chem.* **1974**, *13*, 1211.
(29) Potts, A. W.; Price, W. C. *Proc. R. Soc. London, Ser. A* **1972**, *326*, 165.
(30) Bock, H.; Ensslin, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 404.
(31) Gordon, M. S. *J. Chem. Phys.* **1978**, *69*, 4955.

**Table II.** Comparison of Experimental Valence Orbital Energetics of HCl with Those Obtained from MS-Xα Calculations (Energies in eV)

| | exptl | calcd | | exptl | calcd |
|---|---|---|---|---|---|
| $2\pi$ IP | 12.7[a] | 12.7 | $6\sigma$ term energy (from X-ray spectra) | 6.2[c] | 5.3 |
| $5\sigma$ IP | 16.25[a] | 16.1 | | | |
| $2\pi \rightarrow 6\sigma$ $\Delta E$ | 8.0[b] | 8.2 | energy of cross-section max | 3.3[d] | 3.2 |

[a] Reference 38. [b] Reference 39. [c] Reference 22b. [d] This work.

proximation) also give the empty $t_2$ orbital higher in energy for $SiMe_4$ than for $SiH_4$ by 1.75 eV, consistent with our experimental AE's. From the $t_2$-orbital destabilization of 1.2 eV calculated between the ground state and the electron-attachment transition state for $SiH_4$, the ground-state DVM-Xα eigenvalues give projected AE's of 1.8 and 3.5 eV for $SiH_4$ and $SiMe_4$, respectively, in good agreement with experiment.

**$PH_3$ and $PMe_3$.** Few data are available on the empty orbitals of $PH_3$ and $PMe_3$. Schwarz[22] cites a term energy of 4.4 eV for the empty e orbital, which, by analogy to the empty $t_2$ orbital of $SiH_4$, is expected to have P 3p and 3d and H 1s character and be strongly antibonding. The position of the maximum in the P 2p XAS gives a term energy of 4.9 eV. These term energy values project an AE for this e-antibonding orbital of between 1.5 and 1.0 eV, somewhat lower than the experimental AE. Using the experimental $5a_1$ (HOMO) IP of 10.6[32] and assuming that the lowest energy UV peak around 7.3 eV[33] contains the $a_1 \rightarrow e$ transition, we get a term energy of 4.3 eV. In the MS-Xα calculation on $PH_3$[18] the empty e orbital was not found (since its eigenvalue would be positive for neutral unstabilized $PH_3$). The eigenvalue of this orbital in the DVM-Xα calculation[19] is 0.9 eV, and it has significant P p and d character (see Figure 3 and Table II of ref 19). Assuming a 1.2-eV destabilization in the electron-attachment transition state as in $SiH_4$, this projects an AE of 2.1 eV. XAS energies are unavailable for $PMe_3$, and the DVM-Xα results[19] give virtually identical lowest empty e-orbital eigenvalues for $PH_3$ and $PMe_3$. However, the lower HOMO IP (8.6 eV[32]) together with the UV peak energy of 6.2 eV[33] gives a term energy of 2.4 eV—higher than in $PH_3$ by 1.9 eV, consistent with experiment.

For $PH_3$, the DVM-Xα calculation[19] gives an additional set of unoccupied orbitals (4e and $7a_1$) that have about 30% P 3d and 10% P 3p character and have eigenvalues in the ground state of the neutral molecule of 4.0 eV. Assuming a destabilization of 1.2 eV in the AE transition state projects an attachment energy of 5.2 eV, in good agreement with the peak seen experimentally at 5.5 eV.

