Theoret. chim. Acta (Berl.) 7, 117—123 (1967)

Vacuum Ultraviolet Absorption Spectra of Simple Amides

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Received October 11, 1966

Vacuum ultraviolet absorption spectra of six simple amides were measured. It was found that the positions of the first $\pi \rightarrow \pi^*$ transition bands shift appreciably by the substitutions of methyl groups for hydrogen atoms of the NH_2 and $H-\overset{|}{C}=O$ groups. A general tendency is that the substitution in the NH_2 group shifts the band toward longer wavelengths, in the $H-\overset{|}{C}=O$ group however towards shorter wavelengths. This was explained satisfactorily by considering the nature of the band (intramolecular charge-transfer band) and the hyperconjugation effect of the methyl group.

Vakuum-UV-Absorptions-Spektren von sechs einfachen Amiden wurden vermessen. Substitution von H durch Methyl am C-Atom des Formamids verschiebt den ersten $\pi \rightarrow \pi^*$-Übergang zu kürzeren, am N-Atom zu längeren Wellenlängen. Dies kann durch die Natur der Bande (intramolekularer 'charge transfer') sowie durch Methylhyperkonjugation erklärt werden.

Les spectres d'apsorption U.V. dans le vide ont été mesurés pour 6 amides simples. Le remplacement de H par CH_3 sur l'atome de carbone de la formamide provoque un effet hypsochrome de la première transition $\pi \rightarrow \pi^*$; l'effet est batochrome pour la même substitution sur l'atome d'azote. Ceci peut être expliqué par la nature de la bande (transfert de charge intramoléculaire) et par l'hyperconjugaison du méthyle.

Introduction

Amides are interesting compounds from biochemical point of view, since they are brick stones constructing peptide bonds. Many investigations on them have been made in the fields of nuclear magnetic resonance and infrared spectroscopy [*1*—*6*], but there are only few studies on their electronic absorption spectra. HUNT and SIMPSON [*7*] measured the vacuum ultraviolet absorption spectra of formamide and N,N-dimethylformamide and found strong $\pi \rightarrow \pi^*$ absorption bands. PETERSON and SIMPSON [*8*] measured the polarized electronic absorption spectra of the myristamide crystal and determined the direction of the transition moment of the first $\pi \rightarrow \pi^*$ transition band. NAGAKURA [*9*] made a theoretical study on the π-electron structure of formamide and interpreted the first $\pi \rightarrow \pi^*$ transition band as an intramolecular charge-transfer band accompanying an electron transfer from the amino group to the carbonyl group.

In the present study, we have measured the vacuum ultraviolet absorption spectra of various amides like formamide, acetamide and their methyl derivatives, for the purpose of studying the effect of the methyl substitution upon their intramolecular charge-transfer absorption bands.

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Experimental

Material. Formamide of E.P. grade was dried over anhydrous sodium sulfate, purified by repeated recrystallizations and distillations under reduced pressure. The sample was stored in a refrigerator with drying agent; b.p. 91°/8 mmHg. Acetamide of G.R. grade was distilled under reduced pressure; b.p. 90°/20 mmHg. The sample was stored in a desiccator at low temperature. Commercially available N-methylformamide and N,N-dimethylformamide were dried over anhydrous sodium sulfate and distilled under reduced pressure and ordinary pressure, respectively; b.p. 79°/11 mmHg and 151°/760 mmHg, respectively. N-methylacetamide of G.R. grade was distilled twice under reduced pressure and then stored in a desiccator; b.p. 85°/6 mmHg. N,N-dimethylacetamide of G.R. grade was dried over anhydrous sodium carbonate and then purified by vacuum distillation; b.p. 78°/70 mmHg.

Measurement. Cary recording spectrophotometer model 14M and a vacuum ultraviolet spectrophotometer constructed in our laboratory [*10*] were used for the measurements in the near and vacuum ultraviolet regions, respectively. Optical cells equipped with LiF windows whose path-lengths are 1.0 and 2.5 cm were used for the measurements of gaseous samples. Before the measurements in gaseous state, each of the samples was degassed and dehydrated and thereafter was transferred to an optical cell. The details of the vacuum ultraviolet absorption measurement have been described in a previous paper [*10*].

