orbital calculations[7] and more recently by using configuration interaction on CNDO-type molecular wave functions.[22]

Four components of the 4–8-eV band are resolved in the present work, and the insert to Figure 6 shows that the spectrum fits well to four Gaussian curves, the parameters of which are as follows: peak 1, position 4.49 eV, fwhm 0.667 eV, relative area 0.261; peak 2, position 5.36 eV, fwhm 0.909 eV, relative area 1.0; peak 3, position 5.97 eV, fwhm 0.582 eV, relative area 0.774; peak 4, position 6.71 eV, fwhm 0.881 eV, relative area 0.766. It is obvious from the figure that peaks 1 and 3 and 2 and 4 have similar widths, suggesting that these pairs may have a common initial state. Since transitions from the triply degenerate $9t_2$ set of Ni 3d orbitals are expected at lower energies than peaks due to promotion of electrons from the doubly degenerate 2e set, this would lead to the conclusion that peaks 1 and 3 originate from the $9t_2$ MOs and peaks 2 and 4 from the 2e MOs. However, even though the transition matrix elements will certainly be quite different for the $9t_2$ and 2e orbitals, it is unlikely that they are so different as to result in the experimental $(1 + 3)/(2 + 4)$ intensity ratio of 0.586, considering the 3:2 ($9t_2$:2e) degeneracy ratio and the fact that more of the low-energy transitions involving the 2e orbitals are symmetry forbidden. More likely the observed band widths are the result of heavily overlapping transitions and/or associated vibrational progressions.

The assignment given in ref 7 involved transitions from the CO localized ($5\sigma + 1\pi$) levels giving rise to a number of components of the low-energy band system (i.e., the bands below ~8 eV). However, relative to the ($5\sigma + 1\pi$) ionization onset, the highest energy loss (lowest term value) component of this band system (peak 4) at ~6.7-eV energy loss would then have a term value of ~7.4 eV, which is higher than the term value for any band in the inner-shell spectra (see Tables I–III). Since term values for a particular final virtual valence orbital tend to decrease in going from core excitation to valence excitation,[71] such an assignment can be eliminated on these grounds.

The configuration interaction calculations[22] came to the conclusion that not only is the manifold of π^* orbitals accessible from ~4 to 6 eV but so also are the Ni 4s and 4p orbitals, although many of the possible transitions were calculated to be weak. Their assignment of the most intense peak at ~6 eV was to metal → ligand charge transfer, $9t_2$ (Ni 3d) $\rightarrow$ $2t_1$ (π^*), the first lower energy shoulder at ~5.5 eV to $9t_2$ (Ni 3d) $\rightarrow$ $10t_2$ (π^*), and the lowest energy band to either $9t_2$ (Ni 3d) $\rightarrow$ Ni 4s or $10t_2$ (π^*) triplet coupled. If the lowest energy transition is indeed the latter, then it must gain intensity through vibronic coupling, since exchange transitions are forbidden at the high impact energies and 0° scattering angle used in the present VSEELS work. Unfortunately these calculations[22] did not consider transitions involving the 2e (Ni 3d) electrons. Assuming the above assignment[22] to be correct, the excitations from the lower lying 2e (Ni 3d) orbitals can then be assigned either wholly to the peak centered at ~6.7-eV energy loss (feature 4) or partly to this peak plus some intensity contributing to the 5.97 eV peak (feature 3). These findings of the CI calculations[22] are reflected in the assignments summarized in Table IV. It is hoped that the results reported here will stimulate further theoretical investigations of the valence-shell photoabsorption spectrum of $Ni(CO)_4$ to clarify this situation.

Conclusions

We have obtained the first ISEELS spectra of a gaseous transition-metal complex, $Ni(CO)_4$. The VSEELS spectrum was also obtained over an extended energy range. The inner-shell spectra could be interpreted largely by analogy with those of free CO. In particular the C 1s and O 1s spectra both show intense $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions for $Ni(CO)_4$ and free CO. Vibrational structure associated with a C–O stretching mode was resolved in the $1s \rightarrow \pi^*$ bands of the C 1s spectra. The $Ni(CO)_4$ inner-shell spectra can most readily be explained by invoking localization of the C 1s or O 1s hole on one of the CO groups. The shifts in $1s \rightarrow \pi^*$ transition energies and term values from free CO were interpreted in terms of severe orbital relaxation upon creation of a 1s hole and also the influence of Ni $\rightarrow$ CO π back bonding. The changes in vibrational structure between $Ni(CO)_4$ and CO in the C $1s \rightarrow \pi^*$ band, in particular a lower C–O vibrational frequency in $Ni(CO)_4$, also show direct evidence for metal–ligand back bonding.

Due to the complicating factor of greater orbital relaxation accompanying creation of a 1s hole in $Ni(CO)_4$, quantitative estimates of the extent of back bonding are not possible. However, the ISEELS technique should be very valuable in the investigation of metal–ligand bonding when results for different metal carbonyls can be compared, since then the extent of orbital relaxation should be almost constant for a given series of compounds. We are presently undertaking a study of the group VIA metal hexacarbonyls to investigate further the applicability of ISEELS spectroscopy to studies of transition metal–ligand bonding.

