Ultraviolet Absorption Spectra of Aqueous Solutions and Single Crystals of Thioacetamide and Thiourea

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In a series of previous papers by Nagakura and Tanaka[1-4], electronic absorption spectra of various molecules, in which electron donating and accepting groups are connected with each other directly or through a bridge of conjugated double bonds, were discussed from both experimental and theoretical points of view. In these studies, special attention was paid to absorption bands which can be ascribed to neither of the component groups but to the interaction between the electron donating and accepting groups within a molecule. Since the transition corresponding to this kind of absorption band is apparently accompanied by a great amount of electron transfer from the electron donor to the acceptor, it may be called an intramolecular charge-transfer absorption by analogy with intermolecular cases developed by Mulliken[5]. From both experimental results of polarized ultraviolet absorption spectra and theoretical studies based on the LCMO treatment, it was actually shown that the intramolecular charge-transfer absorption can be found with formamide ($O=CH-NH_2$), acrolein ($H_2C=CH-CH=O$), nitramide (H_2N-NO_2), nitrobenzene ($C_6H_5-NO_2$), benzoic acid (C_6H_5-COOH), *p*-nitroaniline ($O_2N-C_6H_4-NH_2$) and other similar molecules. For example, the strong 370 mμ band of *p*-nitroaniline could reasonably be interpreted as an intramolecular charge-transfer absorption, in view of the fact that the direction of the transition moment associated with the band is parallel to the molecular axis connecting the two nitrogen atoms. A similar interpretation was applied to the 237 mμ band of aniline by Longuet-Higgins and Murrell[6].

1) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).
2) S. Nagakura, ibid., **23**, 1441 (1955); *Molecular Physics*, to be published.
3) J. Tanaka, S. Nagakura and M. Kobayashi, *J. Chem. Phys.*, **24**, 311 (1956); J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956).
4) J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1636 (1957); **79**, 1373 (1958).
5) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952) and other papers.
6) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrell, ibid., **A68**, 969 (1955).

In the present paper, electronic absorption spectra of thioacetamide ($S=C\langle^{CH_3}_{NH_2}$) and thiourea ($S=C\langle^{NH_2}_{NH_2}$) are studied as a subject of much interest from the aspect of intramolecular charge-transfer absorption. In these molecules, the thiocarbonyl (C=S) and amino (NH_2) groups are electron acceptor and donor, respectively, and the appearance of the intramolecular charge-transfer absorption may be expected. Especially thiourea seems to be most suitable for studying the effect of so-called cross-conjugation upon the charge-transfer absorption. This is because this molecule shows absorption bands at relatively longer wavelengths than the similar compounds, say urea ($O=C\langle^{NH_2}_{NH_2}$), do. By the way, the absorption bands of urea appear at wavelengths below 190 mμ and therefore are difficult to be measured with spectrophotometric instruments usually available at present.

Katagiri et al. measured absorption spectra of thioacetamide and thiourea in ethereal solution and pointed out that the weak band of thioacetamide at 318 mμ is conceivably ascribed to the $n\rightarrow\pi^*$ transition[7]. However, the assignment of the $\pi\rightarrow\pi^*$ transition bands of these two molecules has never been made. In the present paper, it is undertaken to obtain a definite conclusion on the assignment of the absorption bands by measuring the polarized ultraviolet absorption with their crystals and, moreover, by combining the experimental results with theoretical consideration based on the semi-empirical molecular orbital method including configuration interaction.

As is well known, thioacetone ($(H_3C)_2C=S$) can not exist as a stable monomer but usually as a trimer[8]. Therefore, it is difficult to obtain peak wavelengths of the absorption spectrum pertinent to the C=S bond, which is one of the important and basic data indispensable for the present study. In order to remove this difficulty, we have undertaken to measure the absorption spectrum of the conjugate acid of thioacetamide ($S=C\langle^{NH_3^+}_{CH_3}$) which is isoelectronic with thioacetone. In this connection, the equilibrium between thioacetamide and a proton is studied in detail and its equilibrium constant is obtained by means of the spectrophotometric method.

7) S. Katagiri, Y. Amako and H. Azumi, Presented at the Symposium on Structural Chemistry, Kyoto, October, 1958.
8) E. Baumann and E. Fromm, *Ber.*, **22**, 2593 (1889).
9) A. Bernthsen, *Ann.*, **192**, 47 (1878).
10) A. Hantzsch, ibid., **296**, 93 (1897).

Experimental

Materials.—Commercial thioacetamide of G. R. grade was purified by repeating recrystallization from ethyl ether, m. p. 109.5~110.5°C (uncorrected). The reported value is 107.5~108.5°C[9]. After the purification it was subjected to spectrophotometric measurements as soon as possible, because it has a tendency to decompose easily. Commercial thiourea of G. R. grade was recrystallized from ethanol, m. p. 177~178.5°C (uncorrected). The reported value is 180°C[10]. Hydrochloric acid and sulfuric acid, which are both of G. R. grade, were used as solvents without further purification.

Measurement. — *Ultraviolet Absorption Spectra of Solutions.* — A Cary recording spectrophotometer model 14 M was used for the ultraviolet absorption measurements of solutions. Measurements were usually carried out at room temperature (20~25°C), the quartz cell with a stopper of 1 cm. light path being used. If necessary, however, the temperature of the absorption cell was kept constant by circulating water of a desired constant temperature through the cell jacket.

Ultraviolet Absorption Spectra of Crystals. — An ultraviolet microscope equipped with a Hitachi model EPU monochromator and a polarizer of Rochon prism type was used for the measurement of polarized ultraviolet absorption in the wavelength region of 220~650 mμ[11]. Crystalline axes and planes were identified by the aid of X-ray rotation photographs and of optical examination with a polarizing microscope.

The single crystal of thioacetamide suitable for the measurement of polarized ultraviolet absorption was prepared by sublimation. The crystal showed a well developed (001) cleavage plane and was about 1×2 mm. in size and about 1~2 μ in thickness. The single crystal of thiourea was prepared directly on a quartz plate by dipping it into the ethanol solution and by evaporating the solvent slowly. Two kinds of crystals were obtained, one of which was hexagonal and the other rectangular. The latter was used for the spectroscopic measurement. Its developed plane was shown to be (110) by X-ray rotation photographs.

