Surface Science 124 (1983) 162–174
North-Holland Publishing Company

A SPECTROSCOPIC STUDY OF THE COORDINATION OF DIMETHYL SULFOXIDE TO A PLATINUM (111) SURFACE

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Received 4 August 1982

Spectroscopic studies of the adsorption of dimethyl sulfoxide, $(CH_3)_2S=O$, on Pt(111) have shown that the molecule is bound to the surface via the sulfur atom in an inverted pyramid configuration. A comparison of XPS and EELS data for the adsorbed multilayer and monolayer with XPS and infrared data on the complex $PtCl_2(DMSO)_2$ is consistent with sulfur bonding. In addition, we detect a considerable increase of the $\nu(S=O)$ frequency in the DMSO monolayer with decreasing coverage, indicating a coverage dependent heat of adsorption. UPS data show that on adsorption to form a monolayer, the highest occupied molecular orbital of DMSO, presumably the sulfur "lone pair" orbital, shifts to a higher binding energy. These results show a remarkable similarity between DMSO bonding to a metal surface and bonding to a single Pt^{2+} species.

1. Introduction

In the field of coordination chemistry, molecules which act as weak donor ligands are of particular interest. Such ligands coordinate to transition metal atoms via a lone pair or π orbital, and act as weak Lewis bases (electron donors). Many of these molecules, such as sulfoxides, formamides, pyridine, nitriles, water, alcohols, ethers and ketones are important coordinating solvents and ligands in homogeneous catalysis reactions. The considerable amount of spectroscopic and structural information available on these weak donor complexes is particularly relevant to surface science. A summary of the data available is included in a recent review by Davies and Hartley [1].

As part of a study of weak donor complexes on a platinum (111) surface, we have examined the correlation between the chemistry of dimethyl sulfoxide, $(CH_3)_2S=O$ or DMSO in the adsorbed states, and the known solid state chemistry of the compound $PtCl_2(DMSO)_2$. DMSO is an unusual molecule in that it can be ambidentate, exhibiting both sulfur (S-bonding) and oxygen (O-bonding) coordination to transition metals. A review article of DMSO coordination compounds by Davies [2] contains most of the known structural and spectroscopic information about these complexes. Several relevant ob-

0039-6028/83/0000-0000/$03.00

servations can be made about DMSO complexes. First, the vibrational stretching frequency of the S = O bond, $\nu(S=O)$ is known to exhibit a red or blue shift from the gas phase frequency of 1055 cm^{-1}, depending on the mode of bonding. For S-bonding, an increase in $\nu(S=O)$ to ~ 1150 cm^{-1} is found in Pt, Pd and Ru complexes. For O-bonded complexes, a decrease in the $\nu(S=O)$ frequency to ~ 950 cm^{-1} is found [2].

In addition to the infrared and X-ray crystallographic evidence for O- and S-bonding, Su and Faller [3] measured XPS data of a large number of transition metal sulfoxide complexes and found that the $O(1s)-S(2p_{3/2})$ splitting was related to the mode of bonding. They observed a decrease in the value of $O(1s)-S(2p)_{3/2})$ relative to the gas phase for S-bonded complexes and an increase relative to the gas phase for O-bonded. These results reflect the change in the charge on the sulfur or oxygen atom due to bonding. In some complexes, for example, $[Pd(DMSO)_4][(BF_4)]_2$, two of the molecules are S-bonded and two O-bonded! [3].

The purpose of the study was to compare spectroscopic results for the multilayer and monolayer states of DMSO on Pt(111) with the compound $PtCl_2(DMSO)_2$ which is known to be S-bonded. In particular we have measured the $O(1s)-S(2p_{3/2})$ splitting with XPS and compare the EELS vibrational frequencies with the infrared absorption in the complex. We demonstrate that the bonding of DMSO to Pt(111) does indeed occur via the sulfur atom, and that there is a coverage dependent heat of adsorption in the monolayer. In particular this study points out the remarkable similarity between the bonding to a metallic surface and in Pt(II) complexes. Further work on the other weak-donor ligands will be published separately.