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Experimental Electronic Structures of Complexes of SO_2: An Electron Spectroscopic Study

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Abstract: He I photoelectron spectra of gas-phase complexes formed by SO_2 with the electron donors trimethylamine, triethylamine, diethyl ether, and diethyl sulfide have been recorded and bands assigned to the different orbitals based on MO calculations. The shift in the ionization energy of the lone pair orbital of the donor in these complexes is shown to vary proportionally with the dissociation energy as well as the magnitude of charge transfer to SO_2. Electron energy loss spectra of the donor–SO_2 complexes have been recorded to characterize the electronic transitions in the vacuum UV region. Only the amine–SO_2 complex shows a band ascribable to a charge-transfer transition. In order to investigate situations where SO_2 acts as an electron donor, He I spectra of complexes with BF_3 and HCl have been measured. The decrease in the Mulliken population of SO_2 as well as the dissociation energy of these complexes varies parallel to the shift in the lone pair ionization energy of SO_2.

The 1:1 charge-transfer complex between trimethylamine and sulfur dioxide has been characterized adequately both in the gas and the condensed phases.[1-3] The gas-phase dissociation energy of the complex[3] is 40.5 kJ mol^{-1}. The complex has essentially a

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pyramidal geometry with an experimental N–S distance of 2.06 Å,[4] and it appears that the pyramidal coordination enhances the overlap between the π^* LUMO (lowest unoccupied molecular orbital) of SO_2 and the nitrogen lone pair of amine. In spite of the extensive molecular orbital calculations on $(CH_3)_3N{\cdot}SO_2$,[5–7] the experimental electronic structure of this complex has not been investigated hitherto. In this paper we report the results of our study of this complex by ultraviolet photoelectron spectroscopy (UVPES). Since the increased Mulliken population of SO_2, $\Delta q(SO_2)$, due to coordination with a Lewis base would be proportional to the interaction strength between SO_2 and the electron donor, we have investigated the UVPES of other SO_2 complexes with a few other donors as well. The donors studied are triethylamine, diethyl ether, and diethyl sulfide. On the basis of ab initio molecular orbital (MO) calculations we have made assignments of the UV photoelectron spectra of the complexes. The calculations showed the dissociation energy of the complex, ΔE, as well as $\Delta q(SO_2)$ vary with the donor in the order $(CH_3)_3N > (C_2H_5)_2O > (C_2H_5)_2S$. We find that the experimentally observed change in the lone pair ionization energy (IE) of the donor to be proportional to ΔE and $\Delta q(SO_2)$. We have obtained information on the electronic transitions in these electron donor–SO_2 complexes by means of electron energy loss spectroscopy (EELS). EELS provides information on the electronic transitions especially in the far or vacuum ultraviolet region, where these complexes are expected to exhibit characteristic features.

In all the complexes discussed above, SO_2 acts as the electron acceptor. We considered it instructive to investigate complexes of SO_2 where it acts as the electron donor via the oxygen. For this purpose, we have studied the UVPES of the complex between SO_2 and BF_3 where the coordination occurs between the oxygen of SO_2 and the boron of BF_3. Another complex where SO_2 acts as the donor is that where the oxygen is involved in hydrogen bonding with a proton donor. We have investigated the UVPES of the 1:1 complex of SO_2 with HCl.

The present study has revealed certain important features of the electronic structures of SO_2 complexes and has enabled a correlation of the strength of the donor–acceptor interaction with the observed changes in the photoelectron spectra. In addition, the study has also established the formation of a few gas-phase complexes of SO_2 for the first time.

Experimental and Computational Details

Ultraviolet photoelectron spectra were recorded with a homebuilt spectrometer[8] consisting of a He I lamp, a 3-mm diameter collision chamber, and a channeltron electron multiplier. Differential pumping allowed for operation of the He I lamp at 1.5 Torr, a sample pressure of 0.1–0.5 Torr, and a pressure of 5×10^{-5} Torr in the rest of the spectrometer. The resolution of the spectrometer was 80 meV FWHM at 19.7 eV. Samples of the complexes were prepared in vacuum by co-condensation of the donor with a small excess of the acceptor at 77 K in a glass ampoule fitted with a Teflon tap. Samples of these mixtures were gently warmed to room temperature and admitted in to the spectrometer by means of a needle valve. The initial spectra contained new features due to the complexes besides features of the excess components which then got pumped away to essentially give the spectra of the complexes. Any features due to the free donor or acceptor remaining in the spectra were removed by an interactive computer program. The stripping procedure was similar to that described in the literature.[9] The spectra of the 1:1 complexes thus obtained were identical whether the initial composition had excess donor or acceptor.

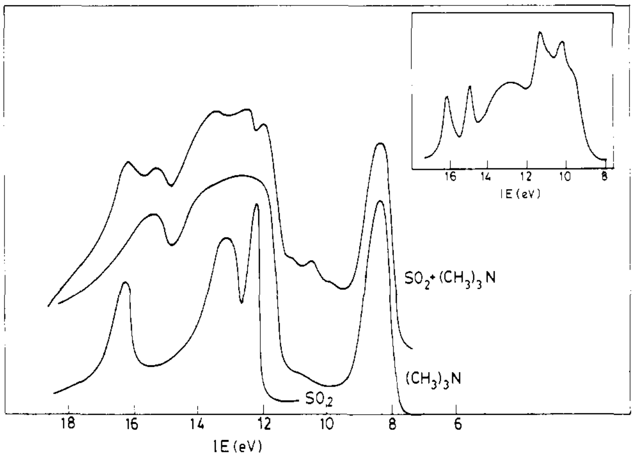

Figure 1. He I spectra of SO_2, $(CH_3)_3N$, and a mixture of SO_2 and $(CH_3)_3N$. The spectrum of the complex is shown in the inset.

