Further Study on the Forms of Umbelliferone in Excited State

Jerzy Grzywacz and Stanisława Taszner
Institute of Physics, Molecular Spectroscopy Group, Gdańsk, University
and
Jerzy Kruszewski
Institute of Chemistry, Gdańsk, University

Z. Naturforsch. **33a**, 1307—1311 (1978); received April 13, 1978

Absorption and emission spectra of umbelliferone in ethanol-water solution are studied in a wide range of water content. No variations in the absorption spectra were found, whereas the emission spectra proved to be highly sensitive to the volume percentage of water. An interpretation is attempted on the basis of electron density calculations by the SCF PPP CI method for the molecule of umbelliferone and a hypothetical tautomer.

1. Introduction

Absorption and emission spectra of umbelliferone in aqueous solutions are reported in [1]. In the pH range corresponding to the neutral form of the molecule considerable shifting was observed. The luminescence of the neutral form proved to be even more longwave shifted than that of the anionic form, though the positions of the absorption maxima of these forms are reverse. This stimulated us to the present investigation of umbelliferone in ethylalcohol-water solutions. The dielectric permittivity of these mixed solutions changes from 24.3 to 35.8, as the water content increases from 0 to 10%.

The absorption and fluorescence spectra were measured with the apparatus described in [1]. In all measurements purified and dehydrated alcohol and twice destilled water were used. The dye concentration was the same in all mixed solutions.

2. Results of Measurements

Figures 1—3 show absorption and emission spectra at different water content in solutions.

The absorption shows no remarkable change when the water content is varied between 0 and 90%. On the other hand, the fluorescence depends strongly on the water content. As the water content increases from 0 to 10%, a long wavelength band emerges at 485 nm at the cost of the short wave band a. 405 nm becoming predominant above 3% of water

An isoemission point is found at 420 nm. Moreover, a band is perceptible at 510 nm as well as the 460 nm band, characteristic for the umbelliferone anion. The latter anionic band becomes more and more predominant above a water content of 10%.

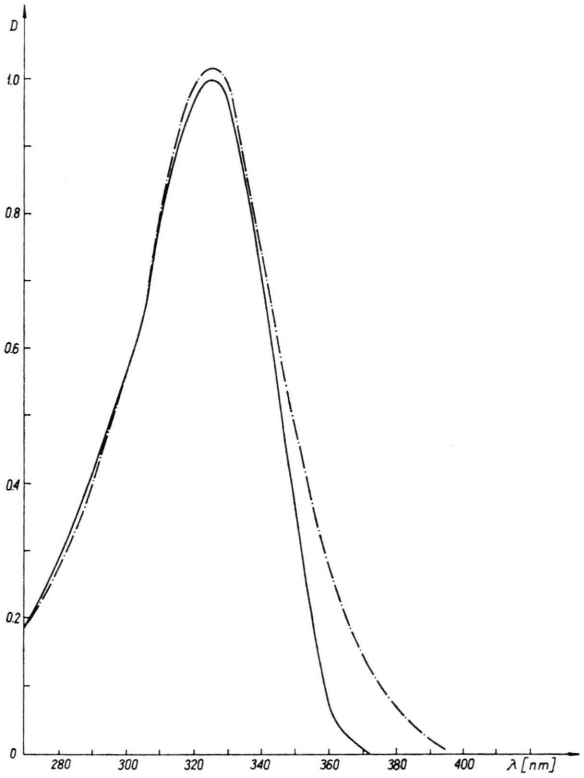


Fig. 1. Absorption spectra of umbelliferone in aqueous-ethanol solutions (concentration $C = 5 \times 10^{-5}$ m/l, cuvette thickness $l = 1$ cm); solid curve 1% water content; dashed curve 90% water content.

Reprint requests to Assist. Prof. Dr. J. Grzywacz, Institute of Physics, University of Gdańsk, 80-952 Gdańsk, Poland.