**$H_2S$ and $Me_2S$.** Hartree–Fock scattering calculations with parameter-free polarization potentials give a resonance of predominantly $b_2$ symmetry at 2.2 eV for $H_2S$,[16] in good agreement with experiment. According to Schwarz[22b] this $b_2$ state has a term energy of 5.1 eV, suggesting an eigenvalue in the AE transition state of less than 1 eV. Similarly, using the calculated HOMO $2b_1$ IP of 10.4 and the calculated $2b_1 \rightarrow 3b_2$ excitation energy of 5.9 eV[20] (both of which are in good agreement with experiment), we obtain a term energy of 4.5 eV. With the valence orbital destabilization calculated for $SiH_4$, this projects a $b_2$ AE eigenvalue of 1.1 eV. As in $SiH_4$ and $PH_3$ the orbital has the shape and symmetry of a $\sigma^*$ orbital (see Figure 3d of ref 20). As noted in ref 20, this orbital can be described "either as a SH $\sigma^*_{SH}$ orbital of $b_2$ symmetry or as a somewhat distorted $3d_{xz}$ function".

In comparing $H_2S$ and $Me_2S$, we note that the $b_1$ HOMO IP of $H_2S$ is 10.5 eV[34] while that for $Me_2S$ is 8.7 eV.[35] If we assume that the broad 2000-Å transition in $Me_2S$[36] has an orbital analogous to the $b_2$ of $H_2S$ as its final state, then the $b_1 \rightarrow b_2$ excitation energies in $H_2S$ and $(CH_3)_2S$ are the same to within a few tenths of an electron volt so that the $b_2$ orbital lies about 1.8 eV closer to the ionization threshold in $Me_2S$ than in $H_2S$, consistent with the experimental AE's of Figure 1.

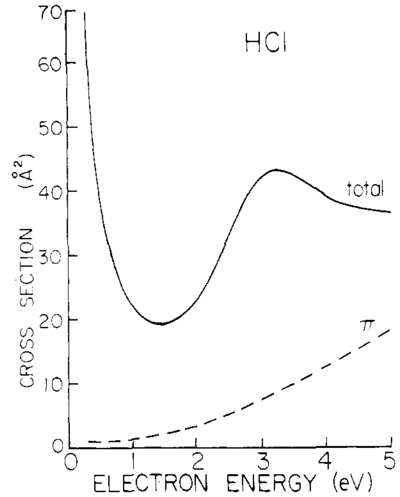


**Figure 3.** Continuum MS-Xα elastic electron-scattering cross sections (σ) for HCl.

**HCl and $CH_3Cl$.** Valence orbital spectral properties for HCl obtained from MS-Xα calculations are compared with experiment in Table II. The equilibrium distance of 1.2744 Å was used, sphere radii were chosen to be 1.80, 0.47, and 1.16 Å for the outer, H, and Cl spheres, respectively, and standard α values[37] were used. The maximum azimuthal quantum number was 3 for both centers. It is apparent that agreement with experiment is good. As shown in Figure 3, the behavior of the scattering cross section in the 3-eV region is in agreement with the ETS results, with its maximum occurring at 3.2 eV, and is qualitatively like that obtained from Hartree–Fock scattering calculations with a parameterized polarization potential[41] (although the parameter dependence of such calculations is large, see ref 16). The Hartree–Fock CI calculations[17] ascribe a maximum in the vibrational excitation cross section around 3 eV to occupation of a strongly antibonding $\sigma^*$ orbital. Clearly, the σ cross section is dominant in Figure 3. Using the XAS term energy of 6.2 eV given by Schwarz[22b] and correcting for the 6.5-eV orbital destabilization we calculate in HCl give a $\sigma^*$-orbital energy of about 0.3 eV in the electron-attachment transition state. The experimental $2\pi$ IP and $2\pi \rightarrow 6\sigma$ AE plus the calculated destabilization of 5.7 eV give an eigenvalue of 1.0 eV. With either data set the electron-attachment transition state orbital energy for the $6\sigma$ orbital of HCl is much lower than the energy of the cross-section maximum. A similar result was observed for $CH_4$ in ref 15: although the calculated energy of the cross-section maximum was in reasonable agreement with experiment, this energy was higher by almost 3 eV than the $t_2$-orbital energy in the AE transition state. This behavior was associated with high delocalization of the empty $t_2$ orbital of $CH_4$. Similarly, the empty $\sigma^*$ orbital of HCl has 82% of its electron density in the outer sphere (in the AE transition state). Thus, for HCl, X-ray or valence term energies lead to underestimations of the ETS resonance energies: the resonance energy of HCl is higher than that of $SiH_4$ although term values apparently indicate that it should be lower. Only for orbitals well localized in space can term values be used to directly estimate resonance energies.