Table I. Occupied Orbital Energies and Assignments of $(CH_3)_3N{\cdot}SO_2$[a]

	calculated MOs		
I_v (eV)	$-\epsilon$ (eV)	character	MO
9.8	10.06	$n_S(n_O)$	21a′
10.3	11.36	n_O	12a″
10.8	11.58	n_N	20a′
11.5	11.89	π_{SO}	11a″
13.0–13.5	14.36	π_{CH_2}	10a″
	14.48	σ_{CN}	19a′
	14.75	π_{CH_2}	9a″
15.0	15.70	π_{SO}	18a′
	15.77	σ_{SO}	8a″
	15.79	σ_{NS}	17a′
16.2	16.68	σ_{CH_2}	7a″
	17.11	π_{CH_2}	16a′

[a] The $(C_2H_5)_3N{\cdot}SO_2$ complex give bands at 9.5, 9.9, 10.6, 11.5, 13.2, 15.2, and 16.0 eV due to $n_S(n_O)$, n_O, n_N, π_{SO}, σ_{CN}, π_{NS}, and π_{CH_2} ionizations, respectively.

Electron energy loss spectra were recorded with a homebuilt spectrometer[8] consisting of a hemispherical electron monochromator (125-mm mean diameter), a collision chamber, a hemispherical electron energy analyzer (140-mm mean diameter), and a channeltron electron multiplier. By means of differential pumping, a sample pressure of 5×10^{-4} Torr could be produced in the collision chamber, while the rest of the spectrometer remained at 2×10^{-6} Torr. An electron beam of 45 V with 300 meV FWHM was employed in the present study.

Hartree–Fock energies of the complexes were computed in the frame work of the SCF-LCAO-MO method using the GAUSSIAN 86 program.[10] The split valence 3-21G basis set was used in all the computations except for $SO_2{\cdot}HCl$; where in addition to 3-21G, a better basis set, 6-31G*, was also used. Monomer geometries were fully optimized and used as input for the calculations on the complexes. In the case of $(CH_3)_3N{\cdot}SO_2$, the geometry was taken from the work of Sakaki et al.[5] In the case of $(C_2H_5)_2O{\cdot}SO_2$ and $(C_2H_5)_2S{\cdot}SO_2$ complexes, free monomer geometries were employed and the donor–SO_2 distances and the various angles (of C_s symmetry) were optimized. Geometries were fully optimized for $BF_3{\cdot}SO_2$ and $SO_2{\cdot}HCl$.

Results and Discussion

He I Spectra of 1:1 Complexes with SO_2 as the Electron Acceptor. In Figure 1, we give the He I spectra of SO_2, $(CH_3)_3N$, and a mixture of the two. SO_2 exhibits features at 12.5, 13.2, and 16.6 eV due to $n_S(n_O)$, π_{SO}, and σ_{SO} ionizations, respectively. Trimethylamine has a characteristic band at 8.4 eV due to the ionization of the nitrogen lone pair. The features in the 9.5–12.0 eV region in the spectrum of the mixture is clearly indicative of

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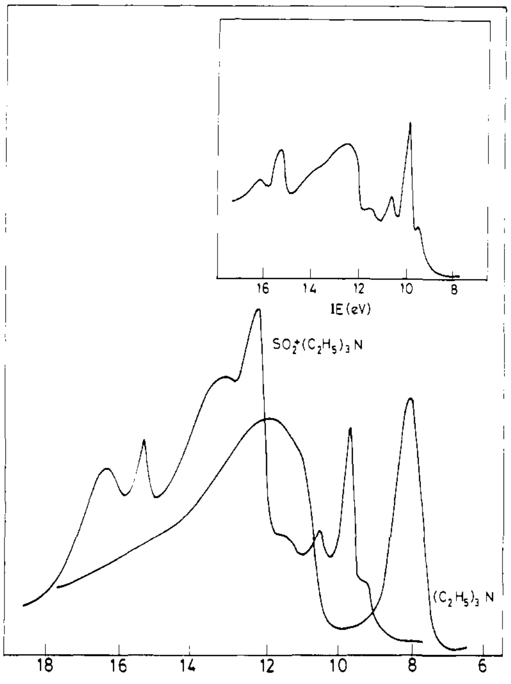

Figure 2. He I spectra of $(C_2H_5)_3N$ and a mixture of SO_2 and $(C_2H_5)_3N$. The spectrum of the complex obtained after stripping is shown in the inset.

complex formation. In the inset of Figure 1, we show the spectrum of the 1:1 complex obtained after stripping. The 1:1 complex gives characteristic features at 9.8, 10.3, 10.8, and 11.5 eV which can be delineated from the features due to the amine and SO_2. On the basis of MO calculations these features are assigned to $n_S(n_O)$, n_O, n_N, and π_{SO} ionizations, respectively. The broad band centered at 13.2 eV is a composite of feature due to various orbitals; the same is true of the bands at 15.0 and 16.2 eV. In Table I, we have listed the assignments of the UVPES of $(CH_3)_3N{\cdot}SO_2$. MO calculations on this complex in the literature[5-7] have shown it be pyramidal in shape with an N–S distance of 2.16 Å. Our calculation give a dissociation energy of 62 kJ mol^{-1} and Δq(SO2) of 0.15 which is comparable to that reported by Sakaki et al.[5] We have also investigated the He I spectrum of the triethylamine–SO_2 complex (Figure 2). The spectrum of the mixture shows additional features in the 9.5–11.5 eV region. The spectrum obtained after stripping (see the inset of Figure 2) is similar to that of the $(CH_3)_3N{\cdot}SO_2$ complex. There is a one-to-one correspondence between features of these two amine complexes of SO_2 as expected (Table I).