Theoretical

In order to explain the change in the vacuum ultraviolet absorptions observed with a series of simple amides, calculations were made on their π-electron structures. The method of the calculation is similar to the one adopted by NAGAKURA [*9*] to the theoretical study of formamide and acrolein. Each of the amides was first divided into two components: electron donating groups [$-NH_2$, $-NHCH_3$, and $-N(CH_3)_2$] and electron accepting groups ($-COH$ and $-COCH_3$). Thereafter interaction between them was considered by the aid of the configurational interaction among the ground (G), locally excited (LE) and charge-transfer (CT) configurations. The configurations are schematically shown in Fig. 1, where χ_N indicates $2p\pi$ atomic orbital of the nitrogen atom of the amino group, and $\varphi^a_{C=O}$ and $\varphi^b_{C=O}$ are the antibonding and bonding molecular orbitals of the carbonyl group, respectively. The actual forms of these molecular orbitals were taken from the calculation made by KON [*11*].

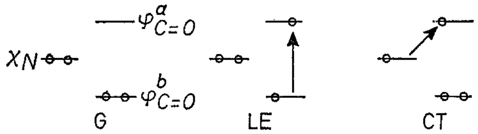

Fig. 1. Configurations adopted in the calculation. *G*: Ground configuration; *LE*: Locally excited configuration; *CT*: Charge-transfer configuration

The wavefunctions of the ground, locally excited and charge-transfer configurations are as follows:

$$\psi_G = |\chi_N(1)\,\bar{\chi}_N(2)\,\varphi^b_{C=O}(3)\,\bar{\varphi}^b_{C=O}(4)|$$

$$\psi_{LE} = 1/\sqrt{2}(|\chi_N(1)\,\bar{\chi}_N(2)\,\varphi^b_{C=O}(3)\,\bar{\varphi}^a_{C=O}(4)| + |\chi_N(1)\,\bar{\chi}_N(2)\,\varphi^a_{C=O}(3)\,\bar{\varphi}^b_{C=O}(4)|)$$

$$\psi_{CT} = 1/\sqrt{2}(|\chi_N(1)\,\bar{\varphi}^a_{C=O}(2)\,\varphi^b_{C=O}(3)\,\bar{\varphi}^b_{C=O}(4)| + |\varphi^a_{C=O}(1)\,\bar{\chi}_N(2)\,\varphi^b_{C=O}(3)\,\bar{\varphi}^b_{C=O}(4)|)$$

$$\varphi^b_{C=O} = 0.5472\,\chi_C + 0.8370\,\chi_O$$

$$\varphi^a_{C=O} = 0.8370\,\chi_C - 0.5472\,\chi_O\,.$$

Here, the bracket represents a Slater determinant, and χ_C and χ_O are the $2p\pi$ atomic orbitals of the carbon and the oxygen atoms of the carbonyl group. Barred and unbarred orbitals denote spin β and spin α, respectively.

The energy of the ground configuration (E_G) was taken as the standard. The energy of the locally excited configuration (E_{LE}) within the carbonyl group was determined to be 7.95 eV, which is the first $\pi \rightarrow \pi^*$ transition energy of formaldehyde observed by WALSH [12].

The energy of the charge-transfer configuration (E_{CT}) can be calculated by the following equations:

$$E_{CT} = I_D - A_{\mathrm{C=O}} - \Delta$$
$$\Delta = 0.2994\,(\mathrm{CC}\,|\,\mathrm{NN}) + 0.7006\,(\mathrm{OO}\,|\,\mathrm{NN})\,.$$