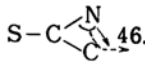
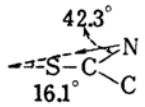
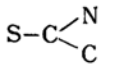
Experimental Results

Absorption Spectra of Thioacetamide in Aqueous and Hydrochloric Acid Solutions. — The results obtained with the aqueous and hydrochloric acid solutions of thioacetamide are summarized in Table I and Figs. 1 and 2. The ultraviolet absorption spectrum of thioacetamide in aqueous solution apparently consists of three bands. Two of them, which appear at 261 and 210 mμ, are fairly strong and may reasonably be attributed to allowed $\pi\rightarrow\pi^*$ transitions. On the other hand, the longest wavelength band at 318 mμ, whose molar extinction coefficient is only 60, may be regarded as an $n\rightarrow\pi^*$ transition band.

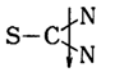
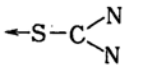
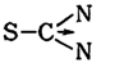
11) For the detail of the instrument, see Ref. 4.

Table I. Absorption spectra of thioacetamide and thiourea in aqueous solutions

a) Thioacetamide

λ_{max} Obs.	λ_{max} Calc.	log ε_{max}* Obs.	f Obs.	f Calc.	Direction of transition moment (Calc.)	Assignment
210 mμ (5.90 eV)	167 mμ (7.44 eV)	3.66	~0.13	0.198		$E_1 \rightarrow E_3$
261 (4.75)	260 (4.77)	4.08	0.216	0.515		$E_1 \rightarrow E_2$
318 shoulder (3.90)	—	1.8	—	—		$n \rightarrow \pi^*$

b) Thiourea

195 mμ (6.36 eV)	212 mμ (5.84 eV)	4.11	>0.3	0.600		$W_1 \rightarrow W_4$
236 (5.25)	225 (5.51)	4.08	0.227	0.529		$W_1 \rightarrow W_2$
?	136 (9.11)	?	?	0.025		$W_1 \rightarrow W_3$

* ε_{max} is the molar extinction coefficient at the absorption peak.

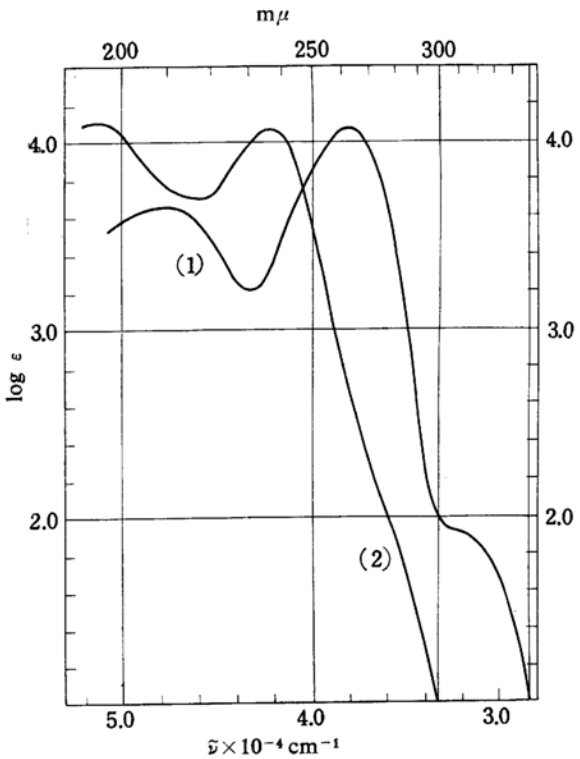


Fig. 1. Ultraviolet absorption spectra of thioacetamide (1) and thiourea (2) in aqueous solutions.

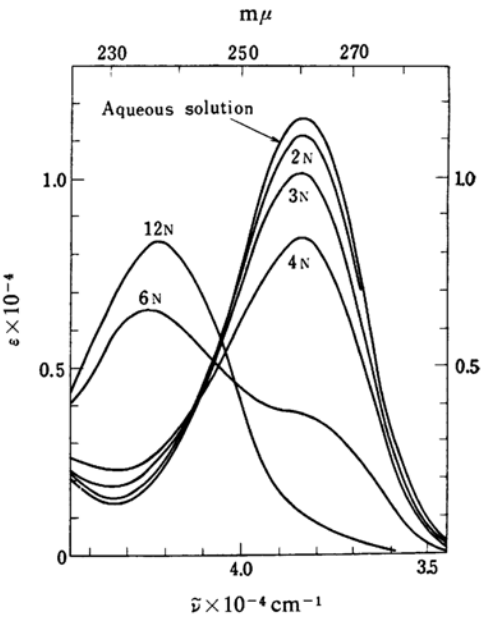


Fig. 2. Ultraviolet absorption spectra of thioacetamide in hydrochloric acid solutions with various acid concentrations.

The absorption spectrum of thioacetamide in hydrochloric acid solution changes considerably from that in aqueous solution. As is seen from Fig. 2, with the increasing concentration of hydrochloric acid, the 261 mμ band gradually decreases its intensity and a new band appears at 237 mμ[12]. Further, an isobestic point can be observed at 245 mμ, though the crossing of absorption curves is not always complete for the solutions of the higher concentrations of hydrochloric acid*. This fact conclusively indicates the existence of an equilibrium between thioacetamide and its conjugate acid. Concerning the mechanism of this equilibrium, there are two possible alternatives which are different from each other in the position where a proton is attached to the parent thioacetamide molecule. They are represented by the following equations:

$$H_2N\text{-}\overset{\overset{S}{\|}}{C}\text{-}CH_3 + H_3O^+ = H_3\overset{+}{N}\text{-}\overset{\overset{S}{\|}}{C}\text{-}CH_3 + H_2O$$

$$H_2N\text{-}\overset{\overset{S}{\|}}{C}\text{-}CH_3 + H_3O^+ = H_2N\text{-}\overset{\overset{{}^+SH}{\|}}{C}\text{-}CH_3 + H_2O$$

Here the former equilibrium is adopted as the more probable one. Some details on this point will be discussed in some later parts of the present paper.

From the experimental results regarding the absorption spectrum of thioacetamide in hydrochloric acid solutions of various concentrations, the basicity constant (pK_B) of thioacetamide can be obtained by the aid of the following equations:

$$K_B = (\overset{+}{H_3N}CSCH_3)/(H_2NCSCH_3)(H^+)$$
$$= (\varepsilon - \varepsilon_B)/(\varepsilon_{HB^+} - \varepsilon)(H^+)$$
$$pK_B = \log\{(\varepsilon_{HB^+} - \varepsilon)/(\varepsilon - \varepsilon_B)\} + pH$$

Quantities (H_2NCSCH_3), ($\overset{+}{H_3N}CSCH_3$) and (H^+) are activities of thioacetamide, its conjugate acid and a proton, respectively. Activity coefficients of thioacetamide and its cation are assumed to be equal to unity because of their low concentrations. The activity of the proton can be evaluated by combining the concentration of the solution determined by titration with the value of activity coefficient taken from the literature[13]. Quantities ε, ε_B and ε_{HB^+} represent the apparent molar extinction coefficient of thioacetamide in dilute hydrochloric acid solution, in aqueous solution and in concentrated hydrochloric acid solution, respectively. The values of the above-mentioned quantities actually used for the evaluation of pK_B are listed in Table II, together with the calculated pK_B value.

