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Electron States of 1:2 Addition Compounds of $TiCl_4$ with Diethyl Ether and Diethyl Sulfide: HeI Photoelectron and Electron Energy Loss Spectroscopy Studies[†]

S. P. Ananthavel and M. S. Hegde*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

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Electron states of 1:2 addition compounds of $TiCl_4$ with diethyl ether and diethyl sulfide in the vapor phase have been studied by HeI photoelectron (UVPES) and electron energy loss spectroscopies (EELS). The peaks in the photoelectron spectra of the complexes are assigned by comparison with the orbital energies from ab initio MO calculations on model compounds $TiCl_4-2(CH_3)_2O$ and $TiCl_4-2(CH_3)_2S$. Lone pair orbitals of chlorine are shifted to lower binding energy by 1.6 eV; the π type oxygen lone pair is shifted to higher binding energy by 1.8 eV and the σ type lone pair of oxygen by 2.4 eV in the $TiCl_4-2(C_2H_5)_2O$ complex. The magnitude of shifts in the Cl and S lone pairs in the $TiCl_4-(C_2H_5)_2S$ are lower than that in the diethyl ether complex. Electronic excitation in $TiCl_4$ and $TiCl_4-2(C_2H_5)_2O$ are obtained by electron energy loss spectroscopy. A band at 3.6 eV observed in the case of the $TiCl_4-2(C_2H_5)_2O$ complex molecule is assigned to the Cl(3p) ligand to Ti^{4+}(3d) charge transfer. An energy level diagram of the $TiCl_4-2(C_2H_5)_2O$ was drawn from the UVPES and EELS results describing the electronic transitions in the complex molecule.

1. Introduction

Formation of addition complexes of $TiCl_4$ with various donors has been known for a long time. Complexes involving acetyl chloride and acetophenone are of particular interest in the context of Friedel−Crafts reactions.[1] Donors such as diethyl sulfide form relatively strong complexes with a binding energy on the order of 23 kcal/mol.[2] For example, NMR studies have shown the formation of a 1:2 complex of $TiCl_4$ with dimethyl ether.[3] An octahedral complex of $TiCl_4$ with dimethyl ether has been proposed. However, there is no report on the electron states of addition complexes of $TiCl_4$ with any donors. Ultraviolet photoelectron spectroscopy (UVPES) and electron energy loss spectroscopy (EELS) can provide information on the nature of interaction, shifts in the orbitals of donors and acceptors, and the extent of charge transfer. In this laboratory we have been investigating donor−acceptor (D−A) complexes and weakly bound hydrogen-bonded complexes by UVPES, EELS, and ab initio MO studies.[4−6] Recently, we have studied UVPES of 1:1 addition compounds of $AlCl_3$ and $GaCl_3$ with donors such as diethyl ether and diethyl sulfide.[7] The chlorine orbitals of $AlCl_3$ and $GaCl_3$ were found to be shifted substantially to lower binding energies, whereas donor orbitals are shifted to higher binding energies. Similarly, electron states of addition complexes of BF_3 and SO_2 with various donors have been studied by UVPES and EELS.[8] In this paper we report the first photoelectron spectroscopic studies of addition complexes of $TiCl_4$ with diethyl ether and diethyl sulfide. The observed ionization energies are compared and assigned with ab initio MO calculations of model compounds $TiCl_4-2(CH_3)_2O$ and $TiCl_4-2(CH_3)_2S$.

2. Experimental and Computational Details

Ultraviolet photoelectron spectroscopy measurements were made with a home-built spectrometer consisting of a HeI lamp, a 3 mm diameter collision chamber, and a channeltron electron multiplier. The resolution of the spectrometer was 60 meV (fwhm) at 15.6 eV ionization energy of N_2.[9] Electron energy loss spectra were recorded with a home-built spectrometer. The spectrometer consists of a hemispherical electron monochromator (140 mm mean diameter), a collision chamber, a hemispherical electron energy analyzer (145 mm mean diameter), and a channelteron electron multiplier. A 40 eV primary electron beam is used in this study. The fwhm of the no-loss peak is about 200 meV. Details of the spectrometer are given elsewhere.[10,11]

