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Infrared Spectra of Urea and Thiourea Thin Films on the Metal Surface

Wataru SUËTAKA

Research Institute for Iron, Steel and Other Metals, Tohoku University, Katahira-cho Sendai

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The infrared spectra of thin urea and thiourea films, several hundred Angstroms thick, on a steel plate were obtained using an optical system in which the beam polarized parallel to the plane of incidence was incident at 70° upon a steel plate covered with film. The spectra obtained showed that the c-axis of the urea crystal was parallel to the metal surface. However, the abnormal behavior of the NH_2 bending and the NH_2 twisting bands suggests that the urea molecule in the film was deformed from the planar structure. The intensities of the infrared bands of thiourea belonging to the B_1 species decreased in the film, and it may be concluded that the c-axis of the crystal is nearly parallel to the metal surface. The considerable rise in frequency of the NH_2 wagging band observed in the thin thiourea film may arise from the deformation of the crystal. As for the thiourea-collodion film, thiourea A_1 bands appeared to be very weak, corresponding to the C=S bond orientation parallel to the metal surface. The dichroism of the thiourea bands in the 3 μ region obtained about the thiourea and thiourea-collodion thin films is in agreement with the Badger-Waldron assignment of the absorption bands.

Infrared spectroscopy of extremely thin film on bulk metal is considered to be a promising method to obtain information about the adsorption on a specified face of a metal single crystal, the catalytic action of bulk metal containing a known number and species of lattice defects, chemical bonding between an adhesive molecule and a metal surface, and the crystal structure of thin film, which may be different from that in the bulk state because of interaction with the substrate. Conventional reflectance measurements, however, can not be an effective method for investigating extremely thin films because of their low sensitivity. The sensitivity of the spectrum can, however, be remarkably increased by the use of a beam polarized parallel to the plane of incidence at high incident angles.[1-3] In the present work, the infrared spectra of thin urea and thiourea films, several hundred Angstroms in thickness, on steel plate were investigated using a beam polarized parallel to the plane of incidence; interesting intensity changes in the spectrum were thus obtained.

Experimental

The reflectance spectra of thin films were obtained by means of a JASCO IR-G infrared spectrophotometer, with an optical system attached, as will be described below. The arrangement of the optical system is shown in Fig. 1. The maximum sensitivity angle of incidence changes with the optical constants of the film and that of the metal, but the incident angle of the

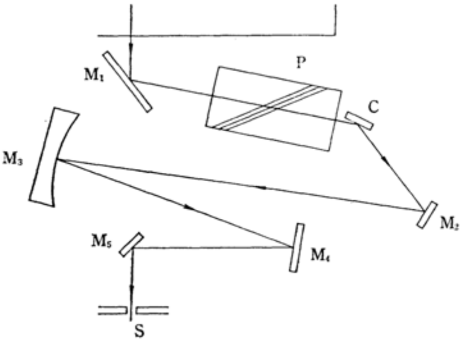

Fig. 1. Arrangement of the optical system for the measurement of reflectance spectrum.
P: Polarizer C: Sample
S: Entrance slit M_3: Spherical mirror
M_1, M_2, M_4, M_5: Plane mirror

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[1] W. Suëtaka, *Sci. Rept. Res. Inst., Tohoku Univ., Ser. A*, **18**, Suppl., 129 (1966).
[2] R. G. Greenler, *J. Chem. Phys.*, **44**, 310 (1966).
[3] S. A. Francis and A. H. Ellison, *J. Opt. Soc. Am.*, **49**, 131 (1959).

system is fixed at 70° for simplicity of construction. The maximum sensitivity angle varies over the range of 60—85° depending on the optical constants.[1] The used angle is not far from the maximum sensitivity angle in any case, and the sensitivity decrease caused by the use of the fixed angle is relatively small.

The urea, thiourea, and ethanol used in the experiments were of a guaranteed grade; the urea and thiourea were further purified by recrystallization in ethanol.

