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Raman Spectra of *N,N*-Dimethylthioacetamide Adsorbed on Silver and Copper Electrode Surfaces

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Surface-enhanced Raman (SER) spectra have been obtained from *N,N*-dimethylthioacetamide (DMTA) adsorbed on Ag and Cu electrode surfaces. Vibrational analysis of the SER spectra of DMTA is made in comparison to the bulk-phase Raman spectrum of DMTA, and the infrared data on Co, Cu, and Hg complexes of DMTA. It is concluded that the DMTA molecule is bonded through its S atom to Ag and Cu surfaces.

Previously we have studied molecular bondings of several isostructural sulfur compounds containing a thiocarbonyl C=S group, namely, thiourea (TU), thioacetamide (TA), *N,N*-dimethylthioformamide (DMTF), thiosemicarbazide (TSC), and thiocarbohydrazide (TCH) on Ag and Cu electrode surfaces.[1–5] We found that in all cases the adsorbate was bonded via its S atom to Ag and Cu surfaces. The predominantly C=S stretching bands for these molecules were shifted to lower frequencies upon adsorption on metal surfaces with amounts comparable to those observed in their organometallic complexes. We believed that there were considerable electronic interactions between the adsorbates and the substrates such that the C=S bond order was reduced, and perhaps some kind of surface complexes was formed. These surface complexes may be the surface analogs of the organometallic complexes of these molecules. In this work we extend our study to *N,N*-dimethylthioacetamide (DMTA), the second simplest tertiary thioamide. The present work is a part of our continuing effort in the understanding of molecular interactions of adsorbates with metal surfaces.[1–8]

Experimental

N,N-Dimethylthioacetamide was synthesized from *N,N*-dimethyl acetamide (Aldrich) and phosphorus pentasulfide (Aldrich), and repeatedly crystallized from hexane.[9] The experimental procedure for the in situ Raman measurements was similar to that described previously.[2,4]

Results and Discussion

Figure 1 shows the surface-enhanced Raman (SER) spectrum of DMTA adsorbed on an Ag electrode at −0.30 V vs. saturated calomel electrode (SCE), whereas Fig.2 shows the SER spectrum of DMTA adsorbed on a Cu electrode at the same potential. The SER spectra were obtained after the electrodes had undergone an oxidation-reduction cycle.

Except for some minor frequency shifts and relative band intensity differences, the general spectral features for the Ag/DMTA and Cu/DMTA systems are similar to each other. This indicates that DMTA adsorbs in a similar fashion on Ag and Cu surfaces.

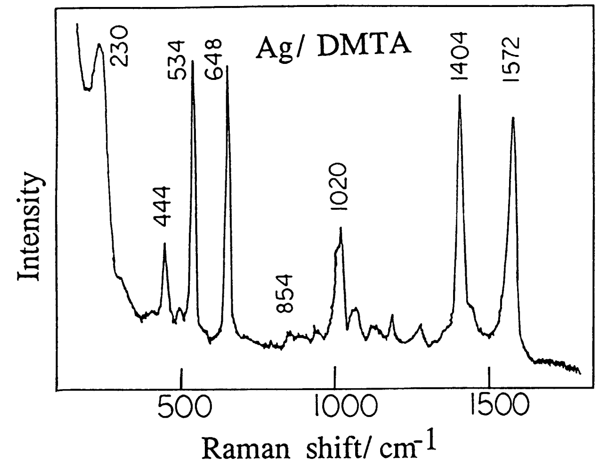


Fig. 1. Surface-enhanced Raman spectrum of DMTA adsorbed on Ag electrode at −0.3 V vs. SCE. The electrolyte was 1.4×10^{-3} M DMTA+0.1 M KCl (acidified with HCl, pH 2.5) (1 M=1 mol dm^{-3}). The electrode was anodized at 0.2 V before the spectrum was taken. The excitation wavelength was Kr$^+$ 647.1 nm.

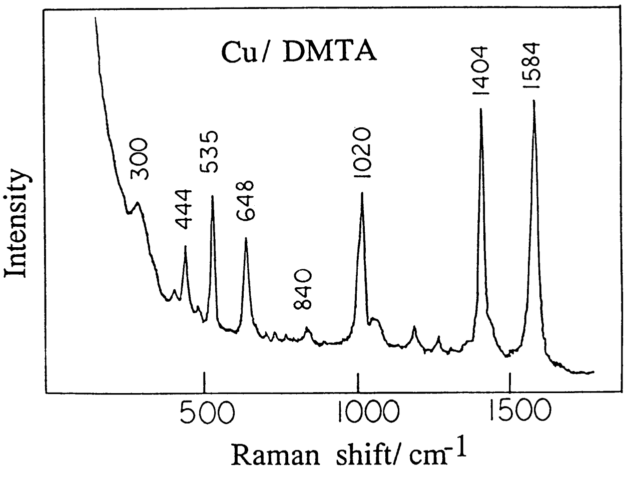


Fig. 2. Surface-enhanced Raman spectrum of DMTA adsorbed on Cu electrode at −0.3 V vs. SCE. The electrolyte was 1×10^{-4} M DMTA +0.1 M KCl (acidified with HCl, pH 2.5). The electrode was anodized at 0.1 V before the spectrum was taken. The excitation wavelength was Kr$^+$ 647.1 nm.