The addition compounds of $TiCl_4$ with diethyl ether and diethyl sulfide were prepared by mixing them in a glass vacuum line. $TiCl_4$ and the donors were purified by vacuum distillation. Different compositions of $TiCl_4$ with diethyl ether (Et_2O) and diethyl sulfide (Et_2S) in the ratio of 1:1, 1:2, and 2:1 were prepared in a glass vacuum line provided with a mercury manometer and collected in separate glass ampules. Vapors of the addition compounds were admitted to the spectrometer through a fine needle valve. In all cases external heating of the sample by a heating tape was necessary to obtain sufficient vapor pressure. The temperature of the ampule was maintained at about 70 °C throughout the experiment. The gas pressure in the HeI collision chamber was about 0.5−1 Torr. The gas inlet line of the spectrometer was also heated to 70 °C. In each case, spectra were recorded a number of times to establish the peak positions. Absence of water vapor in the collision chamber was confirmed by noting the absence of the UV photoelectron spectrum of HCl formed due to the hydrolysis of $TiCl_4$.

In the EELS experiment the complex was also made with a 2:1 composition of diethyl ether and $TiCl_4$ and then a slight excess of diethyl ether was condensed. Initially, EELS of diethyl ether was observed. As the excess ether was removed through the pumping process, the spectrum of the complex molecule was observed. The vacuum in the collision chamber was about $10^{-3}-10^{-4}$ Torr. Also, the needle valve opens to a 1 mm diameter stainless steel capillary leading to the collision chamber. This capillary may also act as a nozzle source. Since the vacuum is sufficiently high (5×10^{-3} to 10^{-4}), almost no collisional dissociation seems to occur, giving EELS of mostly the complex. This is in contrast to the UVPES experiment where the spectrum is of the complex as well as of monomers.

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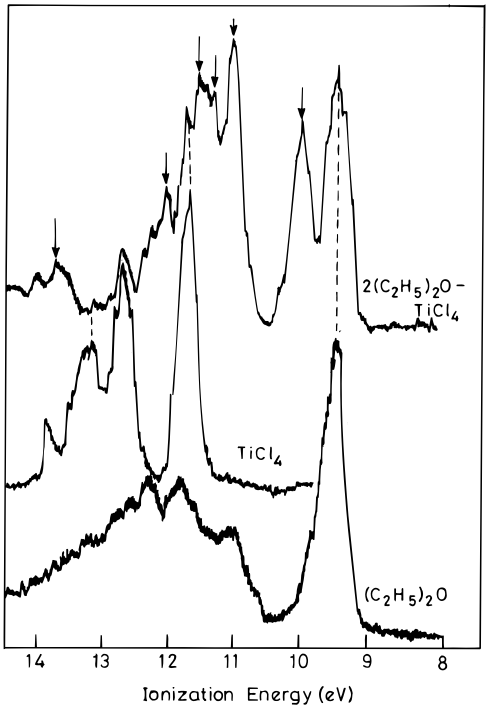

Figure 1. HeI photoelectron spectra of $TiCl_4$, diethyl ether, and the complex between them. The features due to the complex are shown by arrows.

Ab initio MO calculations were done at the RHF/3-21G level using the Gaussian 92[12] system of programs on the model compounds of $TiCl_4$ with $(CH_3)_2O$ and $(CH_3)_2S$. The geometry of the molecule is considered to be octahedral (with D_{2h} symmetry) from an earlier experimental report on the $TiCl_4$−ether complex.[13] The geometry of the sulfide complex is C_{2h}. The geometries were fully optimized. Single-point CIS (configurational interaction with single excitation) calculation has been done on the optimized $TiCl_4$ molecule to obtain excitation energies.

3. Results and Discussion

UVPES Studies of $TiCl_4$ Complexes. HeI photoelectron spectra of $TiCl_4$, diethyl ether, and diethyl sulfide monomers were recorded first. It was essential to heat the gas inlet line as well as the collision chamber to remove adsorbed water vapor before admitting $TiCl_4$ vapor. Despite this precaution, initially, the UVPES of HCl was observed and subsequently the UVPES of pure $TiCl_4$ was obtained. Mixtures of $TiCl_4$ with diethyl ether in various ratios were admitted in the collision chamber. In the 1:1 mixture of $TiCl_4-Et_2O$, the spectrum of $TiCl_4$ was observed. In the 2:1 case (excess $TiCl_4$), the $TiCl_4$ spectrum was also obtained. In the 1:2 composition with a slight excess of $(C_2H_5)_2O$, additional features due to a new species became noticeable. After diethyl ether was pumped out for some time in the spectrometer, a spectrum containing new peaks along with the features of monomers was observed.