2. Experimental

The experiments were performed in two separate UHV apparatuses. Photoemission experiments (UPS, XPS), were conducted in a Vacuum Generators ESCALAB 5 instrument with a base pressure of $< 1 \times 10^{-10}$ Torr. EELS data were taken with a single pass hemispherical analyser in a separate chamber. Each Pt(111) crystal was mounted on a liquid nitrogen cooled sample holder capable of cycling between 90 and 1400 K. Cleaning before each run was accomplished by annealing at 1120 K in oxygen followed by a flash to 1400 K to remove oxide. A crystal was judged to be clean when reproducible molecular and atomic recombination desorption peaks of oxygen were obtained. Auger spectroscopic checks were also made to ensure the absence of calcium.

Dimethyl sulfoxide (DMSO) of analytical quality was outgassed in small glass bottles attached to the gas inlet system and dosed on to the surface via a multichannel array doser. Due to the low room temperature vapour pressure (~ 1 Torr) care had to be exercised in preparing the manifold vacuum to ensure a clean dose. In all cases a multilayer was deposited on the surface near 80–100 K and the crystal temperature was raised stepwise to observe the monolayer phase and finally desorption.

XPS data were taken with Al Kα radiation (1486.6 eV) at 150 W power and 4 mm slits with a pass energy of 30 eV. UPS data were taken with both HeI (21.2) eV) and HeII (40.8 eV) radiation. All data were collected on a Tracor-Northern 1710 MCA and point-plotted on an X–Y chart recorder. The EELS results were obtained with 7–10 meV resolution and an elastic count rate of 1×10^5 Hz was normally used. Thermal desorption spectra were also taken in the EELS apparatus with a selected-area mass probe (differentially pumped).

The complex $PtCl_2(DMSO)_2$ was prepared by dissolving $PtCl_2$ in warm DMSO and then precipitating the complex by addition of water, as white crystals. These were dried in vacuo and verified as $PtCl_2(DMSO)_2$ by infrared spectroscopy. For XPS experiments the powder was dispersed in methylene chloride to form a thin film on a stainless steel sample holder. In these XPS experiments the critical parameter was the O(1s)–S($2p_{3/2}$) binding energy difference, thus eliminating the uncertainty due to charging on the solid complex relative to the adsorbed monolayer on Pt(111).

3. Results and discussion

3.1. Temperature programmed desorption (TPD)

Adsorption of dimethyl sulfoxide on Pt(111) at 100 K and temperature programmed desorption result in two main desorption states, as shown in fig. 1. The main peak near 210 K is the multilayer, which was variable in intensity, depending on the dose. The second peak near 385 K is identified as the monolayer, since it saturated in intensity first as the exposure was increased. In a previous paper we have shown that multilayer temperatures follow a simple function of the boiling point of the particular organic molecule [4]. A high value of 210 K here reflects the high boiling point (462 K) of DMSO. Acetone, which can be looked upon as the carbon analogue of DMSO boils at 329 K, and has a correspondingly lower multilayer temperature of ~ 145 K [5].

The monolayer temperature (385 K) for DMSO/Pt(111) reflects a high heat of adsorption (~ 20–22 kcal $mole^{-1}$) based on a simple first-order desorption process. We have previously determined for alcohols and ethers that the contribution to adsorption heat from an oxygen lone pair type orbital is ~ 10 kcal $mole^{-1}$, with additional small contributions from Van der Waals bonding of the hydrocarbon chains to the Pt surface [4]. It is interesting to compare data for acetone on Pt(111) with DMSO/Pt(111). Acetone bonds to Pt(111) at high coverages in an end-on configuration via an oxygen 2p-like lone pair