Table 1. Vibrational Frequencies (in cm^{-1}) and Potential Energy Distribution for *N,N*-Dimethylthioacetamide

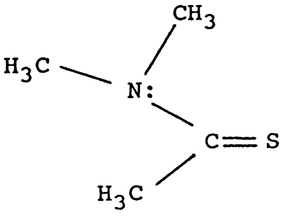
Calcd	DMTA		SERS		Complexes[c]			Assignments
UBF[a]	IR[b]	Raman	Ag	Cu	$\mathrm{CoL_2Cl_2}$	CuLCl	$\mathrm{HgL_4Cl_2}$	(PED %)[d]
			230					$\nu(\mathrm{AgS})$*
				300				$\nu(\mathrm{CuS})$*
300	300 sh	302 b	—	—	290 w	306 sh	284 sh	$\delta(\mathrm{C'NC'})(79)+\delta(\mathrm{CCS})(13)$
446	444 m	444 m	444	444	448 m	435 m	451 m	$\delta(\mathrm{CCS})(59)+\delta(\mathrm{C'NC'})(12)+\nu(\mathrm{CS})(10)$
495	495 m	493 m	495	495	498 m	485 w	498 w	$\delta(\mathrm{NCS})(40)+(\mathrm{CNC'})(21)+a(\mathrm{C'N})(16)$
—	540 vw	537 w	534	535	542 vw	540 vw	535 vw	$\pi(\mathrm{C{-}C})(\text{-})$
661	656 s	656 vs	648	648	655 vs	635 s	640 s	$\nu_s(\mathrm{C'N})(44)+\nu(\mathrm{CS})(25)+\nu(\mathrm{CC})(17)$
867	870 s	864 w	854	840	862 s	845 m	845 m	$\nu_s(\mathrm{C'N})(37)+\nu(\mathrm{CS})(24)+r(\mathrm{C{-}CH_3})(15)$
998	1020 vs	1014 w	1020	1020	1030 vs	1025 s	1030 vs	$r(\mathrm{C{-}CH_3})(38)+r(\mathrm{N{-}CH_3})(22)+\nu(\mathrm{CN})(11)$
1004	1060 w	—	1060	1064	1060 s	1085 sh	1050 w	$\nu_a(\mathrm{C'N})(39)+r(\mathrm{N{-}CH_3})(38)$
1133	1130 s	1125 w	1130	—	1130 w	1115 s	1130 s	$\nu_a(\mathrm{C'N})(26)+r(\mathrm{N{-}CH_3})(26)+\nu(\mathrm{CC})(24)$
1154	1185 s	—	1185	1185	1192 vs	1190 m	1195 m	$r(\mathrm{N{-}CH_3})(36)+\delta_s(\mathrm{N{-}CH_3})(14)+\delta_s(\mathrm{N{-}CH_3})(12)$
1279	1284 vs	1275 w	1279	1262	1285 vs	1262 vs	1270 vs	$\nu(\mathrm{CC'})(28)+\nu(\mathrm{CS})(17)+\delta(\mathrm{NCS})(15)$
1373	1370 s	—	1370	1370	1385 vs	1385 s	1370 s	$\delta_s(\mathrm{C{-}CH_3})(91)$
1405	—	1391 w	1404	1404	—	—	—	$\delta_s(\mathrm{N{-}CH_3})(44)+\nu(\mathrm{CN})(18)+\delta_s(\mathrm{C{-}CH_3})(15)$
1422	1430 s	1418 w	—	—	1430 s	1430 vs	1410 s	$\delta_s(\mathrm{N{-}CH_3})(96)$
1475	1470 s	—	—	—	1465 s	1470 vs	1470 s	$\delta_a(\mathrm{N{-}CH_3})(80)+r(\mathrm{N{-}CH_3})(19)$
1536	1540 vs	1540 b	1572	1584	1580 vs	1590 vs	1610 vs	$\nu(\mathrm{CN})(46)+\delta_a(\mathrm{N{-}CH_3})(16)+r(\mathrm{N{-}CH_3})(15)$

a), b), c) Ref. 10; d) Ref. 10 except *; UBF=Urey–Bradley force; L=DMTA; PED=potential energy distribution; ν=stretch; δ=deformation; r=rock; π=out-of-plane bend; s=symmetric; a=asymmetric; v=very; s=strong; m=medium; w=weak; b=broad; sh=shoulder; C's are used to denote methyl carbons next to the N atom.

