PHYSICAL CHEMISTRY

D. N. SHIGORIN, N. A. SHCHEGLOVA, N. S. DOKUNIKHIN, and V. A. PUCHKOV

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

D. N. SHIGORIN, N. A. SHCHEGLOVA, N. S. DOKUNIKHIN, and V. A. PUCHKOV

THE NATURE OF THE HYDROGEN BOND AND ITS INFLUENCE ON THE ELECTRONIC SPECTRA OF MOLECULES

(Presented by Academician A. N. Terenin, February 11, 1960)

A large number of works have been devoted to the influence of the hydrogen bond on the vibrational spectra of molecules. The results obtained in this field characterize manifestations of the hydrogen bond mainly in the electronic ground state. The quantum-mechanical treatment of the three-atomic model A—H ... B, without π-electrons, given by N. D. Sokolov ([1]), shows that the nature of the H-bond in such systems is determined mainly by acceptor–donor interaction; in this case one takes into account the use by the "unshared"electron pair of the donor atom of the s-orbital of the hydrogen atom. The energy of the hydrogen bond (E) in the system A—H ... B is composed of the energies of the acceptor-donor $E_a(s)$ and dipole E_d interactions, i.e. $E = E_d + E_a(s)$. However, even in order to explain the peculiarities of the manifestation of the hydrogen bond in the vibrational spectra of molecules with π-electrons (the strong shift and broadening of the bands of the groups X—H ..., changes in their intensity, the coplanarity effect, etc.), it was necessary to take into account new factors determining its nature. In works ([2–4]) it was shown that the peculiarities of the manifestation of the hydrogen (and also metal-element) bond can be understood only by taking into account π-electron interaction in the formation of the H-bond.

The mechanism by which the electrons of the group X—H ... (whose electron cloud is deformed in the $\sigma \rightarrow \pi$ direction) participate in the π-electron interaction of the molecule is apparently not standard, but depends on the structural features of the molecular system. The peculiarities of the nature of the H-bond in systems with π-electrons in works ([2–4]) are explained by the fact that the measured p-orbital of the hydrogen atom (in the case of a metal-element bond, the p- or d-orbitals of the metal atom), used by the π-electrons of the C = O group, takes direct part in its formation (Fig. 1). In the case under consideration, an additional (quasiaromatic) ring with π-electron interaction arises, involving 6 electrons of the system. Thus, the H-bond (as well as the metal-element bond) is in the general case formed at the expense of three kinds of interactions: E_d,

$E_a(s)$, and π-electron interaction $E_\pi(p)$ with participation of the p-orbital of the hydrogen atom, i.e. $E = E_d + E_a(s) + E_\pi(p)$. The H-bond model taking into account the participation of the measured p-orbital of the hydrogen atom explains (so far qualitatively) all the peculiarities of its manifestation in vibrational and electronic spectra of molecules. In compounds of the type of the enol form of acetylacetone, tropolone, α-oxyanthraquinone, etc., the share of the energy of π-electron interaction reaches almost 90% of the total energy of the H-bond ([3,4]). Without this basis, it is apparently impossible to study the influence of hydrogen and metal-element bonds on the electronic absorption and emission spectra of molecules with π-electrons.

The influence of hydrogen and metal-element bonds on the electronic spectra of molecules was considered by A. N. Terenin ([5]). The hydrogen bond strongly shifts the absorption bands in electronic spectra into the red region. For example, the corresponding absorption band of α-oxyanthraquinone, in comparison with α-methoxyanthraquinone, is shifted into the long-wavelength region by 45 mμ (Table 1). As a result of the formation of intermolecular hydrogen bonds, the absorption bands of indigo in crystals are shifted into the red region, in comparison with the spectrum of its vapors, by 100 mμ ([6]). The reason for the shift of the absorption band in the electronic spec-

toward longer wavelengths consists in the fact that an H bond, incorporated into a conjugated system of bonds, causes a substantial change in the π-electron interaction throughout the molecule and leads to a change in the positions of the energy levels of the system. Owing to the participation of π electrons in the formation of the H bond, an additional ring with π-electron interaction arises, which is equivalent to lengthening the chain with conjugated bonds or increasing the width of the "potential box," and therefore a shift of the absorption band in the electronic spectrum toward the red should be observed, in accordance with the equation:

$$\nu_{N\to N+1} = \frac{h}{8mL^2}(2N+1),$$

where L is the width of the potential box, and N is the number of atoms in the conjugated chain ([7]).