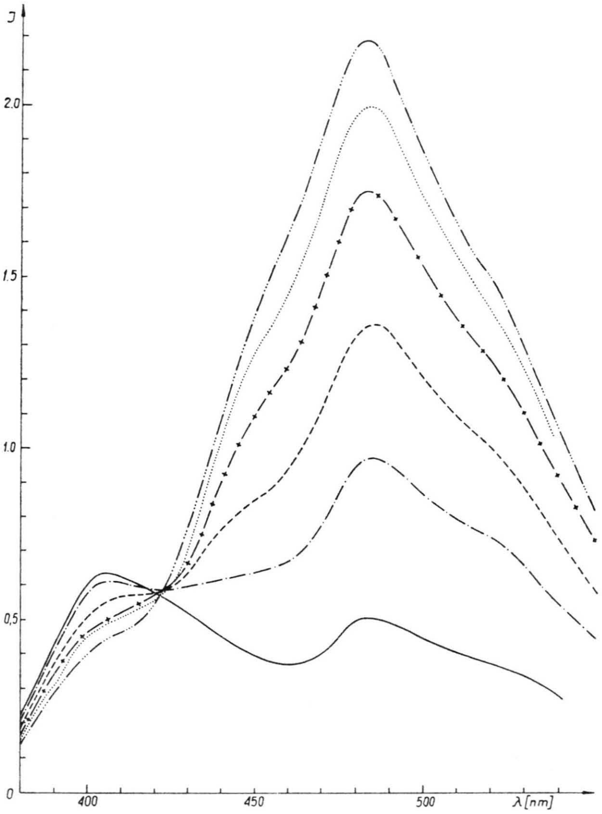


Fig. 2. Emission spectra of umbelliferone in aqueous-ethanol solutions (I = intensity in arbitrary units, λ_{exc} = 324 nm, $C = 5 \times 10^{-5}$ m/l, $l = 0.1$ cm). Curves for water content:

——— 1%
–·–·– 3%
– – – – 5%
–+–+ 7%
······ 8%
–···– 10%

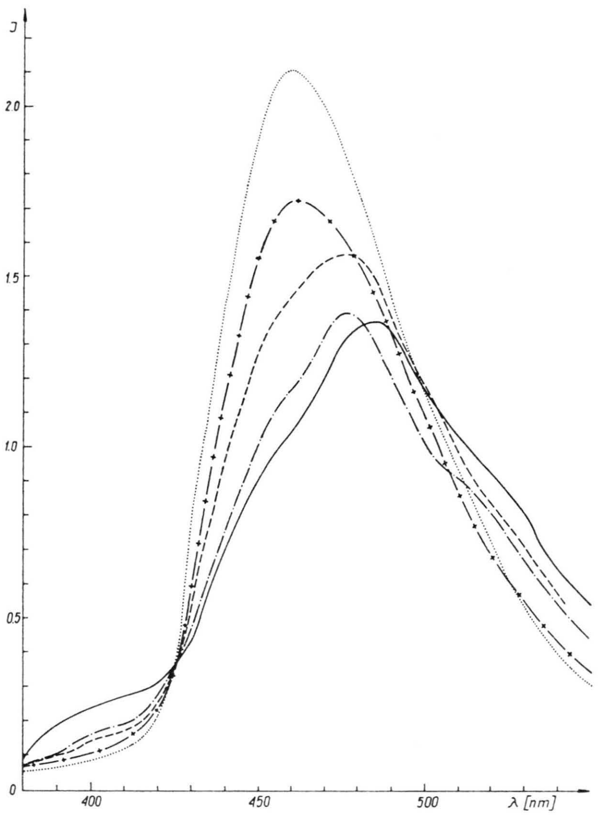


Fig. 3. Emission spectra of umbelliferone in aqueous-ethanol solutions (I = intensity in arbitrary units, λ_{exc} = 340 nm, $C = 5 \times 10^{-5}$ m/l, $l = 0.1$ cm); curves for water content:

——— 10%
–·–·– 20%
– – – – 30%
–+–+ 50%
······ 70%

3. Discussion and Interpretation of the Results

The spectroscopic behaviour of umbelliferone in alcohol-water solutions as reported above is similar to that of other derivatives of cumarin containing a hydroxylic group, especially 4-methylumbelliferone (4-MU). Numerous authors have attempted to interpret the presence of two emission bands as well as the absence of variations in the absorption spectrum as an effect of water and the hydroxylic group.