The film was prepared by dropping a dilute ethanolic solution on a steel surface and evaporating the solvent. The steel plates were polished with a polishing cloth and cleaned by rinsing for a short time in a hot chromate-sulfuric acid solution. The plates were finally cleaned with distilled water. Just before the preparation of the thiourea film, the steel surface was rubbed with clean filter paper to create many active sites for crystal nucleation and to facilitate film formation. Since no apparatus for the measurement of the film thickness was available, the thickness of the film was roughly estimated by assuming that the solute compound remained on the metal surface without any loss by evaporation, thus forming an equal-thickness film. The thiourea-collodion film was not uniform, but consisted of fine crystals dispersed over the metal surface.

Results and Discussion

Urea. The reflectance spectrum of the thin urea film is shown in Fig. 2. The spectrum of bulk-crystal urea is also shown in this figure for purposes of comparison. The thin film spectrum has a close resemblance to Yamaguchi's results concerning orientated urea film on a KBr window obtained with infrared light polarized perpendicular to the c-axis of the crystal,[4] showing that in the thin film the c-axis is parallel to the metal surface. However, important differences between our spectrum and Yamaguchi's can be seen with regard to the bands appearing at 1590 and 550 cm^{-1} in the thin film or at 1592 and 500 cm^{-1} in the bulk state.

The band at 1590 cm^{-1} is assigned to the NH_2 bending vibration of A_1 species[4,5] and should disappear in the spectrum of thin film if the urea molecule has C_{2v} symmetry, the crystals are of the $V^3{}_d(P\bar{4}2_1m)$ space group, and the c-axis of the crystal is parallel to the metal surface, because on the metal surface the electric vector of the radiation is predominantly perpendicular to the surface[2,3] and the very strong A_1 band at 1682 cm^{-1} in the bulk state disappears in the thin film spectrum. The broad band at 550 cm^{-1} is assigned to the NH_2 twisting vibration of B_2 (out-of-plane) species;[4,5] the intensity of this band is expected to be stronger than that of the band at 583 cm^{-1} (B_1), because, in the spectrum of the bulk crystal, the former is stronger than the latter and the essential change in the ratio of intensity of these two bands should not take place as long as the radiation polarized perpendicular to the c-axis is used. This was the case in Yamaguchi's paper. However, in the spectrum obtained in the present work, the band at 550 cm^{-1} is much weaker in intensity than that at 583 cm^{-1}. These facts do not agree with the crystal structure of urea and may be explained by a hypothesis that, in the thin film on the steel surface, urea molecules are deformed from a planar C_{2v} structure, or NH_2 groups would not be lying on the plane containing C, O, and N atoms, because abnormal behavior is observed for the bands assigned to the vibrations of the NH_2 group.

The thin film of urea was not stable, and while, it

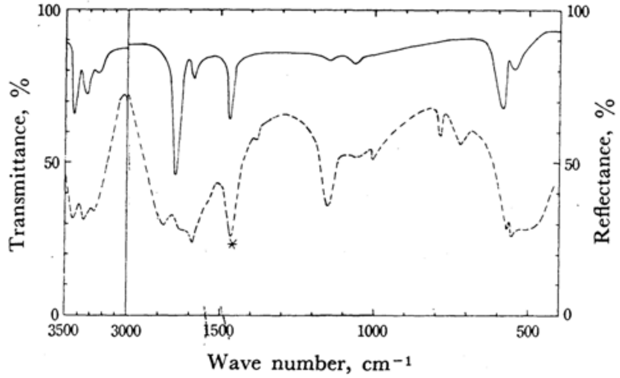

Fig. 2. Infrared spectrum of urea thin film.
——: Reflectance spectrum of thin film on steel. (film thickness: 700Å)
----: Transmittance spectrum of urea crystal (Nujol mull)
* Overlapping with a Nujol band

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[4] A. Yamaguchi, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **78**, 1467 (1957).

[5] J. E. Stewart, *J. Chem. Phys.*, **26**, 248 (1957).

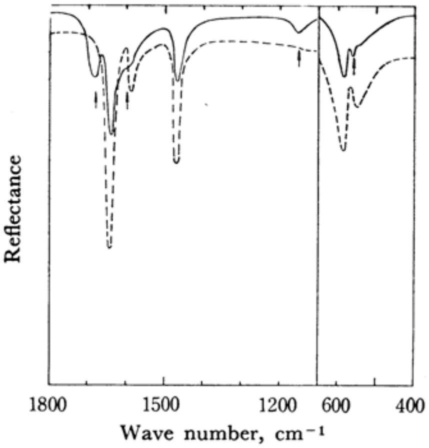

Fig. 3. Change in the infrared spectrum of urea thin film.
----: Fresh film
——: 18 hr. after preparation

changed slowly to islands of fine crystals, the relative intensities of the A_1 bands[*1] increased with the time, as is shown in Fig. 3, where A_1 bands are indicated with arrows. The reflectances are drawn in the same scale but are somewhat displaced vertically in order to avoid overlapping of the curves.