He I spectra of the two amine–SO_2 complexes reveal that the ionization energies of the donor and the acceptor are shifted considerably due to complexation. In the case of $(CH_3)_3N{\cdot}SO_2$, the n_N orbital of the amine is stabilized by 2.4 eV, while the $n_S(n_O)$ orbital of SO_2 is destabilized by 2.7 eV. In the case of $(C_2H_5)_3N{\cdot}SO_2$, the shifts are slightly larger. The shifts of n_N and $n_S(n_O)$ being 2.5 and 3.0 eV, respectively, indicating a slightly higher strength of the donor–acceptor interaction.

He I spectra of diethyl ether and of a mixture of the ether and SO_2 are shown in Figure 3. The first band found in the spectrum of the mixture is broader than that of the free ether; this, in addition to the features at 11.4 and 12.3 eV, clearly suggests the formation of the complex. The spectrum attributed to the pure complex obtained after stripping (given in the inset of Figure 3) shows characteristic bands at 9.8, 11.4, 12.3, and 13.1 eV which are assigned to $n_S(n_O)$, n_O(ether), $\bar{n}_O$, and π_{SO} orbitals, respectively based on MO calculations. The broad band in the region 14.0–15.0 eV is a composite due to ionizations from a number of closely lying orbitals. The band assignments are listed in Table II.

The optimized geometry of the diethyl ether–SO_2 complex is similar to that reported for the dimethyl ether–SO_2 complex.[11] The S–O coordinate bond distance is 2.40 Å, and the SO_2 and C–O–C planes make angles of 96.0° and 144.3° with the intermolecular axis. The dissociation energy (26 kJ mol^{-1}) is smaller than that of $(CH_3)_3N{\cdot}SO_2$ just as the value of $\Delta q(SO_2)$ (0.08).

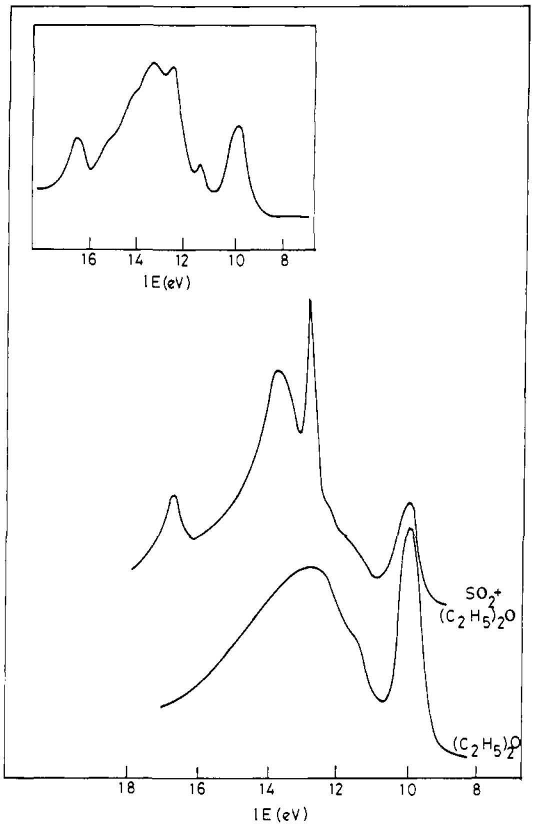

Figure 3. He I spectra of $(C_2H_5)_2O$ and a mixture of SO_2 and $(C_2H_5)_2O$. The spectrum of the complex is shown in the inset.

Table II. Occupied Orbital Energies and Assignments of $(C_2H_5)_2O{\cdot}SO_2$

	calculated MOs		
I_v (eV)	$-\epsilon$ (eV)	character	MO
9.8	11.22	$n_S(n_O)$	22a′
11.4	11.30	n_O(ether)	15a″
12.3	11.90	$\bar{n}_O$	21a′
13.1	12.49	π_{SO}	14a″
14.0–15.0	13.17	π_{CH}	20a′
	13.49	π_{CH_2}	13a″
	14.19	π_{CH}	12a″
	14.62	π_{CH}	11a″
	14.63	π_{CH_2}	19a′
	15.34	π_{CH_2}	18a′
	16.12	π_{SO}	17a′
	16.24	π_{SO}	10a″
	16.65	π_{CH}	9a″
16.3	16.72	π_{SO}	16a′
	17.51	σ_{SO}	15a′

He I spectra of diethyl sulfide and a mixture of diethyl sulfide and SO_2 are shown in Figure 4. The feature at 9.7 eV in the spectrum of the mixture and the broadening of the band at 12.5 eV are indicative of complex formation. This is the first demonstration of the occurrence of a sulfide–SO_2 complex in the gas phase. The stripped spectrum shown in the figure exhibits characteristic features at 9.7, 10.6, 11.5, and 12.3 eV which are assigned to n_S(sulfide), $\bar{n}_S$(sulfide), $n_S(n_O)$, and n_O ionizations based on MO calculations (Table III). The group of bands in the 13.1–15.5 eV range is due to ionizations from a number of closely lying orbitals the same holds for the feature at 16.5 eV.