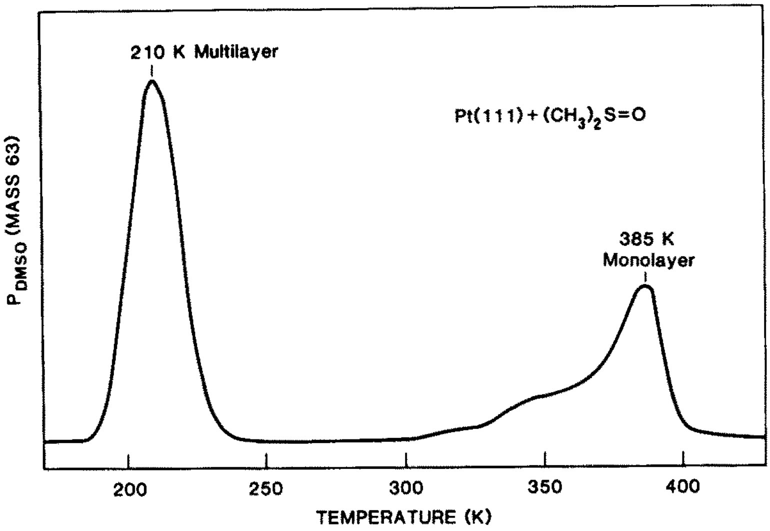


Fig. 1. Temperature programmed desorption of dimethyl sulfoxide adsorbed on Pt(111) at 90 K. Approximately 2–3 layers were adsorbed. The heating rate was 5 K s^{-1}.

orbital [5]. The acetone monolayer desorbs near 210 K, which is consistent with a contribution of 10 kcal/mole from the oxygen lone pair heat plus approximately 1.3 kcal/mole of Van der Waals bonding between each of the methyl groups and the Pt surface [4]. For DMSO however, an adsorption heat of ~ 20 kcal/mole is far too large to be rationalized on the basis of an oxygen-bonded species, since the Van der Waals and lone pair heat contributions would be expected to be similar to acetone. In short, the monolayer desorption temperature of fig. 1 is much larger than acetone and implies a different form of bonding than the oxygen-bonded end-on configuration of acetone/Pt(111) [5].

3.2. XPS evidence for S-bonding

In an earlier study on bonding in metal–sulfoxide complexes, Su and Faller [3] examined and compared XPS and infrared data of some twenty-six complexes. Based on the XPS data, they claimed O- or S-bonded DMSO could be distinguished on the basis of the value of O(1s)–S($2p_{3/2}$) binding energy. This parameter was independent of charging and allowed a comparison of the complex with the spectrum of DMSO itself, which was in the form of a condensed film on a metal substrate. Su and Faller concluded that for a sulfur-bonded complex the value of O(1s)–S($2p_{3/2}$) was ~ 365.0 eV, while for an oxygen-bonded complex a value of ~ 365.8 eV was obtained. DMSO itself

Table 1
X-ray photoelectron spectroscopic results for dimethyl sulfoxide adsorbed on Pt(111) and the complex $PtCl_2(DMSO)_2$

Compound	Present results $O(1s)-S(2p_{3/2})$ (eV)	Su and Faller [3] $O(1s)-S(2p_{3/2})$ (eV)	Shift relative to free DMSO (eV)
Multilayer DMSO	364.8 ± 0.05	365.3	0
$PtCl_2(DMSO)_2$	364.4 ± 0.05	364.9	−0.4 (S-bonded)
Monolayer DMSO	364.4 ± 0.05	–	−0.4 (S-bonded)

had a value of 365.3 eV. Changes in this parameter are related directly to the charge on the oxygen or the sulfur atom in the complexes relative to the free DMSO molecule [2]. For a S-bonded species the sulfur atoms becomes more positively charged, increasing in binding energy and lowering the value of