Here I_D and $A_{\mathrm{C=O}}$ represent the ionization potential of the electron donating group and the electron affinity of the electron accepting group, respectively. Δ is the electrostatic interaction term. The values of I_D were taken to be 10.15, 8.97 and 8.24 eV for the amino, methylamino and dimethylamino groups, respectively, which are the ionization potentials of ammonia, methylamine and dimethylamine, respectively [13]. The $A_{\mathrm{C=O}}$ value was determined to be -1.20 eV by NAGAKURA [9] for the $\mathrm{H{-}\underset{|}{C}{=}O}$ group. The electron affinity of the $\mathrm{H_3C{-}\underset{|}{C}{=}O}$ group may be thought to be smaller than that of $\mathrm{H{-}\underset{|}{C}{=}O}$ group because of the hyperconjugation effect of the methyl group. In the present calculations, it was taken to be -2.0 eV. The two center Coulomb repulsion integrals, (CC | NN) and (OO | NN), were evaluated as 8.294 and 6.192 eV, respectively, by using PARISER and PARR's approximation [14] and the geometrical parameters given in Fig. 2 [15, 16]. The energy values of the charge-transfer configurations were determined as follows:

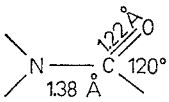

Fig. 2. Structure of amide used in the calculation

$E_{CT} = 4.528$ eV (formamide), 3.348 (N-methylformamide), 2.618 (N,N-dimethylformamide), 5.428 (acetamide), 4.148 (N-methylacetamide), 3.418 (N,N-dimethylacetamide).

Off-diagonal matrix elements each of which represents the interaction between the two configurations were evaluated by the aid of the formulation by POPLE [17] and also by LONGUET-HIGGINS and MURRELL [18]. The values are as follows:

$$H_{G,CT} = 1.183\,\beta_{\mathrm{CN}} = -\,3.077\ \mathrm{eV}\,.$$
$$H_{CT,LE} = -\,0.547\,\beta_{\mathrm{CN}} = 1.422\ \mathrm{eV}\,.$$

Here β_{CN} represents core resonance integral between the $2p\pi$ atomic orbitals of the carbon atom of the carbonyl group and that of the nitrogen atom of the amino group. This value was determined to be $-\,2.60$ eV by NAGAKURA [9].

Solving the secular equations we evaluated the wavefunctions and the energy levels of the six simple amides. They are tabulated in Tab. 1.

Results and Discussion

The observed absorption spectra of the simple amides are shown in Figs. 3—5. The peak wavelengths of the strong and broad bands are given in Tab. 2. In this

Table 1. *Energy levels and wavefunctions of amides*

State	Energy (eV)	Coefficients of the wavefunctions		
		ψ_G	ψ_{LE}	ψ_{CT}
		Formamide		
0	−1.60	0.8851	−0.0686	+0.4603
1	5.45	−0.4401	−0.4447	+0.7801
2	8.63	−0.1512	+0.8931	+0.4238
		N-methylformamide		
0	−1.88	0.8504	−0.0753	+0.5207
1	4.73	−0.5119	−0.3467	+0.7860
2	8.46	−0.1213	+0.9349	+0.3334
		N,N-dimethylformamide		
0	−2.10	0.8237	−0.0795	+0.5615
1	4.28	−0.5569	−0.3002	+0.7744
2	8.39	−0.1070	+0.9505	+0.2955
		Acetamide		
0	−1.42	0.9054	−0.0637	+0.4197
1	5.98	−0.3847	−0.5409	+0.7479
2	8.82	−0.1794	+0.8387	+0.5142
		N-methylacetamide		
0	−1.68	0.8750	−0.0707	+0.4789
1	5.22	−0.4637	−0.4096	+0.7859
2	8.56	−0.1406	+0.9095	+0.3912
		N,N-dimethylacetamide		
0	−1.87	0.8528	−0.0749	+0.4789
1	4.77	−0.5076	−0.3517	+0.7859
2	8.47	−0.1229	+0.9331	+0.3380