The average value of pK_B is obtained to be 1.2 at 24.5°C. Concerning the evaluation of this value, there are some ambiguities on the adoption of activity coefficients and on the medium effect upon the absorption spectrum of thioacetamide in concentrated hydrochloric acid. However, the pK_B value of thioacetamide evaluated here seems to be reasonable compared with the value of thiourea quoted in the literature[14].

Polarized Ultraviolet Absorption Spectra of Thioacetamide Crystal.—According to the structural analysis data of thioacetamide crystal by Truter[15], the molecules lie on the (001) plane as is schematically shown in Fig. 3. The polarized ultraviolet absorption spectra of thioacetamide parallel to *a* and *b* axes are shown in Fig. 3. From this figure it is easily seen that the 261 mμ band has stronger intensity in the direction of *b*-axis than in the direction of *a*-axis, and that the reverse is the case for the 210 mμ band, though the dichroism is not so conspicuous for this band as for the 261 mμ band. For these two bands, unfortunately, it is

Table II. Evaluation of the pK_B value of thioacetamide

Concentration of HCl (N)	$(\varepsilon-\varepsilon_B)/(\varepsilon_{HB^+}-\varepsilon)$ 260 mμ	270 mμ	280 mμ	Average	(H^+)	pK_B
3	0.156	0.157	0.146	0.153	3.665	1.38
4	0.406	0.393	0.372	0.390	7.104	1.26
6	2.90	2.45	2.68	2.68	22.41	0.92

Average pK_B value: 1.19.

* This may be due to the medium effect of the acid.

12) The band corresponding to the 210 mμ band of thioacetamide can not be observed in hydrochloric acid solution, because hydrochloric acid is not transparent in the wavelength region below 220 mμ. However, the spectrum in concentrated sulfuric acid solution which is transparent until 200 mμ shows only one absorption band at 240 mμ, namely the one corresponding to the 237 mμ band in hydrochloric acid solution. This seems to support the opinion that the 210 mμ band of thioacetamide disappears in strongly acidic solution.

13) H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2179 (1933); G. Åkerlöf and J. W. Teare, ibid., **59**, 1855 (1937).

14) pK_B=1.0 for thiourea: "Handbook of Chemistry (Kagakubinran)", edited by the the Chemical Society of Japan, Maruzen, Tokyo (1958), p. 871.

15) Private communication from Dr. M. R. Truter.

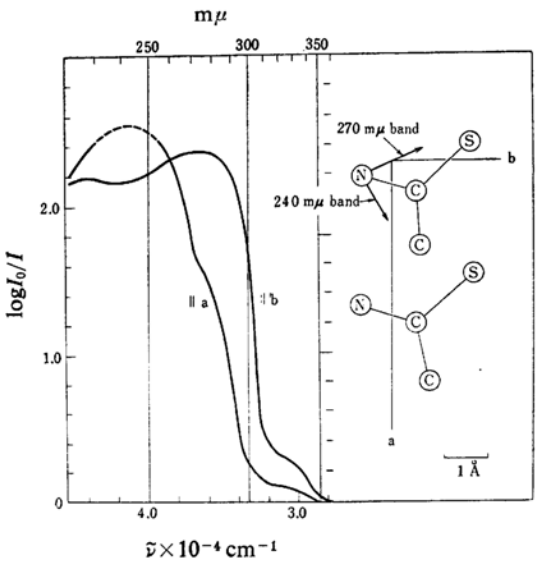


Fig. 3. The polarized ultraviolet absorption spectrum of thioacetamide and the projection of the molecules to the (001) plane. Arrows show the observed directions of transition moments.

difficult to determine exactly the direction of the transition momont from the combination of these spectral data with the crystal analysis result. This is because they overlap with each other and it is difficult to obtain the accurate value of oscillator strength for each band separately. However, it is well accepted that the transition moment of the 261 mμ band is directed very closely to the line connecting the nitrogen and the sulfur atom, thus the absorption intensity being greater in the b-axis spectrum than in the *a*-axis spectrum, while the transition momen of the 210 mμ band is approximately parallel to the line joining the nitrogen atom to the methyl carbon atom, thus the absorption intensity being a little stronger in the *a*-axis apectrum than in the *b*-axis spectrum.

A weak absorption band probably due to $n\rightarrow\pi^*$ transition appears in the 320~340 mμ region and its intensity is much stronger in the direction of *b*-axis than in the direction of *a*-axis. Concerning this weak band, however, one must be careful in determining the direction of the transition moment from the observed absorption intensity ratio, because weak forbidden bands often appear strongly in crystals by borrowing intenisty from allowed transition bands situated nearby[16]. Therefore it seems most likely that the weak band appearing at 320~340 mμ may not exhibit the dichroic property intrinsic to itself but rather the dichroic property characteristic of the 261 mμ band. In fact, the intensity ratio (about 5/1= I_b/I_a) measured with the weak band is completely consistent with the above-mentioned direction of transition moment of the 261 mμ band.

Absorption Spectra of Thiourea in Aqueous Solution.—As is seen from Table I and Fig. 1, absorption bands of thiourea have a conspicuous tendency to appear at shorter wavelengths compared with the corresponding band of thioacetamide. The same tendency seems to be found also in the case of comparing the absorption spectrum of urea with that of acetamide, though a definite conclusion can not be obtained for the case of these two molecules because of some difficulties from the experimental point of view. Another characteristic of the absorption spectrum of thiourea is the fact that the longest wavelength band of thioacetamide, which is probably associated with $n\rightarrow\pi^*$ transition, disappears.