The formation of thin film containing deformed urea molecules may partly result from interaction with the substrate, but the interaction may not sufficiently be strong to maintain the deformed thin film and so the film may tend to have a random orientation.

Thiourea. The spectrum of the thin thiourea film is shown in Fig. 4. The spectrum of bulk-crystal thiourea is also shown in this figure for purposes of comparison. The strong bands at 3256, 3156, 1610, and 1470 cm^{-1} in the bulk spectrum are abnormally weak in the thin film spectrum, as can be seen in this figure.

The assignment of the infrared bands of thiourea based on the assumed C_{2v} structure has been reported by several investigators.[5-7] The bands at 3156 and 1470 cm^{-1} are attributed to B_1-type vibrations in all of these papers. The band at 3256 cm^{-1} is considered to be attributable to the vibration of B_1 species for a reason which will be discussed below. Stewart and Nishikawa *et al.* agree in assigning the band near 1610 cm^{-1} to the NH_2 bending vibrations of both the A_1 and the B_1 species.[5,7] Yamaguchi and her collaborators attributed the band at 1610 cm^{-1} to the vibration of A_1 species, and the band at 1625 cm^{-1} to the vibration of B_1 species.[6] In the present work, only one band, at 1610 cm^{-1}, is observed in the 6 μ region; this band is considered to be the overlapping of the band of the A_1 species and that of B_1.

Thiourea crystallizes in a lattice of symmetry, $V^{16}{}_h$, with four molecules per unit cell on sites of C_s symmetry.[8,9] The infrared anisotropy observed in this work indicates that the c-axis of thiourea crystals in the thin film is nearly parallel to the metal surface, because only the B_1 bands almost disappear in the thin-film spectrum.

Nishikawa and his collaborators indicated that

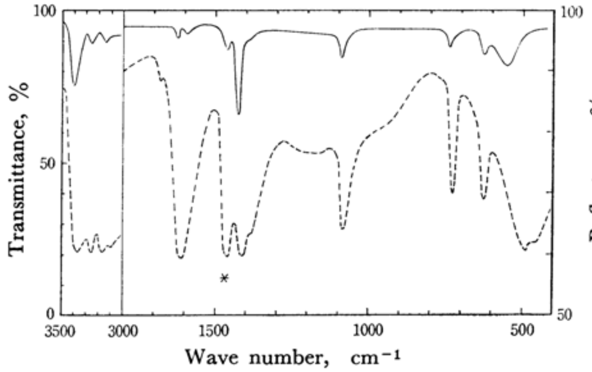

Fig. 4. Infrared spectrum of thiourea thin film.
——: Reflectance spectrum of thiourea thin film on steel (film thickness: 500Å)
----: Transmittance spectrum of thiourea crystal (Nujol mull)
* Overlapping with a Nujol band; contribution to the intensity from Nujol is small.

[*1] Absorption bands due to A_1-species vibration of urea in the C_{2v} structure.

6) A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

7) M. Nishikawa, H. Mima and T. Kanzawa, *Chem. Pharm. Bull. (Tokyo)*, **10**, 1199 (1962).

8) R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **81**, 386 (1932).

9) L. Deměny and I. Nitta, This Bulletin. **3**, 128 (1928).