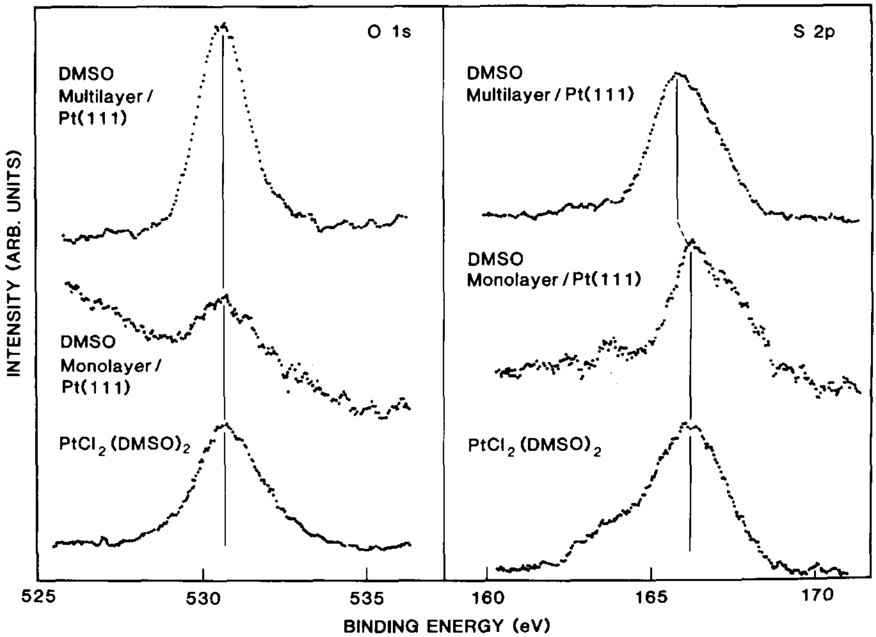


Fig. 2. O(1s) and S(2p) peaks for adsorbed DMSO (multilayer and monolayer) and the complex $PtCl_2(DMSO)_2$. All O(1s) peaks have been aligned with the DMSO monolayer to correct for relaxation in the multilayer case and charging on the solid complex. The $S(2p_{3/2})$ position was estimated manually without deconvolution. The slight shoulder near 163 eV in the $PtCl_2(DMSO)_2$ spectrum is due to a sulfur impurity.

O(1s)–S($2p_{3/2}$). When oxygen is coordinated to the metal, the O(1s) binding energy increased, increasing the value of O(1s)–S($2p_{3/2}$).

On the basis of these data, we repeated the measurements of Su and Faller [3] on a condensed DMSO film (multilayer) and the complex $PtCl_2(DMSO)_2$, to eliminate any instrumental energy scale linearity differences, and took new data for monolayer DMSO/Pt(111). The results are shown tabulated in table 1 and in fig. 2. The results show a value of 364.8 ± 0.05 eV for O(1s)–S($2p_{3/2}$) in the condensed phase, and a smaller value of 364.4 ± 0.05 eV for both $PtCl_2(DMSO)_2$ and a saturated monolayer on Pt(111). The decrease of 0.4 eV below the condensed phase is identical to the results of Su and Faller and we conclude that the DMSO monolayer is sulfur bonded to platinum (111).

It is interesting, but not surprising to note a discrepancy in the linearity of the two energy scales of the two spectrometers. Our value for DMSO of 364.8 ± 0.05 eV is 0.5 eV lower than Su and Faller's (table 1). The decrease in the value of O(1s)–S($2p_{3/2}$) of 0.4 eV between the multilayer and the Pt complex is identical, however, and it is this value which determines the type of bonding. In determining the energy scales of fig. 2 we have aligned the O(1s) values for the $PtCl_2(DMSO)_2$ compound and the DMSO multilayer with the absolute O(1s) value for the monolayer. We have determined, by measuring the relaxation shift of C, S and O core levels between the multilayer and monolayer, that the S(2p) level *increased* in binding energy relative to the other levels by 0.4 eV. This is presumably related directly to the increasing positive charge on the S atom caused by bonding to platinum [2].

3.3. Vibrational spectroscopy: EELS and IR data

Infrared data on DMSO complexes show clearly that the type of coordination may be determined by the value of the $\nu(S=O)$ stretching frequency. In free DMSO, a value of 1055 cm^{-1} is found for $\nu(S=O)$ and this can either increase or decrease depending on S- or O-bonding. For S-bonding the S = O bond order increases and $\nu(S=O)$ is found near 1150 cm^{-1}. For O-bonded complexes a red-shift to ~ 950–1000 cm^{-1} is found for $\nu(S=O)$.