Initially, the 485 nm band was attributed to an exciplex arising in excited state due to protonisation of the 4-MU molecule [2, 3]. Another structure has been proposed by Nakashima and Sousa [4], who interpreted the unknow form as a phototautomer of the neutral 4-MU molecule. This assumption has been tested by Trozzolo, Dienes and Shank [5] by means of laser spectroscopy. Zinsly [6] attributes the 485 nm band to an ion pair. His point of view is shared by Beddard, Carlin and Davidson [7], who established as a necessary condition for the occurence of the 485 and 510 nm bands in the emission of the cumarine derivatives the presence of a hydroxylic group in the solvent. This proves that no monoprotonated exciplexes occur, and it permits the surmise that the 485 nm maximum is attributable to a phototautomer or zwitterion. In Ref. [7] the following reaction scheme in the excited state has been suggested:

$$\begin{tikzcd} & & A_n^{-*} \\ N^* \arrow[r] & X^* \arrow[ur] \arrow[dr] & \\ & & Y^* \arrow[uu] \end{tikzcd}$$

where N^*, A_n^{-*} = neutral and anion molecules in the excited state, X^*, Y^* = forms emitting fluorescence at 485 and 510 nm.

As shown by our measurements, umbelliferone in alcohol-water solutions behaves very much like 4-MU. The emission spectrum of umbelliferone also exhibits an interesting band at 485 and 510 nm. Hence, all the conclusions drawn from the unknown form of 4-MU can be extended to the corresponding form of umbelliferone. Since it is very difficult to decide experimentally whether the emission at 485 nm is due to a zwitterion or phototautomer, we have taken recourse to semiempirical methods of calculations of the π-electron distributions in the ground and excited singlet state. The calculations visualize the changes occuring in the electron cloud and dipole moment by excitation to the state S_1. They moreover permit the calculation of the theoretical absorption spectrum. We carried out the calculations by the π-electron SCF method in the approximation of Pople, Parr and Pariser, by mixing of single excited configurations. Using an ODRA 1204 computer, the program was carried out according to the following scheme:

1. The set of parameters in Table 1 was chosen ensuring the best agreement between the measured and calculated absorption spectrum of umbelliferone (Figure 4).
2. The π-electron density distribution as well as the theoretical value of the dipole moment of umbelliferone in the ground and excited state were calculated (Table 2, 3).
3. For the fixed set of parameters, the absorption spectrum of the tautomer as well as its density distribution and dipole moment in the ground and excited state were obtained (Table 4, 5).
4. The same calculations were performed for the zwitterion molecule.

Table 1. Semi-empirical parameters from PPP method applying the Mataga-Nishimoto approximation for calculating the integrals γ.

Atom	$-I^z_\mu$ (eV)	$\gamma^z_{\mu\mu}$ (eV)	Z	$\beta^z_{\mu c}$ (eV)
C	11.42	10.84	1	− 2.15
C=O	13.8	11.6	1	− 2.0
$C-O^-$	21.2	11.8	2	− 2.3
C−OH	32.1	23.2	2	− 1.6
C−O−C	35.5	23.2	2	− 2.0
$C=OH^+$	29.0	23.2	1	− 2.0

I^z_μ valence state ionization potential,
$\gamma^z_{\mu\mu}$ monocentric electronic repulsion integral,
$\beta^z_{\mu c}$ core resonance integral,
Z number of electrons on the fixed atom.

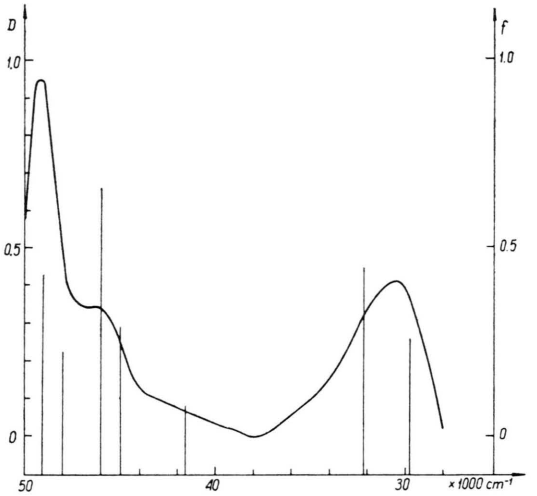


Fig. 4. Comparison of experimentally measured absorption spectrum of umbelliferone in ethanol (solid line) and the calculated spectrum (vertical lines). f = oscillator strength, D = optical density.