Given the above caution, direct scattering calculations will probably be necessary to explain the 0.4-eV difference observed

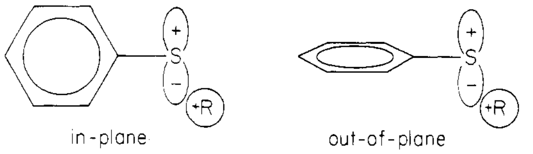
---

(32) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1972**, 711.
(33) Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1974; Vol. 1, p 232.
(34) Potts, A. W.; Price, W. C. *Proc. R. Soc. London, Ser. A* **1972**, *326*, 181.
(35) Cullen, W. R.; Frost, D. C.; Vroom, D. A. *Inorg. Chem.* **1969**, *8*, 1803.
(36) McDiarmid, R. *J. Chem. Phys.* **1974**, *61*, 274.
(37) Schwarz, K. *Phys. Rev. B: Solid State* **1972**, *B5*, 2466.
(38) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: London, 1970.
(39) Romand, J. *Ann. Phys.* (*Paris*) **1949**, *4*, 527. Mulliken, R. S. *J. Chem. Phys.* **1940**, *8*, 382.
(40) Gianturco, F. A.; Thompson, D. G. *J. Phys. B* **1977**, *10*, L21.
(41) Hitchcock, A. P.; Brion, C. E. *J. Electron Spectrosc.* **1978**, *13*, 193.

between the resonance energies of $CH_3Cl$ and HCl. Nonetheless, electron energy loss studies in the X-ray region indicate that the $\sigma^*$-orbital term energy is smaller in $CH_3Cl$ than in HCl (5.3 vs. 6.2 eV[42]) so that a higher AE for $CH_3Cl$ is reasonable.

**Implications.** The measurement and analysis of the electron-attachment energies for the empty $\sigma^*$ orbitals of $SiH_4$ to HCl and $SiMe_4$ to MeCl provide a basis for understanding the nature of $\pi$-type interactions between empty ligand orbitals and occupied orbitals of transition metals or aromatic systems. The nature of the ligand orbital changes across each series from Si to Cl, with the change being greatest on going from S to Cl. Although continuum MS–X$\alpha$ calculations accurately predict the electron-scattering resonance energy in both $SiH_4$ and HCl, it is only in $SiH_4$ that the resonance energy can be correlated with an orbital eigenvalue or with orbital term energies from X-ray or UV data. We see this clearly if we employ the Schwarz[22b] term energies for the $\sigma^*$ orbitals of this set of molecules and add to them the eigenvalue destabilizations obtained from MS–X$\alpha$ calculations for $SiH_4$ and HCl (assuming a linear change in this destabilization across the series). The calculated $\sigma^*$-orbital energies in the electron-attachment transition states drop steadily across the $SiH_4$–HCl series, while the ETS resonance energies are first nearly constant and then increase. Thus, the ETS resonance energies become progressively higher than the corresponding orbital energies as we cross the series.

For the Si, P, and S compounds the resonance in the electron transmission spectrum is associated with a $\sigma^*$ molecular orbital having approximately the symmetry of a d function. Thus, when a ligand derived from one of these compounds is substituted on an organic $\pi$ system such as benzene, the ligand–$\pi$ system interactions may be thought of as a p–d interaction but is more properly described as a hyperconjugative interaction since the presence of the d-like orbital does not imply the existence of other d-type orbital components. For example, the $3b_2$ $H_2S$ $\sigma^*$ orbital of $3d_{xz}$ symmetry does not imply the presence of an orbital of $d_{yz}$ symmetry. Thus, in a phenyl alkyl sulfide, the analogue of the $H_2S$ empty $3b_2$ orbital could have either of two geometries, in plane or out of plane, depending upon whether the R group is small (in plane) or is so bulky as to be forced out of the plane of the ring.