However, in order to study more fully the influence of the H bond on the absorption and emission spectra of molecules with π electrons, it is necessary to determine what happens to the hydrogen bond upon excitation. For this purpose let us consider the most typical case of a coplanar system with π-electron interaction, in which there is a $C = O$ group participating in the formation of the H bond and "bearing responsibility" for electronic excitation. An example of such a system is α-oxyanthraquinone (Fig. 1). Indeed, a study of the electronic-vibrational spectra of anthraquinone and some of its derivatives in frozen solutions at $T = 77°$K showed that the corresponding components of the intense bands are separated from one another on the average by 1664 cm^{-1},

Fig. 1. Electronic model of a ring with an H bond in α-oxyanthraquinone. The dots denote electrons participating in the formation of the ring with π-electron interaction; the p^*-orbital of the H atom is used.

Figure 1: Fig. 1. Electronic model of a ring with an H bond in α-oxyanthraquinone. The dots denote electrons participating in the formation of the ring with π-electron interaction; the p^*-orbital of the H atom is used.

which characterizes the valence vibration of the $C = O$ group in the ground electronic state ([8]). From these data it follows that a large share of responsibility for the position of the electronic level of anthraquinone molecules and its derivatives in the excited state falls on the $C = O$ group. Upon excitation of the molecule as a result of the $n \to \pi^*$ transition (with subsequent transition of the molecule to the triplet state), the π bond of the $C = O$ group is sharply weakened. This is shown by analysis of the electronic-vibrational spectra of anthraquinone and some of its derivatives. The distribution of the intensity of the bands in the spectrum can be explained, in accordance with the Franck–Condon principle, by an increase in the internuclear equilibrium distance (in the $C = O$ group) for the excited electronic level. On the other hand, in α-oxyanthraquinone the probability of participation of the electron pair of the hydroxyl group $O—H$ ... in the π-electron interaction of the system also increases. Thus (Fig. 1), at the moment when a molecule absorbs a quantum of light, changes arise in its structure (redistribution of electron density, internuclear distances, angles) that may lead to strengthening of the ring with the H bond. In the excited state of the molecule, participation of the p-orbital of the hydrogen atom ($O—H \ldots O = C$) in the π-electron interaction of the system apparently becomes still more probable and considerably more effective ([8]). In this connection, the fraction of electronic energy and the rate of its conversion into vibrational energy, as well as the probability of redistribution of the latter over vibrational sublevels, will be increased. Therefore the lifetime of each excited vibration will be shortened, which may lead to blurring of the fine vibrational structure in the luminescence spectra of compounds containing an H bond (since $\tau \Delta E \simeq h$).

Fig. 1. Electronic model of a ring with an H bond in α-oxyanthraquinone. The dots denote electrons participating in the formation of the ring with π-electron interaction; the p^*-orbital of the H atom is used.

Indeed, the luminescence spectra of α-oxy derivatives of anthraquinone (1-oxy, 1,4- and 1,5-dioxy) do not have a fine vibrational structure ([8]). They (Fig. 2, see insert p. 1341) are strongly shifted into the red region and have the form of rather blurred bands. The blurring of these bands is directly related to the state of the carbonyl group directly participating in the formation of the H bond, whereas the luminescence spectra