In our calculations, we paid especial attention to the phototautomer molecule. Umbelliferone is an aromatic π-electron system in which considerable

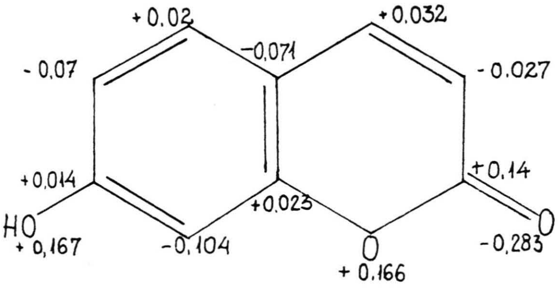


Table 2. Charge distribution for umbelliferone in the ground state.

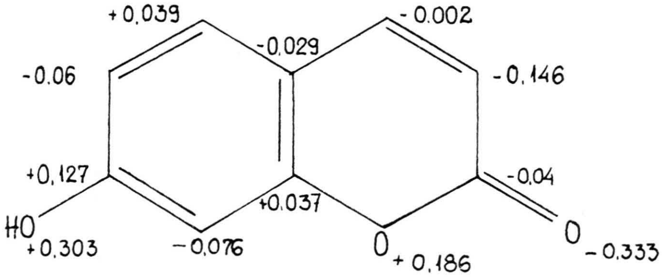


Table 3. Charge distribution for umbelliferone in excited state.

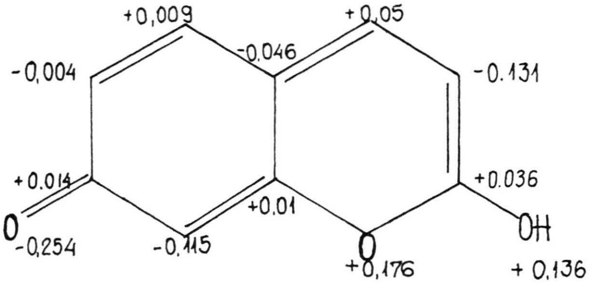


Table 4. Charge distribution for tautomer in the ground state.

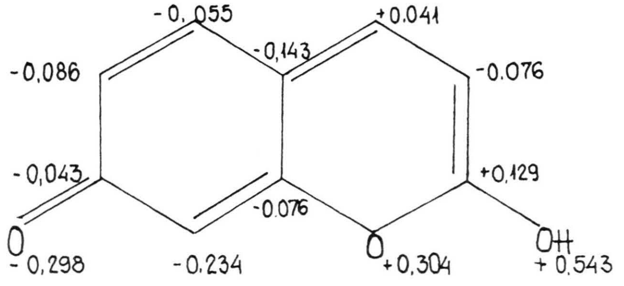
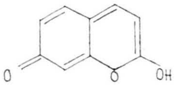
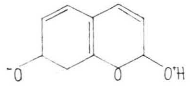


Table 5. Charge distribution for tautomer in excited state.

delocalization is known to take place. By comparison, the zwitterion exhibits a more marked separation of charge. The theoretical absorption spectra of the zwitterion and phototautomer (Table 6) obtained with the set of semiempirical parameters chosen are an evidence in favour of the tautomer. The absorption spectrum of the latter is much more strongly shifted towards longer wavelengths in accord with the emission at 485 nm.

Table 6. Absorption spectra calculated by PPP CI method for: A) tautomeric form, B) zwitterion form (f = oscillator strength).

A		B	
			
λ (nm)	f	λ (nm)	f
425.3	0.616	347.0	0.469
304.4	0.185	318.6	0.247
289.0	0.148	251.1	0.007
271.8	0.010	246.0	0.402
248.0	0.418	217.8	0.299
220.9	0.111	215.3	0.935
209.9	0.420	201.1	0.170
197.6	0.023	199.7	0.265

On the initial assumption that the form X* is a phototautomer, one can propose an interpretation of the two emission bands based on the calculated dipole moments of the molecules as well as the π-electron distribution in the ground and excited state S_1:

The isoemission point in the emission spectra of umbelliferone at various contents of water (1—10%) can be interpreted as due to tautomeric equilibrium in the excited state. The varying polarity of the medium surrounding the molecule is the deciding factor for the equilibrium. The stabilization of tautomeric forms by the solvent has been described in the paper of Kobayashi and Kawabata [8], who established that the stabilization is caused by dipole-dipole interaction between the dipoles of the solute and the polar solvent. The energy difference ΔE^S between the two forms in a solvent with dielectric constant ε is given by the expression