In the first case there will be no $\pi^*$–$\sigma^*$ (or p–d) interaction whereas there will be in the second case. This distinction is observable on comparison of the electron transmission spectra[42] of phenyl methyl sulfide and phenyl-*tert*-butylbenzene.

Table III. Correlation of Properties of $Cr(CO)_5L$ with AE's of L

| L | AE of L, eV | $t_{2g}$ splitting,[a] eV | $\pi$ acceptance of L,[b] mdyn/Å |
|---|---|---|---|
| CO | 2.0[c] | 0 | 0.74 |
| $NMe_3$ | 4.8[d] | 0.31 | 0.0 |
| $PH_3$ | 1.9[d] | 0.13 | |
| $PMe_3$ | 3.1[d] | 0.14 | 0.48 |
| $Me_2S$ | 3.3[d] | 0.20 | 0.15 |

[a] Reference 44. [b] Reference 45. [c] Reference 6. [d] Present results.

In contrast to groups containing second-row atoms, analogous first-row hydrides and methides of C, N and O have no low-energy $\sigma^*$ orbitals to generate broad intense XAS peaks or low-energy ETS resonances. As noted by Schwarz,[22b] the lowest energy $\sigma^*$ orbitals of such molecules lie above the Rydberg orbitals. Such molecules have only broad maxima in the elastic scattering cross section at high energy (e.g., ~8 eV in $CH_4$[43]) and often give no observable ETS resonance. They are thus expected to be poor electron acceptors.

Analysis of the properties of substituted carbonyls such as $Cr(CO)_5L$, where L is a two-electron-donor ligand such as $PH_3$, shows a correlation between ligand AE and Cr 3d–L $\pi$ bonding effects. Representative data are given in Table III. When L is a reasonably strong $\pi$ acceptor (e.g., $PMe_3$), the effective symmetry at the Cr atom is nearly octahedral and the occupied metal 3d orbital (of $t_{2g}$ symmetry in octahedral symmetry) is almost unsplit. When L is a poor $\pi$ acceptor (e.g., $NMe_3$), the splitting of this orbital is substantial.[44] Trends in the AE's of other ligands L are qualitatively consistent with their observed effects on Cr 3d orbital binding energies; e.g., $Me_2S$ has a moderately high AE, has moderate $\pi$-acceptor ability, and gives an intermediate "$t_{2g}$" orbital splitting. IR and Raman spectra may also be used to generate scales of $\sigma$-donor and $\pi$-acceptor strength for ligands L.[45] CO is found to have the strongest $\pi$-acceptor character, and N bases are found to be the weakest. Again, a general correlation is observed between the AE of the ligand and its $\pi$-acceptor character.

**Acknowledgment.** This work was supported by NSF Grant No. CHE-81-21125 and by the Computer Science Center, University of Maryland.

**Registry No.** $Si(CH_3)_4$, 75-76-3; $SiH_4$, 7803-62-5; $P(CH_3)_3$, 594-09-2; $PH_3$, 7803-51-2; $(CH_3)_2S$, 75-18-3; $H_2S$, 7783-06-4; $CH_3Cl$, 74-87-3; HCl, 7647-01-0.

---

(42) Modelli, A.; Jones, D.; Colonna, F. P.; Distefano, G. *Chem. Phys.* **1983**, *77*, 153.

(43) Barbarito, E.; Basta, M.; Calicchio, M.; Tessari, G. *J. Chem. Phys.* **1979**, *11*, 54.

(44) Cowley, A. H. *Prog. Inorg. Chem.* **1979**, *26*, 45.

(45) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315.