TABLE 1. BANDS IN THE 3 μ REGION OF THIOUREA

Stewart		Nishikawa *et al.*		Present work		
Frequency cm^{-1}		Frequency cm^{-1}		Frequency cm^{-1}		Dichroism
3365	B_1 ν(NH)	3375	A_1 ν(NH)	3370	A_1, B_1	no
3258	A_1 ν(NH)	3275	B_1 ν(NH)	3256	B_1	//
3156	B_1 ν(NH)			3156	B_1	//
3097	A_1 ν(NH)			3096	B_1	//

// parallel to the c-axis.

the NH_2 wagging band of B_2 species of thiourea at 460 cm^{-1} shifted to 613 cm^{-1} upon the change in crystal structure from rhombic to rhombohedral accompanied by adduct formation.7) The broad band at 555 cm^{-1} observed in the thin-film spectrum is considered to correspond to the broad band at 470 cm^{-1} of the bulk spectrum. In the reflectance spectrum, the band peak may shift from its true position to a small extent, as has been described in a previous paper,1) but the shift observed here is too large to be explained by the effect of the measuring method. The band at 470 cm^{-1} obviously corresponds to that at 460 cm^{-1} in Nishikawa's paper and may be assigned to the NH_2 wagging vibration. In consequence, the band shift observed in the thin-film spectrum may be attributed to the deformation of the crystal structure in the thin film on steel. The change in spectrum in the 3 μ region with the change in crystal structure was also reported in Nishikawa's paper, but, in the thin-film spectrum, the absorption bands in the same region were very weak except for a band at 3370 cm^{-1} and we could not detect any change in the spectrum similar to Nishikawa's results.

The spectrum of the thin thiourea-collodion film is shown in Fig. 5. As for thiourea bands, only the bands which appeared abnormally weak in the thiourea thin-film spectrum and which are to be attributed to the vibrations of B_1 species appear in the spectrum, except for the band at 3370 cm^{-1}, showing the formation of orientated crystals. The spectrum of thiourea in the thiourea-collodion film was almost the same as that of pure thiourea, and the crystal structure of thiourea in the thiourea-collodion mixture is considered to be rhombic.

There is some confusion in the assignment of the absorption bands of thiourea in the 3 μ region. Badger-Waldron's paper about the infrared dichroism in the 3 μ region of the thiourea single crystal10) indicates that the band at 3370 cm^{-1} is to be attributed to the vibrations of both A_1 and B_1 species, and the bands at 3256, 3156 and 3090 cm^{-1}, to B_1 species. Stewart and Nishikawa *et al.*, however, gave different assignments of the bands in the 3 μ region, as Table 1 shows.

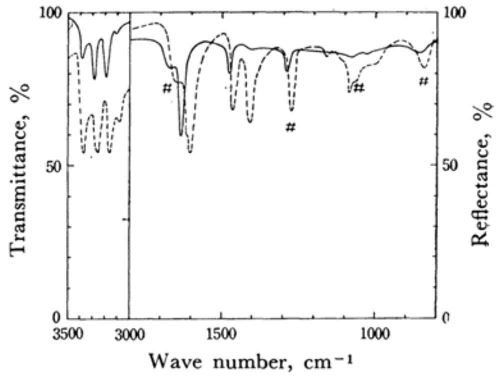

Fig. 5. Infrared spectrum of thiourea-collodion film.
——: Reflectance spectrum of thin film on steel (weight fraction of thiourea: 0.57)
----: Transmittance spectrum of film* on KBr window (weight fraction of thiourea: 0.59)
* Film thickness is much larger than in the film on steel.
♯ Nitro cellulose band

The bands at 3370, 3256 and 3156 cm^{-1} in the spectrum of bulk thiourea are nearly the same in intensity. On the contray, in the thin thiourea film spectrum, in which B_1 bands almost disappeared, only the band at 3370 cm^{-1} remained as an important band in the 3 μ region. On the other hand, the same band in the thiourea-collodion thin film spectrum, in which A_1 bands were abnormally weak, was somewhat weak in intensity relative to other bands in the 3 μ region. The intensity change in the bands in the 3 μ region mentioned above thus shows that the Badger-Waldron assignment is the most reasonable.

The bands of thiourea in the thiourea-collodion mixture, the intensity of which decreased upon a change in the state from bulk to thin film, should, therefore, be attributed to the A_1 species.*2 The above-mentioned results show that, in the thiourea-collodion thin film on steel, the C=S bonds of thiourea were nearly parallel to the metal surface.

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10) R. M. Badger and R. D. Waldron, *J. Chem. Phys.*, **26**, 255 (1957).

*2 B_2 bands were weak, and the dichlorism could not be observed.

The difference in the orientation of the thiourea molecule in the thiourea-collodion film from that in the thiourea thin film may arise from the thiourea-nitrocellulose interaction.

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