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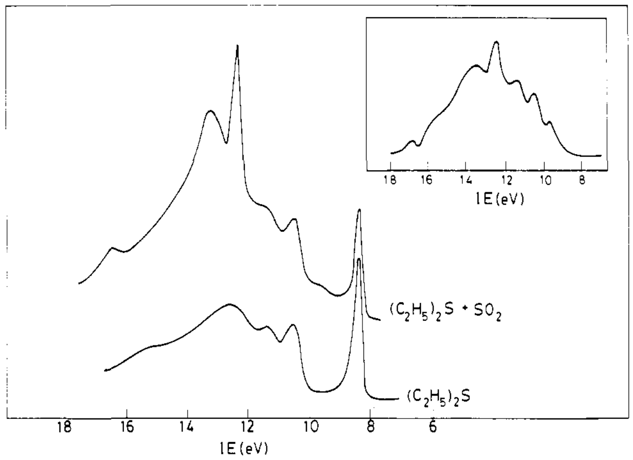

Figure 4. He I spectra of $(C_2H_5)_2S$ and a mixture of SO_2 and $(C_2H_5)_2S$. The spectrum attributed to the 1:1 complex obtained after stripping is shown in the inset.

Table III. Occupied Orbital Energies and Assignments of $(C_2H_5)_2S\cdot SO_2$

	calculated MOs		
I_v (eV)	$-\epsilon$ (eV)	character	MO
9.7	9.51	n_S(sulfide)	25a′
10.6	11.20	$\bar{n}_S$(sulfide)	24a′
11.5	11.59	$n_S(n_O)$	16a″
12.3	12.05	n_O	23a′
13.1–15.5	12.59	σ_{CS}	15a″
	12.99	π_{SO}	14a″
	14.09	π_{CH_2}	13a″
	14.36	π_{CH_2}	22a′
	14.44	σ_{CS}	12a″
	14.73	σ_{CC}	21a′
	15.86	π_{CH}	20a′
	16.45	π_{SO}	19a′
	16.47	σ_{CH_2}	11a″
16.5	16.72	σ_{SO}	10a″
	17.15	σ_{SO}	18a′

The optimized geometry of the $(C_2H_5)_2S\cdot SO_2$ complex gives an S–S distance of 3.32 Å, the SO_2 and C–S–C planes making angles of 100.2° and 131.2° with the intermolecular axis. The computed dissociation energy is 3 kJ mol^{-1}. Accordingly, the increase in the Mulliken population of SO_2 is only 0.03. The small values of the dissociation energy and $\Delta q(SO_2)$ are consistent with the relatively small shifts found in the donor and acceptor ionization energies on complex formation. Our calculations on the 1:1 complex formed between SO_2 and H_2S give a dissociation energy of 9.6 kJ mol^{-1} with an S–S distance of 2.92 Å. The S–O and S–H distances as well as the O–S–O and H–S–H angles are not affected to any significant extent due to complexation.

An examination of the He I spectra of the 1:1 complexes of SO_2 with diethyl ether and diethyl sulfide shows that the n_O and n_S ionization energies of these donors are shifted by 1.8 and 1.1 eV respectively; the shift in the $n_S(n_O)$ ionization energy of SO_2 is 2.7 and 1.0 eV, respectively, in these two complexes. In Figure 5, we have plotted the shift in the ionization energy of the lone pair orbital of the donor, ΔI_v, against the dissociation energy (ΔE) of the complex. In the same figure, we have also plotted ΔI_v against the increase in the Mulliken population of SO_2. The plots show that the shift in the IE of the lone pair orbital of the donor molecule varies monotonically with the magnitude of the donor–acceptor interaction as predicted by Mulliken's theory.[12]

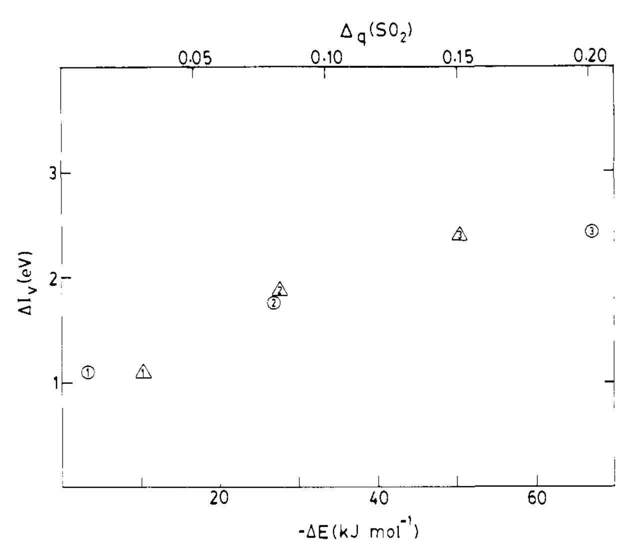

Figure 5. Plot of the shift in the lone pair orbital ionization energy of the donor due to complexation, ΔI_v, against the dissociation energy (ΔE) of the complex (open circles). Plot of ΔI_v against the increase in the Mulliken population of SO_2, $\Delta q(SO_2)$ (open triangles) is also shown: 1, $(CH_3)_3N\cdot SO_2$; 2, $(C_2H_5)_2O\cdot SO_2$; 3, $(C_2H_5)_2S\cdot SO_2$.