The EELS data for multilayer and monolayer DMSO are shown in fig. 3 and a summary of the frequencies with assignments is shown in table 2 together with IR data taken on liquid DMSO and $PtCl_2(DMSO)_2$. The multilayer spectrum of fig. 3 shows the major bands of DMSO, including the $\nu(C-S)$ peak at 690 cm^{-1}, $\nu(C-H)$ modes at 3020 cm^{-1} and methyl rocking and deformation regions near 1040 and 1430 cm^{-1}. It is clear from the IR of the liquid film in table 2 that the 1040 cm^{-1} mode in the EELS spectrum is composed of overlapping bands of $\nu(S=O)$ expected near 1055 cm^{-1} and methyl rocking near 930–950 cm^{-1}. In the monolayer we clearly see $\nu(S=O)$ split away from the methyl rocking modes and increase in frequency to 1110 cm^{-1}. In addition, we see a new band at 430 cm^{-1} assigned as the $\nu(Pt-S)$

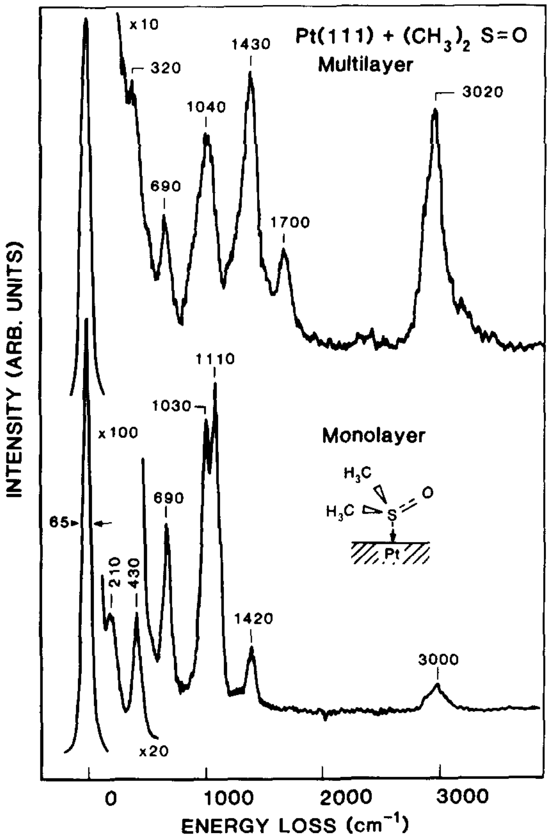


Fig. 3. EELS vibrational spectra of the multilayer and monolayer states of dimethyl sulfoxide on Pt(111). The temperatures were 90 K (multilayer) and 300 K (monolayer). The beam energy was 4 eV. The band near 1700 cm^{-1} in the DMSO multilayer was not reproducible and has not been assigned in the text.

stretch and a weak torsion mode at 210 cm^{-1}. All of the other ν(C–S) and methyl modes are essentially unchanged in frequency. We therefore conclude that the blue-shift in $\nu(S=O)$ to 1110 cm^{-1} from ~ 1040 cm^{-1} is conclusive evidence for sulfur bonding and is comparable with the value of ~ 1140 cm^{-1} for the S-bonded complex $PtCl_2(DMSO)_2$.

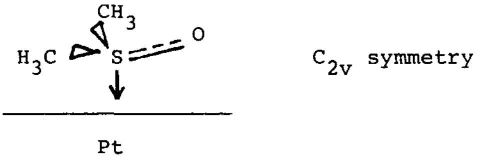
An S-bonded DMSO species on Pt(111) would have C_{2v} symmetry, with all of the S–C and $S=O$ bonds pointing away from the surface in an inverted

Table 2
Vibrational spectroscopy data for free DMSO, adsorbed DMSO/Pt(111) and $PtCl_2(DMSO)_2$