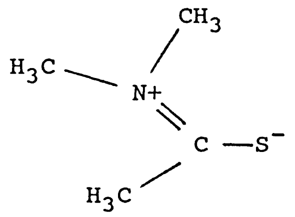
The IR, Raman, and SER frequencies for DMTA, and the vibrational band assignments for DMTA and its Co, Cu, and Hg complexes are given in Table 1. The potential energy distributions (PED's) and the assignments of the bands are also given. The PED calculation was performed by Ray and Sathyanarayana using C_s point group and a Urey-Bradley force field.[10] The present assignments for the SER spectra of the DMTA adsorbed on Ag and Cu surfaces are made by comparing the SER spectra with the solid phase Raman spectrum and with the IR vibrational frequencies of its metallic complexes.[10]

Metal complexes of DMTA were not so well studied when compared to those of TU, TA, DMTF, TSC, and TCH.[11] However, useful information still can be derived from the few complexes of DMTA that had been studied. Madan and Mueller[12] reported the preparation of several Co(II) complexes of DMTA, $\mathrm{Co(DMTA)_2X_2}$ [where X=$\mathrm{NO_3}$, Cl, Br or I], and $\mathrm{Co(DMTA)_4\ (ClO_4)_2}$. From the electronic absorption spectra and magnetic measurements of these complexes, they concluded that the DMTA ligand was coordinated to the central Co(II) atom through the S atom. Ray and Sathyanarayana[10] studied the IR spectra of the complexes of DMTA with the chlorides of Co(II), Cu(I), and Hg(II). They found that the C–N stretching frequency occurring at 1540 cm^{-1} in DMTA was increased to 1580—1610 cm^{-1} in the complexes. Additionally, two C=S bands at 870 and 656 cm^{-1} were decreased to 862—845 and 652— 635 cm^{-1}, respectively, in metal complexes. They concluded that the bonding to the metal ions was through the S atom in these complexes. Aarts et al.[13] synthesized DMTA complexes of Au(I), Au(DMTA)X (where X=Cl, Br or I). Again, their IR results indicated that the coordination of DMTA to Au(I) was through the S atom. The ν(CN) frequency of the free molecule at 1535 cm^{-1} was shifted to higher frequencies 1557 to 1572 cm^{-1} whereas the ν(CS) frequency at 657 cm^{-1} was shifted to lower frequencies 650—648 cm^{-1}. The observed metal-sulfur stretching ν(AuS) frequency was at 300 cm^{-1}.

The experimental observations are not difficult to rationalize in view of the fact that the electronic structure of DMTA can be represented by the resonance hybrid structures **I** and **II**, with a greater contribution comes from the polar structure **II**.[14] When the bonding is through the S donor site, the ν(CS) will be shifted to a lower frequency whereas ν(CN) to a higher frequency.



I



II

In the SER spectra of sulfur compounds with a thiocarbonyl group, the C–N and C=S stretching modes were most susceptible to frequency shifts upon adsorption on metal surfaces[1–5] for the same reason we have just mentioned. Thus, the C–N and C=S stretching modes will be monitored for shifts when DMTA is adsorbed on Ag and Cu electrode surfaces. In particu-

Table 2. Metal–Sulfur Vibration of Adsorbate (A) on Ag and Cu Surfaces

A	ν(AgS)/cm^{-1}	ν(CuS)/cm^{-1}
Thiourea	221	287
Thioacetamide	190	280
N,N-Dimethylthioformamide	230	288
Thiosemicarbazide	239	294
Thiocarbohydrazide	221	287
N,N-Dimethylthioacetamide	230	300

lar, the 1540 cm^{-1} Raman band with 46% PED ν(CN) is shifted to 1572 (+32) and 1584 (+44) cm^{-1}, respectively (The values in parentheses refer to the shifts from the corresponding Raman bands for DMTA). There are two bands that have a relative large contribution (about 25% PED) of the C=S stretching, one is at 656 and the other at 864 cm^{-1}. The band at 656 cm^{-1} is shifted to 648 (−8) on both Ag and Cu surfaces, whereas the 864 cm^{-1} band is shifted to 854 (−10) and 840 (−24) cm^{-1} on Ag and Cu surfaces, respectively. From this observation, we can conclude that the DMTA molecule is bonded through its S atom to the Ag and Cu electrode as was observed in previous cases.[1—5]

We assign the low-frequency vibrational modes at 230 cm^{-1} in the Ag/DMTA system and at 300 cm^{-1} in the Cu/DMTA system to the ν(AgS) and ν(CuS) modes, respectively. The intensity of these modes is increased as the applied potential becomes more cathodic, a behavior which is similar to those observed for other systems.[3,4] The frequency values of the metal to sulfur vibrations compare well with the same modes for TU, TA, DMTF, TSC, and TCH on Ag and Cu surfaces (see Table 2).

In conclusion, we have studied the adsorption of DMTA on Ag and Cu electrode surfaces. DMTA, like the other C=S compounds previously studied,[1—5] is also S-bonded to Ag and Cu surfaces.

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