Table 1

Compound	Absorption λ mμ	Absorption $\Delta\lambda$ mμ	Emission at $T = 77°$K λ mμ	Emission at $T = 77°$K $\Delta\lambda$ mμ	Presence of vibrational structure at $T = 77°$K	IR spectrum of vapors ν cm^{-1}
Anthraquinone	312/π330/p		457/p		Fine vibrational structure	
α-Methylanthraquinone	331/p		455/p		Same	
α-Phenylanthraquinone	322/p		455/p		Same	
α-Methoxyanthraquinone	340/π368/p	0/π0/p	455/p	0/p	Same	
α-Hydroxyanthraquinone	385/π402/p	4534	550/π552/p	97	Strongly broadened band	Strongly broadened band with a maximum at 3050–3100 cm^{-1}

* π –vapors; p –solution

α-derivatives of anthraquinone (α-methyl-, α-methoxy- and α-phenylanthraquinone), which do not contain an H-bond, have a fine vibrational structure (Fig. 2, Table 1). The formation of an H-bond in the molecule of α-hydroxyanthraquinone has such a profound effect on the entire system that it makes it impossible for a fine vibrational structure due to the second carbonyl group to appear.

In the IR absorption spectra, the bands of the stretching vibrations of the groups O–H···and C = O···are shifted into the long-wavelength region and are broadened. Thus, parallelism is observed in the manifestation of the H-bond in the electronic and vibrational spectra (Table 1).

Comparison of the absorption and emission spectra of compounds with and without an H-bond shows that the magnitudes of the shifts of the corresponding

bands in the absorption spectra are considerably smaller than in the emission spectra. For example, the shift $\Delta\lambda$ for α-hydroxyanthraquinone relative to α-methoxyanthraquinone in the absorption spectra is 34 mμ, whereas in the emission spectra it is 97 mμ (Table 1). The electronic emission spectra of vapors of anthraquinone derivatives were first studied in the laboratory of A. N. Terenin ([9]). The magnitude of the "Stokes" shift for compounds with an H-bond is considerably greater than for those without one ([10]). The emission bands are more strongly broadened than the absorption bands. The noted features of the absorption and emission spectra are observed most characteristically in molecules with a coplanar arrangement of the ring bearing the H-bond with respect to the π-electronic system of the molecule. The facts presented can evidently be explained only by the fact that the changes in the structure of the molecule and in its electronic state, which begin at the moment of absorption of an energy quantum $h\nu_p$, are completed in the system only by the moment of emission of its light quanta $h\nu_i$.

It may be assumed that in systems with a hydrogen (or metalloelement) bond the excited electronic level of the system ($^1\Gamma_p^*$), arising from the moment of absorption of an energy quantum, and the electronic level at which the molecule begins to emit energy ($^1\Gamma_i^*$), are not identical. Strengthening of the ring with a hydrogen (or metalloelement) bond in the excited molecule leads to a lowering of its electronic level, as is shown schematically in Fig. 3. A kind of photochemical process occurs with a change in the structure of the molecule; at the same time, the possibility of proton transfer from one oxygen atom to another is not excluded. In molecules with a symmetrical structure (the enol form of acetylacetone, tropolone, etc.) that are in the excited state, movement of the hydrogen atom from one potential well to another is possible. The potential barrier that the hydrogen atom overcomes classically in passing from one well to another must be lowered because of the closeness and equal depth of the potential wells ([11]). However, this question requires special investigation. In the case under consideration, the motion of the electrons is by no means independent of the motion of the nuclei; nonradiative transitions occur with transformation of part of the electronic energy into the vibrational energy of the nuclei. Under these conditions the law of mirror symmetry of Levshin does not

must be strictly obeyed ([12]). What has been said is confirmed by experiment. Indeed, in molecules analogous to those considered, the law of mirror symmetry is not fulfilled ([10]). The question of the relation between luminescence and absorption spectra was considered in works ([14–15]).

Everything that has been said for an intramolecular bond can occur provided that the coplanarity factor is fulfilled. Therefore, in the case of groups H—N—H ... O = C— or H—N—H ... N ≡ N—, etc., for which the coplanarity condition is insufficiently fulfilled, the indicated phenomena may not be observed. In such systems it is possible not to have strengthening of the H-bond upon excitation, but rather its weakening and even rupture, owing to violation of the acceptor–donor interaction and the impossibility of participation of the

Fig. 3. Scheme of possible electronic levels

Figure 2: Fig. 3. Scheme of possible electronic levels

group N—H in π-electron interaction.