Vibrational mode	EELS frequency (cm^{-1})		Infrared frequency (cm^{-1})	
	DMSO [a] condensed on Pt(111)	DMSO [b] monolayer on Pt(111)	DMSO [c] condensed	$PtCl_2(DMSO)_2$ [d] solid
ν(C–H)	3020	3000	3000 2920	Not measured
$\delta_d(CH_3)$	1430	1420	1436 1410 1310	1410 1420
ν(S = O)	1040	1110	1055	1134, 1157
$\rho_r(CH_3)$		1030	950 930	1020, 980, 920, 940
ν(C–S)	690	690	690	690, 740
ν(Pt–S)	–	430	–	Unknown
Torsion	320	210	–	–

[a] Multilayer film on Pt(111) at 100 K.
[b] Monolayer on Pt(111).
[c] Liquid film.
[d] Nujol Mull.
ν = stretching mode, δ_d = deformation, ρ_r = rocking.

pyramidal geometry as shown below,



In the gas phase, DMSO is pyramidal and is known to undergo very little distortion upon coordination. With an adsorption geometry shown above, each of the vibrational modes ν(C–H), $\delta_d(CH_3)$, ν(S = O), $\rho_r(CH_3)$, ν(C–S) and ν(Pt–S) would have components of the dipole moment perpendicular to the metal surface and be EELS-active, as is observed.

Additional information about the adsorbed S-bonded state was obtained from annealing experiments. In fig. 4 we show the 600–1500 cm^{-1} region in more detail as the monolayer is progressively removed. This was accomplished by slowly annealing the crystal in increasing temperature increments in the range 330–360 K where the desorption rates were substantial. An unusual sequence of spectra was obtained in which ν(S = O) progressively shifts from its saturation monolayer value of ~ 1110 cm^{-1} to a low coverage value near

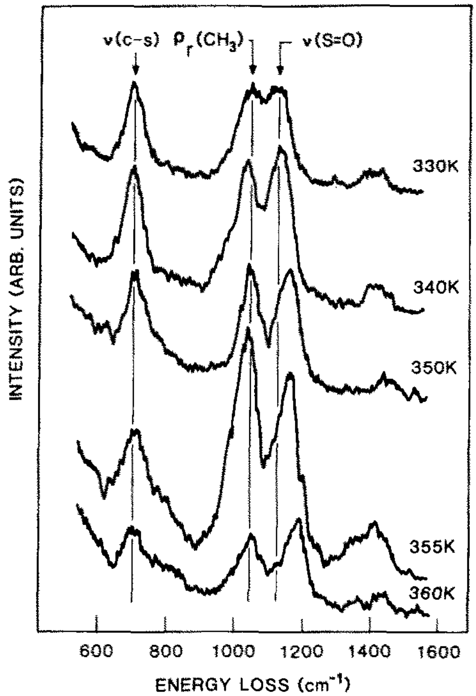


Fig. 4. Coverage dependence of the $\nu(S=O)$ and $\rho_r(CH_3)$ region. The monolayer was heated sequentially to the temperatures indicated to reduce the coverage. Note the increasing splitting and blue-shift of $\nu(S=O)$ as the coverage decreases, from 1110 cm^{-1} at 330 K to 1160 cm^{-1} at 360 K.

1160 cm^{-1}. The shift can be clearly seen in fig. 4 where $\nu(S=O)$ moves away to higher frequency from the CH_3 rocking mode as the coverage is reduced. The other CH_3 modes and $\nu(C-S)$ remained unchanged during this process.

The increase in the $\nu(S=O)$ frequency is directly related to the charge on the sulfur atom and the $S=O$ bond order. In compounds such as $[(CH_3)_3SO]^+I^-$, the $\nu(S=O)$ frequency is as high as 1240 cm^{-1} [6]. We interpret the increase in the $\nu(S=O)$ frequency with decreasing coverage as an increase in the heat of adsorption as the DMSO molecules become more dispersed on the Pt surface. As a result of this frequency shift we could expect the Pt–S bond to strengthen somewhat and the positive charge on the S atom to increase. No lower coverage data were taken with XPS or UPS, however, owing to poor signal-to-noise. Finally, the strong intensity of the methyl rocking mode near 1030 cm^{-1} in the monolayer spectrum of figs. 3 and 4 deserves comment. It is well known that the $\nu(S=O)$ stretching mode is considerably coupled with the methyl rocking mode, in DMSO [2]. A strong band is expected for $\nu(S=O)$ on the basis of a large dipole moment change, but the $\rho_r(CH_3)$ mode near 1030 cm^{-1} must be borrowing intensity by coupling with $\nu(S=O)$. An isolated methyl rocking mode would not be expected to be so intense in the infrared.