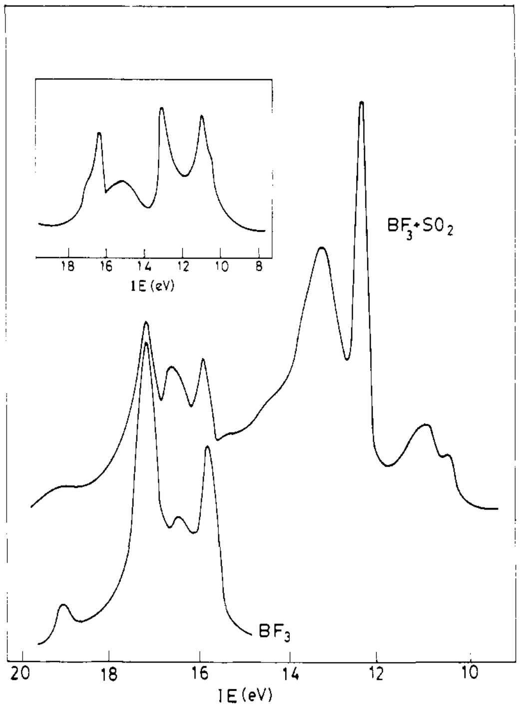

Figure 6. He I spectra of BF_3 and a mixture of BF_3 and SO_2. The spectrum of the complex obtained after stripping is shown in the inset.

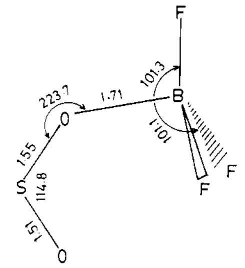

Figure 7. Optimized structure of the $BF_3\cdot SO_2$ complex.

1:1 Complexes of SO_2 as the Electron Donor. In order to investigate the electronic structures of complexes where SO_2 may act as an electron donor, we first studied the interaction of SO_2 with BF_3 which is a classic vacant-orbital acceptor. For this purpose, we recorded the He I spectra of several mixtures of SO_2 and BF_3. In Figure 6 we show the spectrum of a mixture of BF_3 and SO_2 along with the spectrum of pure BF_3. The spectrum of BF_3 shows bands at 15.9, 16.7, 17.1, and 19.1 eV due to various

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Table IV. Occupied Orbital Energies and Assignments of $BF_3{\cdot}SO_2$

	calculated MOs		
I_v (eV)	$-\epsilon$ (eV)	character	MO
10.4	13.02	n_F	10a″
	14.41	n_F	23a′
11.0	15.33	n_F	22a′
13.1	15.44	n_F	9a″
	15.56	n_F	21a′
15.2	16.34	n_F	8a″
	16.67	n_F	7a″
16.2	17.65	$n_S(n_O)$	20a′
17.0	18.34	π_{SO}	6a″
	19.22	π_{SO}	19a′

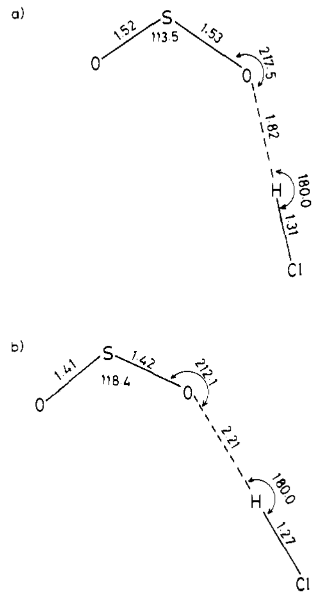

Figure 8. 3-21G and 6-31G* optimized structures of $SO_2{\cdot}HCl$ complex: (a) 3-21G structure and (b) 6-31G* structure. The experimental SOH angle and O–Cl distance are 210° and 3.38 Å, respectively.

n_F orbital ionizations. The features on the low energy side in the spectrum of the $SO_2 + BF_3$ mixture indicate the formation of a complex. The spectrum obtained after stripping is shown in the inset of Figure 6.

We have carried out MO calculations on the $BF_3{\cdot}SO_2$ complex with full geometry optimization, and the optimized structure is shown in Figure 7. The computed dissociation energy of the complex is 81.5 kJ mol^{-1}. The Mulliken population of SO_2 decreases on complexation as expected when SO_2 is an electron donor, and accordingly the value of $\Delta q(SO_2)$ is −0.16 (unlike in donor–SO_2 complexes where it has a positive value). The calculated eigen values are sensitive to the O–B bond length, and at the optimized distance (1.7 Å) the HOMO (highest occupied molecular orbital) of the complex turns out to be the nonbonding orbital of oxygen. At slighty shorter O–B distances, the HOMO is the fluorine lone pair. An examination of the He I spectrum of the complex indicates that the lowest energy features are almost certainly associated with the fluorine lone pair ionization. A UVPES study on the $BF_3{\cdot}H_2O$ system[13] with a comparable dissociation energy has shown that the first few features in the complex spectrum are due to the ionizations from the fluorine lone pair orbitals. In order to interpret the He I spectrum of $BF_3{\cdot}SO_2$ (on the basis of Koopman's approximation), we obtained the ordering of MOs in the complex with a O–B distance of 1.6 Å. The assignments based on this ordering are listed in Table IV. The IEs of the fluorine lone pair orbitals are shifted to lower values since BF_3 accepts electron density from SO_2. The formation of the $BF_3{\cdot}SO_2$ complex is reported here for the first time in the literature.

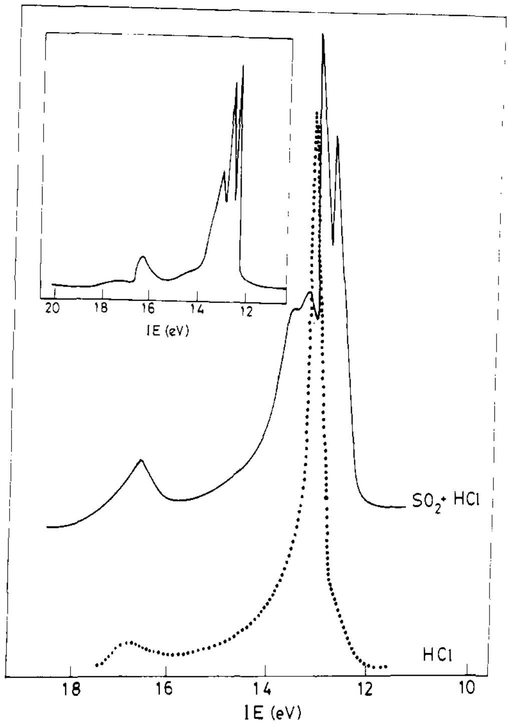

Figure 9. He I spectra of HCl and a mixture of SO_2 and HCl. The spectrum of the complex obtained after stripping is shown in the inset.