Photoelectron spectra of $TiCl_4$, $(C_2H_5)_2O$, and the complex are given in Figure 1. The HeI photoelectron spectrum of $TiCl_4$ shows peaks at 11.75, 12.78, 13.31, and 13.86 eV due to $t_1(n_{Cl})$, $t_2(n_{Cl})$, $t_2{}^1(n_{Cl})$, and $a_1(\sigma_{Ti-Cl})$ orbital ionizations, respectively.[14] The first ionization energy of diethyl ether at 9.61 eV is due to a π type oxygen lone pair. The next peak at 11.1 eV is due to a σ type lone pair on oxygen, and the features between 11.8 and 14.3 eV are due to σ_{CC}, π_{CH_2}, π_{CH_3}, and σ_{CO} ionizations.[15] The spectrum of the complex is different from that of $TiCl_4$ and $(C_2H_5)_2O$. Additional peaks marked by arrows at 10.0, 11.0, 11.4, 11.7, 12.07, and 13.5 eV are observed.

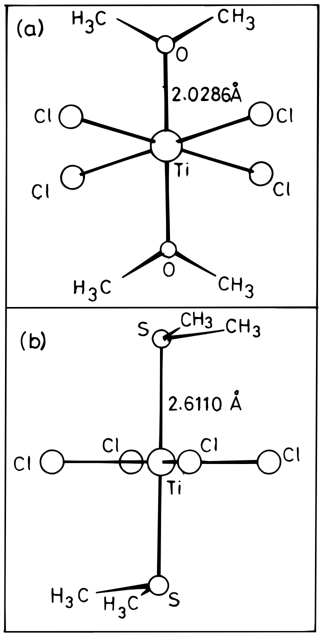

Figure 2. Optimized structure of (a) $2(CH_3)_2O-TiCl_4$ and (b) $2(CH_3)_2S-TiCl_4$ complexes.

To assign the various bands in the HeI spectrum of $TiCl_4-2(C_2H_5)_2O$ and to understand the nature of the interaction, ab initio MO calculations were done on the model compound $TiCl_4-2(CH_3)_2O$. With the available computational facility, the calculation on the $TiCl_4-2(C_2H_5)_2O$ system could not be done even at the 3-21G level. The calculation showed that the σ type $3a_1$ orbital of $(CH_3)_2O$ is involved in the bonding with $TiCl_4$. It is expected that ordering of the valence orbitals would not be significantly different for the complexes of $TiCl_4$ with $2(CH_3)_2O$ and $(C_2H_5)_2O$.

An earlier experimental report on the complexes of $TiCl_4$ with dimethyl ether suggested that it forms a complex with nearly octahedral geometry with two dimethyl ether units bonded with Ti.[13] In view of this, the geometry of the complex is considered to be D_{2h}. Both the monomers and the complexes are fully optimized at the 3-21G level. The optimized geometry of the complex is given in Figure 2a. The optimized Ti−O distance is 2.0286 Å, which is much less than the sum of the van der Waals radii of Ti and O. The binding energy of the complex is 70.34 kcal/mol. The structure has been confirmed to be a true minimum by frequency calculations. The orbital energies of $TiCl_4$ monomer do agree with the reported values.[16] The calculated orbital energies of the model compound $TiCl_4-2(CH_3)_2O$ is given in Table 1. The first two orbitals are due to the chlorine lone pair followed by the oxygen lone pair. The chlorine orbitals are shifted to lower binding energies by about 2 eV. All the chlorine orbitals are shifted to lower binding energies. The π type oxygen lone pair is shifted by 1.5 eV to higher binding energy and that of the σ type oxygen lone pair orbital is shifted by 2.8 eV.