3.4. UPS data (HeI and HeII)

There is only one known study of DMSO adsorption with UPS: the paper of Lüth et al. [7], in which DMSO, acetone and pyridine were studied on ZnO(1$\bar{1}$00). Lüth et al. found that the two highest lying occupied valence orbitals coalesced into a single band in the adsorbed state, presumably because of a chemisorption induced shift to higher binding energy of the highest occupied orbital.

In fig. 5 we show the results of HeI (21.2 eV) and HeII (40.8) difference spectra of multilayer and monolayer DMSO/Pt(111). In the multilayer, or gas phase, two intense orbitals are observed at low binding energy, labelled A and B. In the monolayer, A and B appear to coalesce into a single band C (fig. 5) which is close to the original position of B. It is difficult to line up the orbitals to correct for relaxation shifts because the deeper-lying orbitals are diffuse and have been known to undergo different degrees of relaxation relative to each

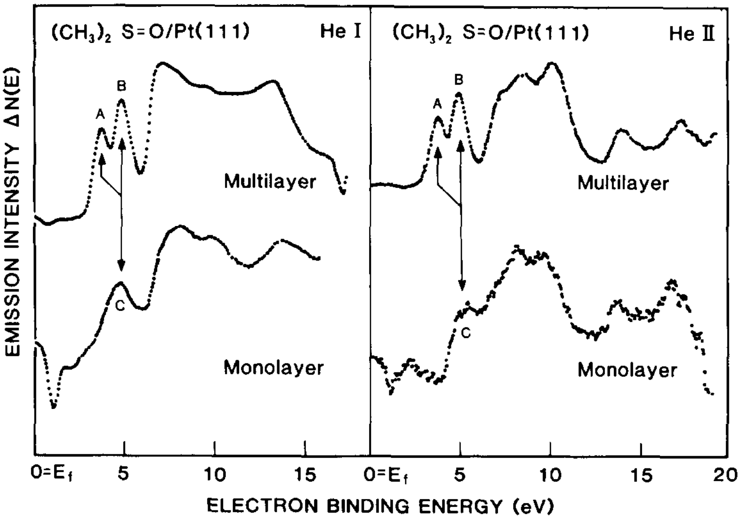


Fig. 5. UPS (HeI and HeII) spectra of the adsorbed multilayer and monolayer dimethyl sulfoxide on Pt(111). Note the coalescence of the two orbitals A and B in the monolayer state.

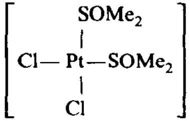
other [7]. We tentatively suggest that orbital A has undergone a chemisorption-induced shift to higher binding energy and has merged with B to form a single peak C, in the monolayer. The question remains, what are A and B?

Photoelectron spectra for DMSO have been measured but there appears to be disagreement in the literature as to the ordering of the orbitals. Mines et al. [8] measured a gas-phase UPS spectrum similar to our multilayer spectrum of fig. 5. They assigned the orbitals A and B near 9.11 and 10.26 eV in the gas phase as the "sulfur and oxygen lone pairs", respectively. Lüth et al. [7] disagreed with this interpretation and claim that DMSO cannot have a sulfur lone-pair orbital. They claim to have calculated the MO's of DMSO and say that "no high-lying sulfur lone-pair orbital is formed". They label peak A as an oxygen lone pair-like orbital with some contribution from an oxygen π^* orbital. Their analysis was based on placing the two extra electrons from the S atom in the unoccupied π^* orbitals of acetone with subsequent rearrangement to a pyramidal shape from the planar configuration. Obviously the UPS results do not give a conclusive picture of S- or O-bonding. Based on the evidence presented in this paper from EELS and XPS we would like to suggest that the orbital A in fig. 5 does have significant sulfur lone-pair character. The strong charge transfer from sulfur to the surface would shift this orbital significantly to higher binding energy, and give the single peak C in fig. 5. It would be useful for a conclusive MO calculation to be done on DMSO to resolve the discrepancies in the literature.