Table V. Occupied Orbital Energies and Assignments of $SO_2{\cdot}HCl$

	calculated MOs			
	$-\epsilon$ (eV)			
I_v (eV)	3-21G	6-31G*	character	MO
12.3	12.00	12.42	n_{Cl}	20a′
	12.01	12.43	n_{Cl}	5a″
12.6	13.21	13.75	$n_S(n_O)$	19a′
13.0	13.45	14.56	n_O	4a″
13.4	14.68	15.11	n_O	18a′
14.5	15.56	16.54	σ_{HCl}	17a′
16.3	17.97	18.71	σ_{SO}	3a″
17.5	18.73	19.47	π_{SO}	16a′

Another complex that we have investigated where SO_2 acts as an electron donor is the hydrogen-bonded complex with HCl which has recently been characterized by microwave spectroscopy.[14] MO calculations on this complex were carried out with two different basis sets (3-21G and 6-31G*) with full geometry optimization. The optimized structural parameters obtained from the calculations (Figure 8) are comparable to the experimental values.[14] The dissociation energy of the complex is 31.1 and 9.0 kJ mol^{-1} from 3-21G and 6-31G* calculations, respectively. We are not aware of any experimental value of the dissociation energy of the complex. The computed decrease in the Mulliken population of SO_2 is 0.06 at the 3-21G level and 0.02 at the 6-31G* level.

He I spectra of HCl as well as a mixture of SO_2 and HCl are shown in Figure 9. The spectrum of HCl shows bands at 12.7 and 16.3 eV due to n_{Cl} and σ_{HCl} ionizations. The observed shift of the first SO_2 band to higher energy and of the first band of HCl to lower energy in the spectrum of the mixture as well as the splitting of the 13.5 eV band are clear indications of the formation of the complex. The spectrum obtained after stripping is shown in the inset of Figure 9. The observed ionization energies and assignments are listed in Table V. The scaled Koopman's IPs (-0.9ϵ) and experimental IEs of the $SO_2{\cdot}HCl$ complex are very close to each other. The first feature at 12.3 eV is due to n_{Cl} ionization. The small decrease in the ionization energy on complexation is due to the increase in the electron density around chlorine on the formation of the hydrogen bond. The shifts in

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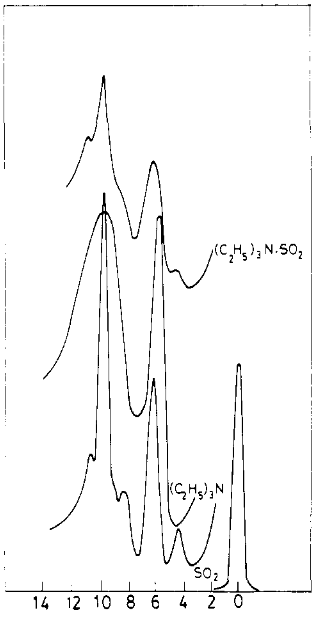

Figure 10. Electron energy loss spectra of $(C_2H_5)_3N$, SO_2, and $(C_2H_5)_3N\cdot SO_2$ complex.

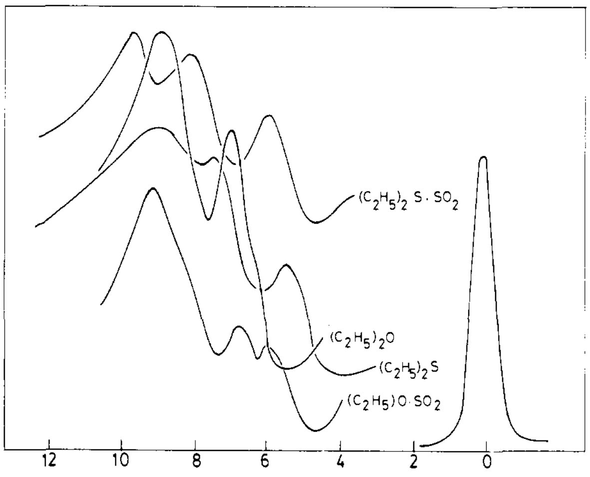

Figure 11. Electron energy loss spectra of $(C_2H_5)_2O$, $(C_2H_5)_2O\cdot SO_2$, $(C_2H_5)_2S$, and $(C_2H_5)_2S\cdot SO_2$.

the SO_2 ionization energies are small.