Assuming that the magnitude of the shifts in dimethyl ether should be similiar to diethyl ether in the complex, assignment of the HeI spectra of the $TiCl_4-2(C_2H_5)_2O$ adduct is done based on the orbital ordering from the above calculation. Accordingly, ionization energies of the $TiCl_4-2(C_2H_5)_2O$ complex and their assignments are given in Table 2. The first two bands observed in this experiment are assigned to the chlorine lone pair. Both these orbitals are shifted by about 1.8 eV. The band at 11.40 eV is assigned to the π type lone pair of oxygen, which is shifted by 1.8 eV. The peak at 11.7 is due to the shifted n_{Cl} orbital of $TiCl_4$. The feature at 12.7 is due to the σ_{Ti-Cl} orbital. These

TABLE 1: Vertical Ionization Energies, Calculated (3-21G) Orbital Energies, and Assignments for the Model Compounds

molecule	*I* (eV)	$-\epsilon$ (eV) 3-21G	assignment
$TiCl_4$	11.75	13.27	t_1 (n_{Cl})
	12.78	14.60	$3t_2$ (n_{Cl})
	13.31	14.99	1e (n_{Cl})
	13.86	15.63	$2a_1$ (σ_{Ti-Cl})
$(CH_3)_2O$	10.14	10.7	n_O (π)
	11.94	11.3	n_O (σ)
	13.4	14.9	π_{CH_3}
	14.2	15.3	π_{CH_3}
	16.0−16.5	16.7−17.4	σ_{CO}
$TiCl_4-(CH_3)_2O$		10.9	b_{1g} (n_{Cl})
		12.0	b_{2u} (n_{Cl})
		12.2	b_{3u} (n_O)
		12.8	b_{2g} (n_{Cl})
		13.8	$2b_u$ (σ_{Ti-Cl})
		14.2	b_{3g} (n_O)
$(CH_3)_2S$	8.7	8.8	n_s (π)
	11.3	9.7	n_s (σ)
	12.6	13.9	σ_{CS}
	14.1	15.9	π_{CH_3}
$TiCl_4-(CH_3)_2S$		11.3	b_{1g} (n_{Cl})
		11.4	b_u (n_s)
		11.7	a_u (n_{Cl})
		12.2	b_g(n_{Cl})
		12.3	b_u (σ_{Ti-Cl})
		12.8	n_s

TABLE 2: Vertical Ionization Energies and Assignments for the Complexes of $TiCl_4$ with Et_2O and Et_2S

molecule	*I* (eV)	assignments
$TiCl_4$	11.75	t_1 (n_{Cl})
	12.78	$3t_2$ (n_{Cl})
	13.31	1e (n_{Cl})
	13.86	$2a_1$ (σ_{Ti-Cl})
$(C_2H_5)_2O$	9.61	n_O (π)
	11.08	n_O (σ)
	11.92−14.74	σ_{CC}, π_{CH_2}, π_{CH_3}, σ_{CO}
$TiCl_4-(C_2H_5)_2O$	10.00	n_{Cl}
	11.0	n_{Cl}
	11.4	n_o (π)
	11.7	n_{Cl}
	12.07	σ_{Ti-Cl}
	13.5	n_o (σ)
$(C_2H_5)_2S$	8.5	n_s (π)
	10.70	n_s (σ)
	11.48	σ_{C-S}
	12.54	π_{CH_3}
$TiCl_4-(C_2H_5)_2S$	9.85	n_s (π)
	10.30	n_{Cl}
	11.20	n_{Cl}
	12.40	n_{Cl}
	13.1	n_s (σ)
	13.6	σ_{Ti-Cl}

two peaks are shifted to lower binding energy by 1.6 and 1.8 eV, respectively. Thus, all four bands of $TiCl_4$ are shifted to lower binding energy. The 13.5 eV peak is assigned to the σ type lone pair of oxygen, which is shifted to higher binding energy by 2.4 eV. A higher shift of σ type lone pair of oxygen is reasonable, since this is the bonding orbital. This is in agreement with the calculated orbital energies of the $TiCl_4-2(CH_3)_2O$ complex.

He I photoelectron spectra of $TiCl_4$, diethyl sulfide, and the complex are presented in Figure 3. The spectrum of the complex $TiCl_4-2(C_2H_5)_2S$ is different from that of the donor and acceptor with additional features marked by arrows. The calculations are done on the model compound $TiCl_4-2(CH_3)_2S$. The geometry is optimized at the 3-21G level. The D_{2h} form of this complex is not found to be the minimum energy structure.