Polarized Absorption Spectra of Thiourea Crystal.—According to the X-ray crystal analysis study by Wyckoff and Corey and by Kunchur and Truter[17], the molecules of thiourea lie on the (110) plane as is shown in Fig. 4. The polarized ultraviolet absorption spectra of thiourea measured by the use of the incident radiation polarized parallel and perpendicular to the *c*-axis of the crystal are shown in Fig. 4. From this figure it is easily

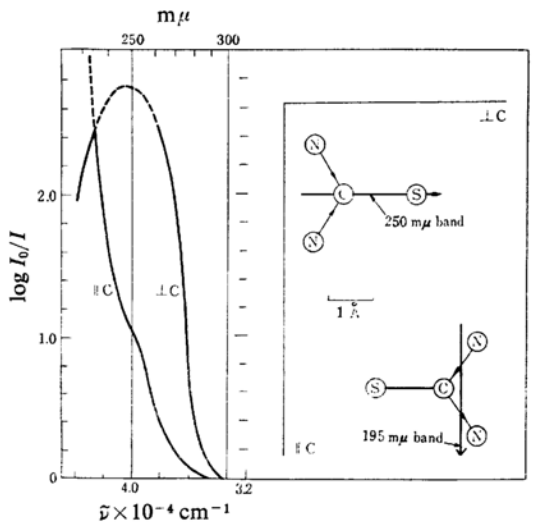


Fig. 4. The polarized ultraviolet absorption spectrum of thiourea and the projection of the molecules to the (110) plane. Arrows show the observed direction of transition moments.

16) D. S. McClure and O. Schnepp, *J. Chem. Phys.*, **23**, 1375 (1955).

17) R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **81**, 386 (1932). N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, **1958**, 2551.

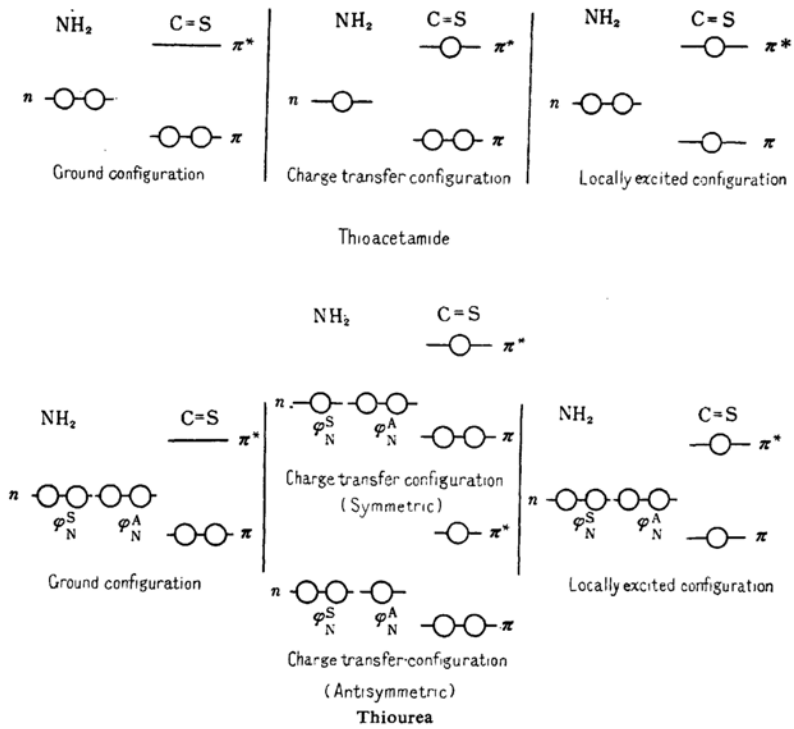


Fig. 5. Electron configurations for thioacetamide and thiourea.

seen that the observed intensity of the longer wavelength band is overwhelmingly great in the direction perpendicular to the *c*-axis compared with that in the direction parallel to the same axis, while the reverse is the case for the shorter wavelength band. This means that the transition moment of the longer wavelength band is evidently perpendicular to the *c*-axis, namely parallel to the C=S bond axis. On the other hand, the transition moment of the shorter wavelength band is determined to be perpendicular to the C=S bond axis.

Theoretical

In the present calculation, only π-electrons are taken into account and moreover the approximation of zero-differential overlap is adopted. In actual calculations, four and six π-electrons are taken for thioacetamide and thiourea, respectively. Now let us explain the actual calculation procedure in some detail, initially taking thioacetamide as an example.

Following Longuet-Higgins and Murrell's procedure[6], three electron configurations are constructed for this molecule in terms of π-electron molecular orbitals (φ_1, φ_2) of the electron accepting groups (C=S) and the nonbonding $2p$ atomiic orbital (χ_N) on the nitrogen atom of the electron donating group (NH_2)[18]. These configurations (a), (b) and (c) corresponding to ground, charge-transfer and locally excited configurations, respectively, are schematically shown in Fig. 5. As is well known, the wave functions for these configurations are written as follows:

$$\psi_G = 1/\sqrt{4!}\sum(-1)^p P\varphi_1(1)\alpha(1)\varphi_1(2)\beta(2) \times\chi_N(3)\alpha(3)\chi_N(4)\beta(4) \quad (1)$$

$$\psi_{CT} = 1/\sqrt{4!}\sum(-1)^p P\varphi_1(1)\alpha(1)\varphi_1(2)\beta(2) \times\chi_N(3)\alpha(3)\varphi_2(4)\beta(4) \quad (2)$$

$$\psi_{LE} = 1/\sqrt{4!}\sum(-1)^p P\varphi_1(1)\alpha(1)\varphi_2(2)\beta(2) \times\chi_N(3)\alpha(3)\chi_N(4)\beta(4) \quad (3)$$

Here, $\sum(-1)^p P$ is the usual antisymmetrizing summation over all permutations of the electrons. The wave functions φ_1 and φ_2 in Eqs. 1—3 can be determined following the procedure described in the Appendix.

Next one must take into account configuration interaction in terms of the three electron configurations mentioned above. According to this procedure, the energy levels of the molecule turn out to be obtained as solutions of the following secular equation:

18) According to the X-ray crystal analysis data of thioacetamide, hydrogen atoms of amino group are almost coplanar with heavy atoms.[15] This means that the nonbonding electrons of nitrogen may reasonably be assumed to belong to the pure $2p\pi$ atomic orbital.

$$\begin{vmatrix} H_G-E & H_{G\cdot LE} & H_{G\cdot CT} \\ H_{G\cdot LE} & H_{LE}-E & H_{LE\cdot CT} \\ H_{G\cdot CT} & H_{LE\cdot CT} & H_{CT}-E \end{vmatrix}=0 \qquad (4)$$

where, $H_G=\int\psi_G H\psi_G d\tau$, $H_{G\cdot LE}=\int\psi_G H\psi_{LE}d\tau$, etc.