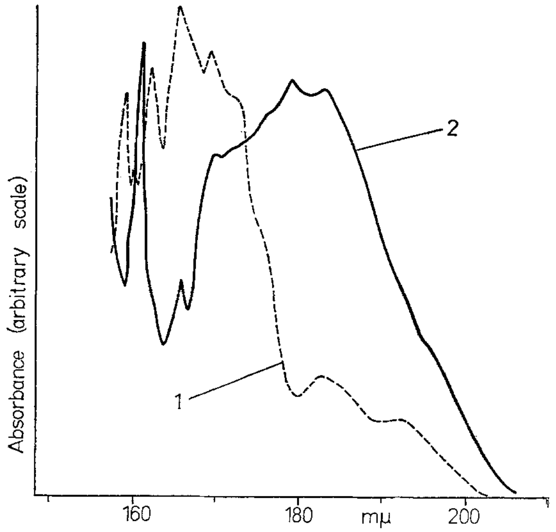

Fig. 3. Vacuum ultraviolet absorption spectra. 1: Formamide; 2: N-methylacetamide

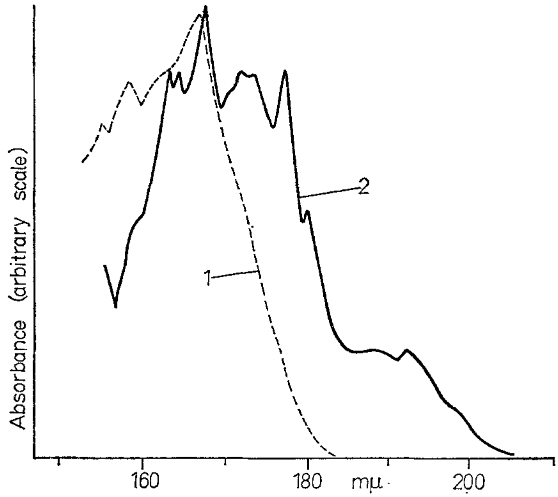

Fig. 4. Vacuum ultraviolet absorption spectra. 1: Acetamide; 2: N-methylformamide

table, the calculated transition energies for the first $\pi \rightarrow \pi^*$ transition bands are also shown for the purpose of comparison. This table shows that the present theoretical consideration can well explain the observed peak wavelength shifts due to the methyl substitution, except for the case of N-methylfomamide where the theoretical transition energy is considerably smaller than the observed one.

According to the investigation on the myristamide crystal by PETERSON and SIMPSON and the theoretical study on formamide by NAGAKURA, the first $\pi \rightarrow \pi^*$ transition band of amide can be regarded as an intramolecular charge-transfer band. As is seen in the wavefunctions of the first excited states given in Tab. 2, the present calculation also supports this interpretation. On the basis of this

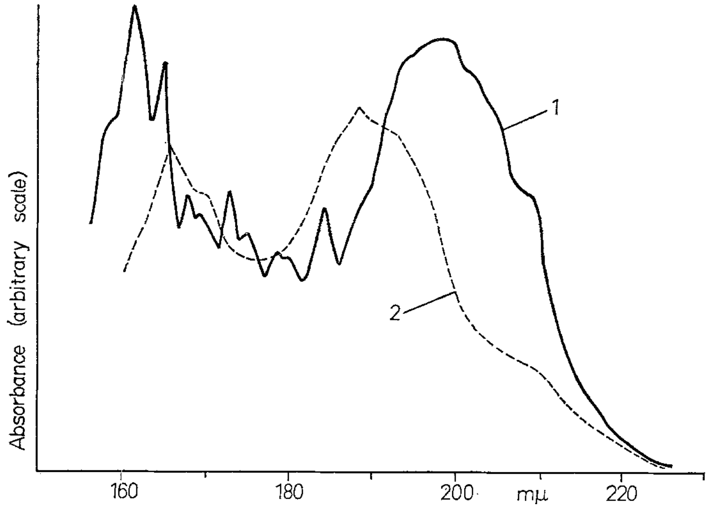

Fig. 5. Vacuum ultraviolet absorption spectra. 1: N,N-dimethylformamide; 2: N,N-dimethylacetamide

Table 2. *Observed and calculated transition energies* (eV) *for* $\pi \rightarrow \pi^*$ *transitions of amides*

	First transition (obs.)	Second transition (obs.)	First transition (cald.)
N,N-dimethylformamide	6.22 6.29	7.70	6.38
N,N-dimethylacetamide	6.60	7.52	6.64
N-methylacetamide	6.77 6.92	7.69 ?	6.90
N-methylformamide	7.08 7.16 7.22		6.61
Formamide	7.16 7.22		7.05
Acetamide	7.48		7.39

interpretation, the hyperconjugation effect of the methyl group upon the observed peak wavelengths can be qualitatively explained in the following way.