$$\Delta E^{S} = \Delta E^{V} - (\mu_A{}^2 - \mu_B{}^2)\, a^{-3} \cdot \left\{x(1-l\,x)^{-1} + b\, f_e\left[1-\exp\left(-\frac{c}{2}\right)\right]\right\}, \qquad (1)$$

where ΔE^V is the difference in energy of the two forms in the vapour state, a = the Onsager radius, μ_A and μ_B the dipole moments of the respective tautomeric forms, b is a parameter which ensures fitting to the experimental values, and

$$x = \frac{\varepsilon - 1}{2\varepsilon + 1}; \quad f_e = \left[\frac{(\varepsilon-2)(\varepsilon+1)}{\varepsilon}\right]^{1/2};$$

$$l = 2\frac{n_D{}^2 - 1}{n_D{}^2 + 2}; \quad c = \mu_S(\mu_A - \mu_B)(r^3\, kT)^{-1};$$

r = averaged distance between the point dipoles of the solute and of the solvent molecules,
n_D = refractive index of solute molecule,
μ_S = dipole moment of solvent.

In Eq. (1) the first term of the sum in parentheses corresponds to interaction of the polarizable molecule and dipolar solvent, and the second term to dipole-dipole interaction between the solute and solvent molecules. In the ground state, umbelliferone has a calculated dipole moment close to zero (0,6 D) and no tautomeric equilibrium is observed for a lack of dipole-dipole interaction. Throughout the entire ε-range of the solvent only one ground state form of umbelliferone occurs. In the excited state the dipole moment of umbelliferone is non-zero, amounting to as much as 2.61 D, that of the tautomer being 4.26 D so that dipole-dipole interaction is present, stabilizing the one or other form according to the ε-value of the medium. As the medium changes from $\varepsilon = 24.3$ to $\varepsilon = 35.8$ (at 25 °C), the content of the more strongly polar phototautomeric form increases whereas that of excited umbelliferone decreases.

The charge density distribution in the excited tautomer molecule permits an interpretation of the changes in emission spectra at high water contents in the solution (Figure 3). A positive charge of 0.543 being localized on the oxygen atom of the hydroxylic group in the tautomer, detachment of a proton and formation of an excited anion can occur already in an aqueous medium with weakly basic properties. In the ground state of umbelliferone the oxygen atom of the OH carries a charge of 0.167, i.e. several times smaller than that occuring in excited tautomer, and considerably weaker acidic properties are observed [1]. The distribution of charges in excited umbelliferone thus anables us to predict how it transforms into a tautomer in a medium of higher polarity.

4. Concluding remarks

Some supplementary tests are still required to prove unequivocally the existence of the tautomer and the presence of tautomeric equilibrium. Thus, it is necessary to check whether the curve of

$$\ln \frac{N_\mathrm{A}}{N_\mathrm{B}} = f\left\{x(x - l\,x)^{-1} + b\,f_\mathrm{e}\left[1 - \exp\left(-\frac{c}{2}\right)\right]\right\} \qquad (2)$$

is a straight line (N_A and N_B denoting the numbers of molecules of the respective tautomers). To this aim, it will be necessary to measure the intensity of the emission spectra as a function of the content of water very accurately. This in turn will require a special setup for measurements of the emission spectra ensuring complete operation stability of the lamp and the whole device over periods of time. We hope to proceed to such measurements in near future.

Acknowledgement

This work was performed within the Problem MR I 5.

[1] J. Grzywacz and S. Taszner, Bull. Acad. Polon. Sci. Ser. Math. Astr. Phys. **25**, 447 (1976).

[2] C. V. Shank, A. Dienes, A. M. Trozzolo, and J. Myer, Appl. Phys. Lett. **16**, 405 (1970).

[3] R. K. Baur, A. Kowalczyk, and M. Berndt, Bull. Acad. Polon. Sci. Ser. Math. Astr. Phys. **22**, 637 (1974).

[4] M. Nakashima, J. A. Sousa, and R. Clapp, Nature London Phys. Sci. **235**, 16 (1972).

[5] A. M. Trozzolo, A. Dienes, and C. V. Shank, J. Amer. Chem. Soc. **96**, 4699 (1974).

[6] P. E. Zinsli, J. Photochem. **3**, 55 (1974).

[7] G. S. Beddard, S. Carlin, and R. S. Davidson, J. Chem. Soc. Perkin **2**, 262 (1977).

[8] M. Kobayashi and S. Kawabata, Spectrochim. Acta **33a**, 549 (1977).