Suppose the energy of the ground configuration is taken as a standard. The value of H_{CT}, the energy of the charge-transfer configuration, can be evaluated by the following equation:[2]

$$H_{CT}=I_N-A_{C=S}-\{d^2_{11}(CC \mid NN)+d^2_{12}(SS \mid NN)\} \qquad (5)$$

where I_N and $A_{C=S}$ are the ionization potential of the nonbonding electron of the amino nitrogen atom and the electron affinity of the C=S group, respectively. The former is set equal to the ionization potential of ammonia which is determined as 10.15 eV by Watanabe from the photoionization experiment.[19] The quantities d_{11} and d_{12} are coefficients of atomic orbitals in φ_1 or φ_2 molecular orbital and are evaluated to be 0.6902 and 0.7236 (see Appendix), respectively. Two center Coulomb integrals (CC | NN) and (SS | NN) are calculated with the aid of uniformly charged sphere approximation, by taking the C–N and C=S bond distances as 1.324 and 1.713 Å, respectively, and further by taking ∠SCN as 121.6°[15]. The value of $A_{C=S}$ is assumed to be −0.32 eV which seems to be reasonable compared with that of the C=O bond, −1.20 eV.[2]

The energy value of the locally excited configuration, H_{LE}, is set equal to the observed excitation energy corresponding to the $\pi\rightarrow\pi^*$ transition pertinent to the C=S group. It is natural to take this value from the experimental result on the absorption spectrum of thioacetone. Unfortunately, however, this expectation can not be satisfied, because thioacetone usually exists as trimer like $Me_2C<^{S-C(Me)_2}_{S-C(Me)_2}>S$ [8]. Then in the present calculation this value is taken to be 5.24 eV from the experimental result of the absorption spectrum of thioacetamide in hydrochloric acid solution. As mentioned above, thioacetamide in this condition exhibits the peak absorption at 237 mμ. This absorption band is conceivably ascribed to the protonated thioacetamide represented by $R>^{S}C-\overset{+}{N}H_3$. Since in this protonated cation the resonance effect of the amino group can be neglected to the first approximation, the 237 mμ band may be regarded as due to the $\pi\rightarrow\pi^*$ transition pertinent to the C=S bond. The present consideration on this point is consistent with the observation by Katagiri et al.[7] that thiocamphor shows a peak absorption at 242 mμ (5.12 eV).

Following the procedure developed by Longuet-Higgins and Murrell,[6] and also by Pople,[20] values of $H_{G\cdot CT}$, $H_{G\cdot LE}$ and $H_{CT\cdot LE}$ can easily be evaluated as follows:

$$H_{G\cdot CT}=\sqrt{2}\,d_{12}\beta_{CN}=1.414\times0.7236\times(-2.1)=-2.15 \text{ eV}$$

$$H_{G\cdot LE}=0$$

$$H_{CT\cdot LE}=-d_{11}\beta_{CN}=-0.6902\times(-2.1)=1.45 \text{ eV}$$

Here β_{CN} is the core resonance integral between the π-electron orbital of carbon and the nonbonding orbital of nitrogen. In the present calculation β_{CN} is assumed to be an appropriate value of −2.1 eV.

By inserting the energy integral values into Eq. 4 and by solving it, the three energy levels of thioacetamide can be determined. Further, wave functions corresponding to these energy levels can easily be evaluated following the usual procedure in the variation method. The results are shown in Table III. Here values in parentheses are squares of coefficients of corresponding component wave functions. In view of the fact that these values represent magnitudes of contributions of electron configurations to a certain state of the molecule, it may be said that the lowest state (E_1) is principally composed of the ground configuration and the contribution of the charge-transfer configuration to that state is only 17%.[21] On the other hand, in the E_2 state contributions of the charge-transfer and locally excited configurations are almost equal and amount to 43%.

From the energy values for the states of thioacetamide given in Table III, excitation energies corresponding to $E_1\rightarrow E_2$ and $E_1\rightarrow E_3$ transitions can be calculated to be 4.77 eV and 7.44 eV, respectively. Values of the transition moments Q_{1i}'s and oscillator strength f_{1i}'s associated with these transitions are calculated by the following equations[22]:

$$Q_{1i}=\int\Psi_1 er\,\Psi_i\,d\tau \qquad i=2,\ 3 \qquad (6)$$

$$f_{1i}=4.704\times10^{-7}\,\tilde{\nu}_{1i}Q^2_{1i} \qquad (7)$$

where $\tilde{\nu}_{1i}$ is the wave number (cm^{-1}) of the absorption peak under consideration and Q_{1i} is represented in Debye units. The calculated

19) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

20) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

21) This apparently corresponds to the fact that the electronic structure of thioacetamide can be represented by a resonance hybrid between the following two structures:

$$H_3C>^{S}C-NH_2 \quad\longleftrightarrow\quad H_3C>^{S^-}C=\overset{+}{N}H_2$$

22) R. S. Mulliken, *J. Chem. Phys.*, **7**, 14 (1939); J. R. Platt and H. B. Klevens, *Rev. Modern Phys.*, **16**, 182 (1944).

TABLE III. ENERGY LEVELS AND WAVE FUNCTIONS FOR THIOACETAMIDE

Energy level	Symmetry	Wave function
$E_1=-0.9929$ eV	A'	$\Psi_1=0.9036\,\phi_G-0.0971\,\phi_{LE}+0.4173\,\phi_{CT}$
		$(0.8165 \quad 0.0094 \quad 0.1741)$
$E_2=3.7811$ eV	A'	$\Psi_2=-0.3740\,\phi_G-0.6538\,\phi_{LE}+0.6578\,\phi_{CT}$
		$(0.1399 \quad 0.4275 \quad 0.4327)$
$E_3=6.4519$ eV	A'	$\Psi_3=-0.2090\,\phi_G+0.7503\,\phi_{LE}+0.6271\,\phi_{CT}$
		$(0.0437 \quad 0.5630 \quad 0.3933)$

TABLE IV. ENERGY LEVELS AND WAVE FUNCTIONS FOR THIOUREA

Energy level	Symmetry	Wave function
$W_1=-1.7653$ eV	A_1	$\Phi_1=0.8555\,\phi_G-0.1454\,\phi_{LE}+0.4968\,\phi^S{}_{CT}$
		$(0.7319 \quad 0.0211 \quad 0.2468)$
$W_2=3.7397$ eV	A_1	$\Phi_2=-0.4328\,\phi_G-0.7275\,\phi_{LE}+0.5324\,\phi^S{}_{CT}$
		$(0.1873 \quad 0.5293 \quad 0.2835)$
$W_3=7.3357$ eV	A_1	$\Phi_3=-0.2840\,\phi_G+0.6705\,\phi_{LE}+0.6854\,\phi^S{}_{CT}$
		$(0.0807 \quad 0.4496 \quad 0.4698)$
$W_4=4.0700$ eV	B_1	$\Phi_4=\phi^A{}_{CT}$

values of f_{1i}'s are listed in Table I in comparison with the observed valuse which are obtained from absorption curves with the aid of the following equation:

$$f_{1i}^{obs}=4.32\times10^{-9}\int\varepsilon d\tilde{\nu} \qquad (8)$$

where ε denotes the molar extinction coefficient. Directions of transition moments can also be evaluated readily from magnitudes of their components parallel and perpendicular to the C=S bond axis in the molecular plane. Consequently it is found that directions of transition moments associated with transitions $E_1\rightarrow E_2$ and $E_1\rightarrow E_3$ are inclined by 16° to the C=S bond and by 46° to the N–C bond, respectively. These theoretical results are schematically shown in Table I.