Fig. 3. Scheme of possible electronic levels

An increase in interaction upon excitation is also possible in bridges with an H-bond arising between molecules possessing π-electrons, as, for example, in the case of β-oxyanthraquinone ([8]). A phenomenon of this kind was detected from the fluorescence spectra by A. N. Terenin and A. V. Shablya, using 9-(n-oxy)-phenylacridine as an example ([13]). Upon excitation in the bridge

$$\begin{array}{c} \\ \text{C—O—H} \ldots \text{N} \end{array} \qquad -\delta_1 + \delta_2 \qquad -\delta_3$$

the hydrogen atom proves to be more strongly bound to the nitrogen atom,

$$\begin{array}{c} \\ \text{C—O} \ldots \text{H} \ldots \text{N} \end{array} \qquad -\delta_4 \qquad +\delta_5$$

owing to the strengthening of the acceptor–donor and especially the π-electron interaction. Here one should also take into account the increase in stability of the molecule donating the proton, owing to delocalization of the electron (negative charge) in the system. In other words, the dissociation constant of the system

$$\text{Ar—OH} \rightleftarrows |\text{Ar—O}|^- + \text{H}^+$$

upon excitation should increase, but this limiting process is possible only under definite conditions.

The phenomenon of strengthening of the interaction in bridges with an H-bond upon excitation apparently plays an important role in processes of energy migration, which is of great significance in high-molecular compounds (polyamides, proteins, etc.), and also for the study of questions connected with the splitting off and transfer of a proton in excited systems.

Thus, investigation of the hydrogen bond in the excited state is of substantial importance for elucidating its nature and for studying a number of phenomena.

Physicochemical Institute
named after L. Ya. Karpov

Received
10 I 1960

CITED LITERATURE

1. N. D. Sokolov, *DAN*, **82**, 369 (1952); *Usp. fiz. nauk*, **57**, 205 (1955).

2. D. N. Shigorin, *Izv. AN SSSR, ser. fiz.*, **14**, 395 (1953); *ZhFKh*, **27**, 554 (1953); *Spectrochim. Acta*, **14**, 198 (1959); *Probl. fiz. khim.*, vol. 1, 173 (1958).

3. D. N. Shigorin, N. S. Dokunikhin, *ZhFKh*, **29**, 1958 (1955).

4. D. N. Shigorin, M. M. Shemyakin, et al., *DAN*, **108**, 672 (1956).

5. A. N. Terenin, *Photochemistry of Dyes*, Publishing House of the Academy of Sciences of the USSR, 1947, p. 158.

6. D. N. Shigorin, N. S. Dokunikhin, E. A. Gribova, *ZhFKh*, **29**, 867 (1955).

7. M. V. Vol' kenshtein, *The Structure and Physical Properties of Molecules*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 539.

8. D. N. Shigorin, N. A. Shcheglova, R. N. Nurmukhametov, *DAN*, **120**, 1242 (1959).

9. A. V. Karyakin, *ZhFKh*, **23**, 1332 (1949).

10. Yu. V. Naboikin, B. A. Zadorozhnyi, E. N. Pavlova, *Izv. AN SSSR, ser. fiz.*, **23**, 9 (1959).

11. D. N. Shigorin, *ZhFKh*, **23**, 505 (1949).

12. B. I. Stepanov, *Luminescence of Complex Molecules*, Minsk, 1955, p. 172.

13. A. N. Terenin, A. V. Shablya, *Disc. Faraday Soc.*, No. 27, 83 (1959).

14. B. I. Stepanov, *Izv. AN SSSR, ser. fiz.*, **22**, 1367 (1958).

15. B. S. Neporent, *Izv. AN SSSR, ser. fiz.*, **22**, 1372 (1958).

Note: Figure translations are in progress. See original paper for figures.