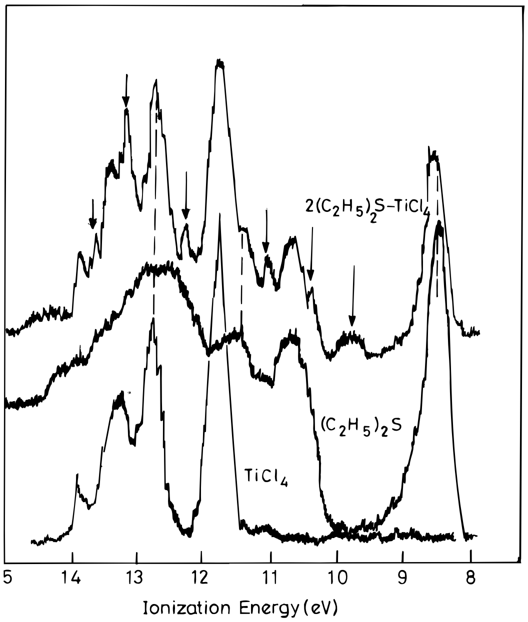

Figure 3. HeI photoelectron spectra of $TiCl_4$, diethyl sulfide, and the complex $2(C_2H_5)_2S-TiCl_4$. The features due to the complex are shown by arrows.

In earlier studies of D−A complexes of diethyl ether with halogens, the interaction was observed between the σ type oxygen lone pair with σ^* of halogens with a C_{2v} symmetry. However, in the case of of diethyl sulfide with halogens, it was the π type lone pair orbital that is bonded to σ^* of the halogens, the complexes having C_s symmetry.[4,5] Accordingly, in this case, the minimum energy geometry of $TiCl_4-2(CH_3)_2S$ was found to have a C_{2h} symmetry. The structure is optimized and is given in Figure 2b. The optimized Ti−S distance is 2.611 Å. The binding energy of the complex is computed to be 26.24 kcal/mol, which agrees with the heat of formation.[2] The interaction energy is less than that of the dimethyl ether complex. In Table 1, calculated orbital energies of $(CH_3)_2S$ and $TiCl_4-2(CH_3)_2S$ are given. Although the sulfur lone pairs in the complex are shifted to higher binding energies, chlorine lone pairs as well as the $\sigma_{(Ti-Cl)}$ bond energy are shifted to lower binding energies. The calculation shows that the highest occupied orbital in the complex is due to n_{Cl} and the second orbital is due to S. The difference in energy however is only about 0.1 eV. It is also clear from this calculation that the π type sulfur lone pair is the bonding orbital with $TiCl_4$.

In Table 2 the observed ionization energies and the assignments for the complex $TiCl_4-2(C_2H_5)_2S$ are given. The first new band due to the complex is assigned to the n_S and the second band to n_{Cl} because the first band is broad and all peaks due to n_{Cl} are expected to be narrower as seen in $TiCl_4-2Et_2O$. Accordingly, the π type sulfur lone pair orbital is shifted by 1.3 eV to higher binding energy and that of n_{Cl} by about 1.4 eV to lower binding energy. The other n_{Cl} bands as assigned in Table 2 are shifted to lower binding energies by 1.4−1.6 eV. The n_{Cl} bands are expected to be shifted by a lower value in $2Et_2S-TiCl_4$ compared to $2Et_2O-TiCl_4$. The assignment given here agrees with this expectation. Furthermore, the shift in the sulfur lone pair orbital by 1.3 eV is lower than the oxygen lone pair shift of 1.8 eV in ether−$TiCl_4$, which agrees well with the lower energy of interaction of $2Et_2S-TiCl_4$.

Interactions of $(CH_3)_2O$, $(CH_3)_2S$, $(C_2H_5)_2O$, $(C_2H_5)_2S$, and such ligands with $TiCl_4$ should be viewed as Lewis base−Lewis acid interactions. $TiCl_4$ is a tetrahedral molecule and forms an octahedral-like molecular complex with the addition of two ligands. The Ti^{4+} ion is classified as a hard acid, and the

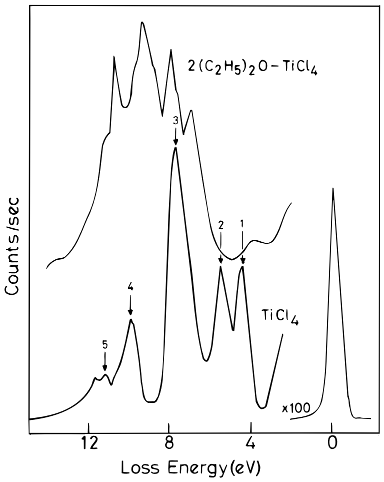

Figure 4. Electron energy loss spectra of $TiCl_4$ and $TiCl_4-2Et_2O$.

