Mean Life Times of the Excited State of $n \rightarrow \pi^*$ Transitions of the Nitroso Group in Cupferron

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The mean life times of the excited state of the $n \rightarrow \pi^*$ transitions of the nitroso group have been computed from observed spectra of cupferron in different solvents. The results are discussed in the light of various possible perturbations of the electronic states.

The color of the monomer C-nitroso compounds and nitrosoamine derivatives originates from the $n \rightarrow \pi^*$ transition bands of the nitroso group, which are observed in the nitrosoamine derivatives around 350 nm and in the monomer of C-nitroso compounds around 700 nm [1]. Haszeldine et al. [2], carried out a systematic study of the UV and IR spectra of N-nitroso compounds, and pointed out that the $n \rightarrow \pi^*$ band of the nitroso group usually observed with nitrosoamines was absent in the UV spectra of N-alkyl-N-nitrosohydroxyl amine. In order to explain this phenomenon, Haszeldine assumed that the non-bonding electron of the nitrogen atom in the nitroso group might be used to form the dimer. However, the presence of dimers in N-nitroso compounds has been denied by Williams et al. [3] and by Hayne et alias [4]. Since it is impossible for cupferron and its salts to be dimerized at the nitrogen atoms of the nitroso group because of the steric hindrance, the $n \rightarrow \pi^*$ transition band near 700 nm could appear. Nevertheless, Yoshimura et al. [5] reported that no absorption bands were observed near 700 nm in the spectrum of cupferron. However, when we conducted absorption measurements, using a spectrophotometer type Beckmann model 15 800 DR monochromator, on solutions of the ammonium salt of cupferron (N-Nitrosophenyl hydroxylamine), a band was observed near 700 nm ($\in$: 0.5 – 70) which could be attributed to the $n \rightarrow \pi^*$ transition of the nitroso group.

In the present work the mean life times of the excited state of the $n \rightarrow \pi^*$ transition of the nitroso group have been computed from observed spectra of cupferron in different solvents. The results are discussed in the light of various possible perturbations of the electronic states.

Mean Life Time of The Excited State

If a molecule is in an excited state, in the absence of an external electromagnetic field, on the average after a time [6]

$$T = 1/A_{mn} \tag{1}$$

it will emit a photon. T is called the MLT of the excited state and A_{mn} is Einstein's coefficient of the transition

$$A_{mn} = \frac{64\,\pi^4\,\nu^3\,e^2}{3\,h}\,D_{mn} = 7.29 \cdot 10^{10}\,\nu^3\,D_{mn} \tag{2}$$

where ν is the frequency of radiation in cm^{-1} and $e^2\,D_{mn}$ is the square of dipole moment of the transition connecting the levels m and n.

$$D_{mn} = 3.98 \cdot 10^{-20}\,\frac{1}{\nu} \int \in(\nu)\,\mathrm{d}\nu \tag{3}$$

where $\int \in(\nu)\,\mathrm{d}\nu$ is the area of the absorption curve. D_{mn} is also related to the oscillator strength, f, given by

$$f = \frac{8\,\pi^2\,m_e\,c\,\nu}{3\,h}\,D_{mn} = 1.085 \cdot 10^{11}\,\nu\,D_{mn}$$

and $$f = 4.32 \cdot 10^{-9} \int \in(\nu)\,\mathrm{d}\nu \quad (\text{Ref.}\ ^{7,8})\,. \tag{4}$$

ν and f values have been determined from absorption measurements. Substituting these values in Eq. (1) to (4), T values have been computed.

The observed characteristics of the absorption band and the T values of the excited state have been collected in Table 1. Two causes can influence the intensity (f value) of the transition [9]: hydrogen bonding and solvent perturbation.

The hydrogen bonding is equivalent to placing a positive charge near the electronic cloud of the nitroso group. The energy arises due to its interaction with the electron cloud. In many cases, the electronic perturbations due to hydrogen bonding and vibration perturbation are expected to be of the same order. The T values decrease with the increase in hydrogen power of the solvent (Table 1).

Solvent perturbation: the oriented solvent dipoles in the case of polar solvents are also expected to disturb the symmetry of the ions, which makes the

Table 1. The wavelengths of the absorption maxima and mean life times of the excited state of the $n \rightarrow \pi^*$ transition of cupferron in different solvents.

Solvent	$\lambda_{\max}$ (nm)	$\nu_{\max}$ (cm^{-1})	$\in$	intensity $f \cdot 10^4$	$T \cdot 10^5$ (s)
Methyl alcohol	760	13158	74	8.65	0.993
Ethyl alcohol	765	13072	26.5	2.97	2.934
iso-Propyl alcohol	765	13072	29.2	3.57	2.440
Dioxan	700	14286	0.5	0.508	14.367

transition forbidden. The *T* values in dioxan are much larger than in ethyl or methyl alcohol, suggesting that the solvent interaction is much smaller than the hydrogen bonding perturbation.

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