The calculation of π-electron structure is carried out also with thiourea by the same method as described in the case of thioacetamide. Therefore, it seems tedious to describe repeatedly the details of the calculation procedure. However, it may be necessary to add some note on the fact that in the case of thiourea two group orbitals, whose wave functions are represented by $\varphi^S{}_N=(\chi_{1N}+\chi_{2N})/\sqrt{2}$ and $\varphi^A{}_N=(\chi_{1N}-\chi_{2N})/\sqrt{2}$, can be obtained from the two nonbonding orbitals belonging to the amino groups. Consequently, in this case two charge-transfer configurations must be taken into account. Suppose that the wave functions of these two charge-transfer configurations and of the ground and locally excited configurations can be designated by $\psi^S{}_{CT}$ and $\psi^A{}_{CT}$[23], ϕ_G and and ϕ_{LE}, respectively (see Fig. 5). Among these wave functions, only $\psi^A{}_{CT}$ is antisymmetric with respect to the symmetry plane perpendicular to the molecular plane and including the C=S bond axis, while $\psi^S{}_{CT}$, ϕ_G and ϕ_{LE} are all symmetric with the same symmetry plane. Therefore it is readily concluded that the electron configuration represented by ψ^A_{-CT} can not mix with the other configurations. On the other hand, three configurations represented by ϕ_G, $\psi^S{}_{CT}$ and ϕ_{LE} interact with one another. The configuration interaction in terms of these three configurations finally results in three new states. The energy values and wave functions of these new states are given in Table IV[24].

From the energy values given in Table IV, excitation energies corresponding to $W_1\rightarrow W_2$, $W_1\rightarrow W_4$ and $W_1\rightarrow W_3$ are evaluated to be 5.51, 5.84 and 9.11 eV., respectively. It is inferred from this that the observed two absorption bands (236 and 195 mμ) in near ultraviolet region may reasonably be ascribed to the $W_1\rightarrow W_2$ and $W_1\rightarrow W_4$ transitions. The directions of transition moments for these two transitions

23) $\psi^S{}_{CT}=1/\sqrt{6!}\,\Sigma(-1)^P p\phi_1(1)\alpha(1)\phi_1(2)\beta(2)\phi^S{}_N(3)\alpha(3)\phi_2(4)\beta(4)\phi^A{}_N(5)\alpha(5)\phi^A{}_N(6)\beta(6)$
$\psi^A{}_{CT}=1/\sqrt{6!}\,\Sigma(-1)^P p\phi_1(1)\alpha(1)\phi_1(2)\beta(2)\phi^S{}_N(3)\alpha(3)\phi^S{}_N(4)\beta(4)\phi^A{}_N(5)\alpha(5)\phi_2(6)\beta(6)$

24) The values of matrix elements used for the evaluation of energy levels of thiourea are as follows:
$H_G=0$
$H^S{}_{CT}=H^A{}_{CT}=4.07$ eV.
$H_{LE}=5.24$ eV.
$H_{G\text{-}CT}=2d_{12}\beta_{CN}=2\times0.7236\times(-2.1)=-3.04$ eV.
$H_{G\text{-}LE}=0$
$H_{LE\text{-}CT}=-\sqrt{2}\,d_{11}\beta_{CN}=-1.414\times0.6902\times(-2.1)=2.05$ eV.
The values of I_N and $A_{C=S}$ necessary for the evaluation of $H^S{}_{CT}$ and $H^A{}_{CT}$ are the same as those employed in the case of thioacetamide (see Eq. 5). The values of (NN | CC) and (NN | SS), however, are newly calculated for thiourea by the method as described in the case of thioacetamide, by the use of the C-N and S-N distances determined by X-ray crystal analysis ($d_{C\text{-}N}=1.35$ Å, $d_{C=S}=1.64$ Å, $\angle NCS=126°$; see Ref. 16 for these data).

can easily be found from the symmetry properties of the upper and lower states for each transition. That is to say, the direction of transition moment for the $W_1 \rightarrow W_2$ transition is expected to be exactly parallel to the C=S bond axis, while that for the $W_1 \rightarrow W_4$ transition is perpendicular to the same axis. Combining this theoretical expectation with the experimental results regarding polarized ultraviolet absorption, it is possible to determine clearly the assignment of these two absorption bands. This point will be explained in the next chapter.

Discussion

Assignment of Absorption Bands of Thioacetamide. — Experimental and theoretical results concerning the absorption spectra of thioacetamide are summarized in Table I and Figs. 1 and 3. From these results it is seen that the directions of transition moments determined theoretically for $E_1 \rightarrow E_2$ and $E_1 \rightarrow E_3$ transitions, whose excitation energies are calculated to be 4.77 eV. (260 mμ) and 7.44 eV. (167 mμ), respectively, are approximately equal to the directions of transition moments observed with the 261 mμ and 210 mμ bands, respectively. This fact gives a powerful support for the assignment that the 261 mμ and 210 mμ bands ought to be ascribed to the transitions $E_1 \rightarrow E_2$ and $E_1 \rightarrow E_3$, respectively. According to the above assignment, the agreement between the theoretical and experimental excitation energies is satisfactory for the 261 mμ band, but some discrepancy is seen for the 210 mμ band. A principal reason for this discrepancy is thought to be the neglect of electron configurations with higher energies, say configurations including two electron jumps. Although there is the above-mentioned difficulty from the quantitative point of view, the assignment of the two absorption bands of thioacetamide may be thought to be finally determined by the present experimental and theoretical studies.

Concerning the assignment of the weak band at 318 mμ, much can not be said. As pointed out by Katagiri et al.[7], however, this band is tentatively due to an $n \rightarrow \pi^*$ transition, namely due to the excitation of a nonbonding electron of the sulfur atom to the excited π-electron orbital of the C=S bond.