EELS Study of the Electronic Transitions of SO_2 Complexes. We have investigated the electronic spectra of SO_2 complexes by employing EELS. Alkylamines, ethers, and thioethers show electronic transitions in the far or vacuum UV region due to n → σ^* and $\sigma \rightarrow \sigma^*$ excitations. Trimethylamine shows the n → σ^* transition around 6 eV.[15] This band appears at 5.8 eV in the EEL spectrum of triethylamine (Figure 10), in agreement with the optical absorption spectrum documented in the literature.[15] The next band found at 9.9 eV is likely to be a Rydberg transition. The EEL spectrum of SO_2 has been reported earlier,[16] and we have obtained an identical spectrum in the present study (Figure 10). The $^1A_1 \rightarrow {}^3B_1$ transition at 3.3 eV in the optical spectrum[17] is not observed in EELS. $(C_2H_5)_3N\cdot SO_2$ shows five transitions at 4.2, 6.3, 8.5, 9.8, and 10.8 eV (Figure 10) of which the first corresponds to the 4.4-eV band found in the optical spectrum.[3] This band is a charge-transfer transition arising from $n_S \rightarrow \sigma^*_{NS}$ excitation. The bands at 6.3 and 8.5 eV are due to $n \rightarrow \pi^*$ transitions involving SO_2, shifted considerably from those in free SO_2 due to complexation.

Table VI. Electronic Transitions of SO_2 Complexes with *n*-Donors

n-donor	transition energy (eV) from EELS	assignment
$(C_2H_5)_3N$	4.2	$n_S \rightarrow \sigma^*_{NS}$
	6.3	$n_S \rightarrow \pi^*_{SO}$
	8.5	$n_S \rightarrow \pi^*_{SO}$
	9.8	R
	10.8	R
$(C_2H_5)_2O$	6.1	$22a' \rightarrow 24a'(n_S \rightarrow \pi^*_{SO})$
	6.9	$15a'' \rightarrow 23a'(n_O \rightarrow \sigma^*_{CO})$
	9.3	$14a'' \rightarrow 24a'(\pi_{SO} \rightarrow \pi^*_{SO}$
$(C_2H_5)_2S$	6.1	$25a' \rightarrow 26a'(n_S \rightarrow \sigma^*_{CS})$
	8.2	$16a'' \rightarrow 27a'(n_S(n_O) \rightarrow \pi^*_{SO})$
	9.7	$14a'' \rightarrow 27a'(\pi_{SO} \rightarrow \pi^*_{SO})$

Table VII. Some Important Features of SO_2 Complexes

	$-\Delta E$ (kJ mol^{-1})	$\Delta q(SO_2)$	ΔI_v (eV)	μ (D)
donor				
$(CH_3)_3N$	62	+0.15	2.4	6.4
$(C_2H_5)_2O$	26	+0.08	1.8	6.0
$(C_2H_5)_2S$	3	+0.03	1.1	5.5
acceptor				
BF_3	82	−0.16	3.7	7.6
HCl	31 (9)[a]	−0.06 (−0.02)[a]	0.1	6.3 (4.2)[a]

[a] 6-31G* values.

EEL spectra of $(C_2H_5)_2O$ and $(C_2H_5)_2O\cdot SO_2$ are given in Figure 11. Diethyl ether exhibits transitions at 6.6, 7.2, and 8.9 eV due to $3b_1 \rightarrow 10a_1(n_O \rightarrow \sigma^*_{CO})$, $3b_1 \rightarrow 8b_1(n_O \rightarrow \sigma^*_{CC})$ and $7b_2 \rightarrow 10a_1(\sigma_{CO} \rightarrow \sigma^*_{CO})$ excitations, of which the first two bands have been reported in the literature.[15] $(C_2H_5)_2O\cdot SO_2$ exhibit three valence transitions at 6.1, 6.9, and 9.3 eV which are assigned to $n_S \rightarrow \pi^*_{SO}$, $n_O \rightarrow \sigma^*_{CO}$ and $\pi_{SO} \rightarrow \pi^*_{SO}$ excitations, respectively.

Diethyl sulfide shows EELS transitions at 5.9, 7.8, and 9.6 eV of which the first band corresponds to the 6.0 eV transition found in the optical spectrum.[15] The transitions are assigned to $4b_1 \rightarrow 9b_2(n_S \rightarrow \sigma^*_{CS})$, $11a_1 \rightarrow 9b_2(\bar{n}_S \rightarrow \sigma^*_{CS})$, and $11a_1 \rightarrow 12a_1(\bar{n}_S \rightarrow \sigma^*_{CC})$ excitations, respectively. Lower energy transitions observed in the optical spectrum are not seen in EELS. The diethyl sulfide–SO_2 complex exhibits transitions (Figure 11) at 6.1, 8.2, and 9.7 eV which are assigned to $n_S \rightarrow \sigma^*_{CS}$, $n_S(n_O) \rightarrow \pi^*_{SO}$, and $\pi_{SO} \rightarrow \pi^*_{SO}$ excitations, respectively.

It is interesting that in the complexes of SO_2 with diethyl ether (and diethyl sulfide) σ^*_{CO} (and σ^*_{CS}) becomes the LUMO after complexation. The σ^* orbital of the donor gets stabilized in the complex by around 1 eV, while the π^* orbital of the acceptor gets destabilized by nearly 4.5 eV. The electronic transitions of all the SO_2 complexes obtained by us from EELS are summarized in Table VI.

Concluding Remarks

The present experimental study of the electronic structures of SO_2 complexes by means of electron spectroscopic techniques has provided some insight on the electronic structures of these interesting electron donor–acceptor complexes of SO_2. It is gratifying that the experimental shift in the ionization energy of the lone pair orbital of the donor varies in the same direction as the dissociation energy as well as the increase or decrease in the charge aquired by SO_2; the dipole moment also varies in the same direction. This is true whether SO_2 acts as an electron donor or as an acceptor. These conclusions are summarized in Table VII. Among the complexes studied, only the strong complex, namely the adduct between triethylamine and SO_2, exhibits a charge-transfer-like transition.

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