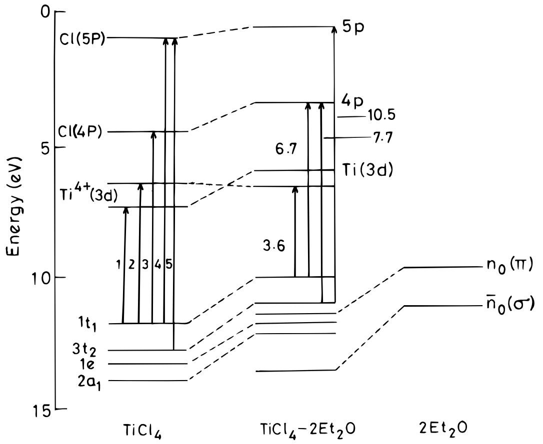

Figure 5. Energy level diagram of $TiCl_4-2Et_2O$ complex and the electronic transitions in $TiCl_4$ and the complex.

tendency for complex formation is in the order O ≫ S > Se > Te.[17] Thus, octahedral complex molecule $TiCl_4-2(CH_3)_2O$ should be more stable than $TiCl_4-2(CH_3)_2S$. The binding energy of the complexes and the shifts in the orbital energies of the donor and acceptor molecules support this argument.

EELS Study of the $TiCl_4$−Ether Complex. EELS of $TiCl_4$ and $TiCl_4-2Et_2O$ complex are given in Figure 4. Five prominent peaks are seen at 4.5, 5.4, 7.4, 9.8, and 11.2 eV. The transitions are assigned with the help of optical absorption studies[13,18,19] and quantum defect calculations.[20] Accordingly, the first peak at 4.5 eV can be assigned to the transition $1t_1 \rightarrow e$, which corresponds to the first transition observed by optical study. The one at 5.4 eV is due the $1t_1 \rightarrow 1t_2$ transition. This matches well with the optical absorption value. CIS calculations gave transition energies at 5.9 and 6.1 eV, respectively, for the above transitions. The intense peak at 7.4 eV is assigned to the $1t_1 \rightarrow 4P$ Rydberg transition. The features at 9.8 and 11.1 eV are assigned to the transitions from the $1t_1$ and $3t_2$ orbitals to the 5P level. An energy level diagram showing the various transitions observed in the EELS is presented in Figure 5. The orbital energies of the $TiCl_4$ molecule is taken from the photoelectron spectra.

The spectrum of the complex is different from that of diethyl ether and $TiCl_4$. The transitions observed are at 3.7, 6.7, 7.7, 8.9, and 10.5 eV. A MO diagram [Figure 5] for the $TiCl_4-2Et_2O$ complex was drawn using the UVPES and EELS data to explain the various transitions observed from the complex molecule. The first peak at 3.7 eV is assigned to the charge-transfer band that is due to the transition from the highest occupied shifted chlorine lone pair orbital to the Ti^{4+}(3d). The peaks at 6.7 and 7.7 eV are assigned to the transitions from the shifted $1t_1$ and $3t_2$ chlorine orbitals to the 4p Rydberg states, which are also shifted due to the complex formation. The peak at 10.5 eV is assigned to the $3t_2 \rightarrow 4p$ transition. Thus, when the tetrahedral $TiCl_4$ molecule goes over to octahedral $TiCl_4-2Et_2O$, the molecule should become more ionic.[17] This can be seen from the decrease in the ionization energies of Cl orbitals as well as destabilized Rydberg states. The charge-transfer band in $TiCl_4$ at 4.6 eV is shifted to 3.6 eV because of the change in the electronic structure of the molecule.

Conclusions

Occupied electron states of $TiCl_4-2Et_2O$ and $TiCl_4-2Et_2S$ have been obtained from UV photoelectron spectroscopy. MO calculations on the model compounds of $TiCl_4-2(CH_3)_2O$ showed that the σ type pair is the bonding orbital with molecule having D_{2h} symmetry. In the $TiCl_4-2(CH_3)_2S$, the π type lone pair of S is involved in bonding with C_{2h} symmetry. From electron energy loss spectroscopy and UVPES of $TiCl_4-Et_2O$ a complete energy level diagram was drawn where the 3.6 eV band observed is assigned to the charge-transfer band from Cl to the Ti(3d) orbital.

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