Assignment of Absorption Spectrum of Thiourea. — The results regarding the absorption spectrum of thiourea are given in Table I and Figs. 1 and 4. This molecule shows fairly strong absorption bands at 236 and 195 mμ. Calculated excitation energies for the $W_1 \rightarrow W_2$ and $W_1 \rightarrow W_4$ transitions are 5.51 (225 mμ) and 5.84 eV. (212 mμ), respectively. In this case, it is dangerous to determine the assignment of these two bands from the theoretical excitation energies alone, because the energy difference between W_2 and W_4 states is only 0.33 eV. and there may be some possibility that energy levels of these two states are reversed with each other by changing to only a small extent some parameters adopted in the present calculation. Fortunately, however, this difficulty is completely removed by considering the result of the polarized ultraviolet absorption measurement on the single crystal.

As is seen from Fig. 4, experimental results on the polarized ultraviolet absorption spectrum shows that the directions of transition moments of the longer and shorter wavelength bands are parallel and perpendicular to the C=S bond axis, respectively. Theoretical consideration in

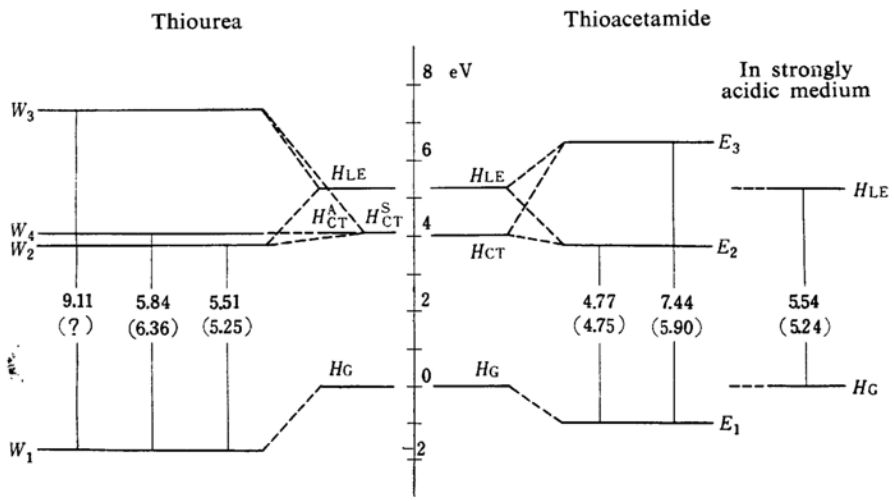
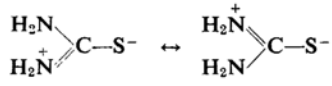


Fig. 6. Energy level diagrams for thioacetamide and thiourea, showing the relation between observed (in parentheses) and calculated transition energies.

the preceding chapter concludes that the transition moments associated with $W_1 \rightarrow W_2$ and $W_1 \rightarrow W_4$ ought to have directions exactly parallel and perpendicular to the C=S bond axis, respectively. These facts lead to the conclusion that the 236 mμ and 195 mμ bands correspond to the $W_1 \rightarrow W_2$ and $W_1 \rightarrow W_4$ transitions, respectively.

Of these two absorption bands, the shorter wavelength (195 mμ) band may be called a typical intramolecular charge-transfer band, because the upper state (W_4) of the corresponding transition is completely constructed from the charge-transfer configuration. This charge-transfer configuration includes electron transfer from the orbital represented by an antisymmetric combination of the nonbonding electron orbitals of the two nitrogen atoms to the φ_2 orbital pertinent to the C=S bond. From the resonance viewpoint, this means that the upper state of the 195 mμ band can be represented approximately by the resonance hybrid between the following two structures:



On the other hand, the 236 mμ band exhibits strongly the character of the locally (C=S) excited band, because in the excited state corresponding to this band the contribution of the locally excited configuration is great and amounts to 53%. In this sense, the 236 mμ band of thiourea may be regarded as the shifted one of the 237 mμ band pertinent to the C=O bond.

The relation between the energy state and the ultraviolet absorption spectrum described hitherto on thioacetamide and thiourea are schematically shown in Fig. 6.

Absorption Spectrum of Thioacetamide in Hydrochloric Acid Solution.—The fact that the 261 mμ and 210 mμ bands ($E_1 \rightarrow E_2$ and $E_1 \rightarrow E_3$ transitions, respectively) of thioacetamide disappear and a new band appears at 237 mμ in concentrated hydrochloric acid solution (240 mμ in concentrated sulfuric acid solution) seems to give an important information regarding the position of the proton attached to the parent molecule. Concerning the position of the proton, there are conceivably two alternatives, namely the nitrogen atom of the amino group and the sulfur atom of the thiocarbonyl group. In the latter case, it may be expected that the electron affinity of the C=S group increases considerably and the energy of the charge-transfer configuration given by Eq. 5 apparently decreases. From this it may be predicted that the 261 mμ band of thioacetamide will shift toward longer wavelengths if the proton be attached to the sulfur atom. The experimental result is completely reverse to this prediction. This seems to support the other possibility, namely the fact that proton is attached to the nitrogen atom. This conclusion is in agreement with the result obtained from the absorption measurement in the infrared region[25].

Appendix

The Molecular Orbital Functions Pertinent to the C=S Bond. — π-Electron orbitals of the C=S bond are represented by the linear combination of the $2p$ atomic orbital of carbon (χ_C) and the $3p$ atomic orbital of sulfur (χ_S):

$$\varphi_1 = d_{11}\chi_C + d_{12}\chi_S \tag{9}$$

$$\varphi_2 = d_{12}\chi_C - d_{11}\chi_S \tag{10}$$

The problem is to calculate the values of coefficients d_{11} and d_{12}. The calculation is carried out by the aid of the combination of Roothaan's LCAO SCF method[26] with Pariser and Parr's approximation[27]. The values of energy integrals actually adopted to the calculation are as follows:

$$\alpha_C = -I_C + \int \chi_C U_S \chi_C d\tau = -11.54 - 7.76 = -19.30 \text{ eV}. \tag{12}$$

$$\alpha_S = -I_S + \int \chi_S U_C \chi_S d\tau = -12.50 - 7.65 = -20.15 \text{ eV}. \tag{11}$$

$\beta_{CS} = -2.0$ eV. (assumed value)

$$(CC|CC) = \int \chi_C(1)\chi_C(2)\frac{e^2}{r_{12}}\chi_C(1)\chi_C(2)d\tau = 11.54 - 0.46 = 11.08 \text{ eV}.$$

$$(CC \mid SS) = \int \chi_C(1)\chi_S(2)\frac{e^2}{r_{12}}\chi_C(1)\chi_S(2)d\tau = 7.37 \text{ eV}.$$

$$(SS \mid SS) = \int \chi_S(1)\chi_S(2)\frac{e^2}{r_{12}}\chi_S(1)\chi_S(2)d\tau = 12.50 - 2.70 = 9.80 \text{ eV}.$$