From the results of the photo-ionization experiments made by WATANABE [13], the ionization potential of the amino group may reasonably be supposed to decrease by the methyl substitution. Furthermore, the hyperconjugation effect of the methyl group may be thought to decrease the electron affinity of the carbonyl group. Therefore, it may be concluded that the energies of the charge-transfer configurations decrease by the methyl substitution for the hydrogen atom of the amino group and increase by the methyl substitution for the hydrogen atom of the $H-\overset{|}{C}=O$ group. This means that the intramolecular charge-transfer band whose excited state is mainly contributed by the charge-transfer configuration shifts toward longer or shorter wavelengths by the methyl substitution for the hydrogen atom of the amino group or of the $H-\overset{|}{C}=O$ group, respectively. The observed wavelengths of the first $\pi \rightarrow \pi^*$ transition given in Tab. 2 may be said to satisfy this expectation. N-methylformamide is an exceptional case, because the observed peak wavelength of its first $\pi \rightarrow \pi^*$ transition is shorter than that of N-methylacetamide. The reason for this discrepancy is not clear in the present stage of investigation.

References

[1] BERGER, A., A. LOEWENSTEIN, and S. MEIBOOM: J. Amer. chem. Soc. 81, 62 (1959).
[2] SUNNERS, R., L. H. PIETTE, and W. G. SHNEIDER: Canad. J. Chem. 38, 681 (1960).
[3] SAIKA, A.: J. Amer. chem. Soc. 82, 3540 (1960).
[4] BROWN, A. J. R., and E. W. RANDALL: J. molecular Spectroscopy **13**, 29 (1964).
[5] MIZUSHIMA, S., T. SHIMANOUCHI, S. NAGAKURA, K. KURATANI, M. TSUBOI, H. BABA, and O. FUJIOKA: J. Amer. chem. Soc. **72**, 3490 (1950).
[6] TSUBOI, M.: Bull. chem. Soc. Japan **22**, 215, 255 (1949); **24**, 75 (1950).
[7] HUNT, H. D., and W. T. SIMPSON: J. Amer. chem. Soc. **75**, 4540 (1953).
[8] PETERSON, D. L., and W. T. SIMPSON: J. Amer. chem. Soc. **79**, 2375 (1957).

[*9*] NAGAKURA, S.: Molecular Physics **3**, 105 (1960).
[*10*] TSUBOMURA, H., K. KIMURA, K. KAYA, J. TANAKA, and S. NAGAKURA: Bull. chem. Soc. Japan **37**, 418 (1964).
[*11*] KON, H.: Bull. chem. Soc. Japan **28**, 275 (1955).
[*12*] WALSH, A. D.: Trans. Faraday Soc. **42**, 66 (1946).
[*13*] WATANABE, K., and T. NAKAYAMA: J. Quant. Spectr. Radiant. Transfer **2**, 369 (1964).
[*14*] PARISER, R., and R. G. PARR: J. chem. Physics **22**, 466, 767 (1953).
[*15*] KIMURA, M., and M. AOKI: Bull. chem. Soc. Japan **26**, 429 (1953).
[*16*] SENTI, F., and D. HARKER: J. Amer. chem. Soc. **62**, 2008 (1940).
[*17*] POPLE, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).
— Proc. physic. Soc. London **A68**, 81 (1955).
[*18*] LONGUET-HIGGINS, H. C., and J. N. MURRELL: Proc. physic. Soc. London **A68**, 601 (1955).

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