3.5. A model for DMSO adsorption on Pt(111)

On the basis of the previous results, we propose that the bonding of DMSO to Pt(111) occurs via the sulfur atom, and that the geometry of the adsorbed molecule is similar to the bonding in the complex $PtCl_2(DMSO)_2$. Table 3 summarizes the X-ray crystallographic data for DMSO [9] and the complex [10]. In the complex $PtCl_2(DMSO)_2$ the Pt–S bond length is 2.24 Å. In the coordinated state a slight increase in both $C-\hat{S}-C$ and $O-\hat{S}-C$ bond angles is noted owing to decreased repulsion caused by transfer of charge out of the sulfur "lone-pair" orbital to the metal. Also the $S=O$ bond is slightly shorter in the complex due to a strengthening of the $S=O$ bond caused by increased overlap of oxygen 2p orbitals with the empty d orbitals of sulfur. Based on the geometrical data of table 3 we propose that the adsorbed dimethyl sulfoxide has a similar geometry to the $PtCl_2(DMSO)_2$ complex. For a pyramidal DMSO complex on Pt(111) with the sulfur apex pointing toward the surface, all of the EELS bands observed in fig. 3 would be expected to be dipole-active. The increase of the $\nu(S=O)$ frequency to 1110–1180 cm^{-1} is entirely consistent with an increase in the $S=O$ bond order caused by increased π-bonding. An increase in the sulfur $2p_{3/2}$ binding energy by 0.4 eV is also

Table 3
Structural data for dimethyl sulfoxide and the complex $PtCl_2(DMSO)_2$

State	Bond lengths (Å)			Bond angles (deg)			
	M–S	S–O	S–C	M–$\hat{S}$–C	M–$\hat{S}$–O	O–$\hat{S}$–C	C–$\hat{S}$–C
$(CH_3)_2S=O$ gas[a]	–	1.477	1.810	–	–	106.7	96.4
 $\left[\mathrm{Cl{-}Pt(SOMe_2)(SOMe_2){-}Cl}\right]$[b]	2.24	1.462	1.782	111.5	114.8	108.6	101.4

[a] Ref. [9].
[b] Ref. [10].

consistent with transfer of charge from sulfur to platinum. Our XPS results are supported by X-ray absorption and emission spectroscopy studies of the charge on sulfur and oxygen. For free DMSO, the sulfur atom has 5.30 ± 0.08 valence electrons [2]. In S-bonded Pd(II) DMSO complexes the positive charge on the sulfur atom increases [2] as a result of coordinative charge transfer. In O-bonded complexes, no change is found on the charge of the S atom [2]. We commented previously that the decrease in O(1s)–S($2p_{3/2}$) for S-bonded DMSO relative to free DMSO is caused solely by an increase in the sulfur binding energy in the XPS experiment. This was determined by measuring the relaxation shift for the C and O levels between the multilayer and monolayer DMSO/Pt(111), and applying this shift to the sulfur $2p_{3/2}$ peak in the two states.

Finally the shift of $\nu(S=O)$ from 1110 cm^{-1} at saturation monolayer coverage to 1160 cm^{-1} at low coverage, is consistent with a variation of the S → Pt charge transfer with coverage. One would expect the low coverage frequency (1160 cm^{-1}) to be similar to the single Pt atom case (~ 1150 cm^{-1}). As the coverage increases there must be indirect interactions through the metal surface between adjacent DMSO molecules which reduces the charge transfer to the surface somewhat, resulting in a decrease in $\nu(S=O)$ of ~ 50 cm^{-1}.

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