Here U and α represent core potential and core Coulomb integral concerning atoms each of which is referred to by a suffix, respectively. β_{CS} is the core resonance integral between the χ_C and χ_S orbitals. I_C and I_S are the ionization potential of the $2p$ electron of carbon and of the $3p$ electron of sulfur, respectively. These values are taken from Pritchard and Skinner's table[28]. Integrals $\int \chi_C U_S \chi_C d\tau$ and $\int \chi_S U_C \chi_S d\tau$ are assumed to be equal to electrostatic attraction between two spherically charged ($-e/2$ each) tangent balls on one atom and the opposite charge ($+e$) on the other

25) E. Spinner, *Spectrochim. Acta*, **12**, 95 (1959).
26) C. C. J. Roothaan, *Rev. Modern Phys.*, **23**, 69 (1951).
27) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
28) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

atom. Following Pariser and Parr's procedure[27], one center Coulomb repulsion integral, (CC | CC) or (SS | SS) is set equal to the difference between the ionization potential and the electron affinity. These two quantities are taken from Pritchard and Skinner's table. The two center Coulomb repulsion integral (CC | SS) is evaluated under the uniformly charged sphere approximation[29], taking the C=S bond distance as 1.71 Å, the value obtained by Truter from the X-ray analysis data on thioacetamide[15].

In order to obtain more accurate values for the core Coulomb integrals, the polarization effect of the σ-electrons of the C=S orbital upon them is taken into account. According to Moffit's method[30], the corrected ionization potentials can be obtained by the following equation[31]:

$$I'_C = -11.54 - 0.1436(11.08 - 7.37) = -12.08 \text{ eV}.$$

$$I'_S = -12.50 + 0.1436(9.80 - 7.37) = -12.15 \text{ eV}.$$

Substituting these values for I_C and I_S in Eqs. 11 and 12, the corrected core Coulomb integrals become as follows:

$$\alpha'_C = -19.84 \text{ eV}. \qquad \alpha'_S = -19.80 \text{ eV}.$$

By using these integral values, the iterative procedure following Roothaan's method is continued until self-consistent results are obtained with d_{11}, d_{12} and orbital energies (ε_1, ε_2). The final results thus obtained are as follows[32]:

$$d_{11} = 0.6902 \qquad d^2_{11} = 0.4764$$

$$d_{12} = 0.7236 \qquad d^2_{12} = 0.5236$$

$$\varepsilon_1 = -12.946 \text{ eV}. \qquad \varepsilon_2 = -1.566 \text{ eV}.$$

$$\varphi_1 = 0.6902\chi_C + 0.7236\chi_S$$

$$\varphi_2 = 0.7236\chi_C - 0.6902\chi_S$$

Further the excitation energy ΔE corresponding to the $\varepsilon_1 \rightarrow \varepsilon_2$ transition can be calculated by the following equations:

$$\Delta E = \varepsilon_2 - \varepsilon_1 - (11 \mid 12) + 2(12 \mid 12) = 5.54 \text{ eV}.$$

$$(11 \mid 22) = d^2_{11}d^2_{12}\{(CC \mid CC) + (SS \mid SS)\} + (d^4_{11} + d^4_{12})(CC \mid SS)$$

$$(12 \mid 12) = d^2_{11}d^2_{12}\{(CC \mid CC) + (SS \mid SS) + 2(CC \mid SS)\}$$

The calculated value, 5.54 eV., may be said to be in fairly good agreement with the observed one, 5.24 eV.

29) R. G. Parr, *J. Chem. Phys.*, **20**, 1499 (1952).

30) W. Moffitt, *Proc. Roy. Soc.* (*London*), **A202**, 534 (1950).

31) In this calculation the following energy values are used:

$I^\sigma_S = 20.0$ eV. $\qquad A^\sigma_S = 4.0$ eV.

$I^\sigma_C = 15.42$ eV. $\qquad A^\sigma_C = 3.32$ eV.

$\beta^\sigma_{CS} = -2.0$ eV.

where I and A represent ionization potential and electron affinity, respectively, and the superscript σ means that the corresponding quantity is concerned with σ-electrons. The quantities on carbon are taken from Pritchard and Skinner's table[28] and those on sulfur are roughly estimated from corresponding values for oxygen which are also obtained from the table.

32) Katagiri et al. calculated independently the wave functions and orbital energies of the C=S bond and obtained the following results:

$\phi_1 = 0.6330\chi_C + 0.7741\chi_S$

$\phi_2 = 0.7741\chi_C - 0.6330\chi_S$

$\varepsilon_1 = -11.98$ eV $\qquad \varepsilon_2 = -1.90$ eV

S. Katagiri, Y. Amako and H. Azumi, Presented at the Symposium on Electronic States, Tokyo, September, 1959.

Summary

Ultraviolet absorption spectra of thioacetamide and thiourea are measured under various conditions. In aqueous solution, three bands (210, 261 and 318 mμ) for thioacetamide and two bands (195 and 236 mμ) for thiourea are observed. Further, polarized ultraviolet absorption spectra are measured with their crystals. On the basis of the results regarding the polarized ultraviolet absorption spectra, the directions of transition moments can be determined as follows: 1) the directions of transition moments of the 261 and 210 mμ bands of thioacetamide are approximately parallel to the axis connecting the nitrogen and sulfur atoms and connecting the nitrogen and methyl carbon atoms, respectively, 2) the directions of transition moments of the 236 and 195 mμ bands of thiourea are parallel and perpendicular to the C=S axis, respectively. From the combination of the experimental results concerning the directions of transition moments with theoretical consideration based on semi-empirical LCAO treatment including configuration interaction, the assignment of the four absorption bands under consideration are finally determined. One of the noticeable conclusions is that the 195 mμ band of thiourea can be regarded as a typical intramolecular charge-transfer absorption.

It is shown that in the hydrochloric acid solution of thioacetamide the 261 mμ band decreases its intensity and a new band appears at 237 mμ. By measuring the dependence of intensities of these two bands upon the acid strength of the solution, it is concluded that the 237 mμ band is due to the conjugate acid of thioacetamide. The pK_B value of thioacetamide is determined spectrophotometrically to be 1.2 at 24.5°C. From the comparison of the wavelength of the peak absorption of thioacetamide with that of its conjugate acid, it is seen that the proton is conceivably attached to the amino group.

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