

Field diagram for a molecule appearing in charge transfer state in polar solution

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Paper dedicated to Professor Jozef Heldt on the occasion of his 70th birthday

Abstract

A theoretical consideration of potential energy of a molecule appearing in charge transfer state has been performed and the expressions for potential energy of the S_0 and the S_1 states versus the strength of reaction field of the solvent have been derived. The field diagram plotted on the basis of these expressions represents, in a natural way, inhomogeneous broadening of electronic spectra for charge transfer systems in a solution where this factor is of great importance. The accounting of the charge transfer process was carried out treating it formally as a permanent growth of the excited state electric dipole moment of the solute with the strength of its reaction field. The field diagram of the S_0 and the S_1 singlet states and appropriate probability distributions over different fields of reaction was shown to open a door for describing the basic properties of molecules appearing in charge transfer states taking into account inhomogeneous broadening of its spectra.

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1. Introduction

It is well known in spectroscopy that the large width of absorption and emission bands of complex organic molecules is largely due to existence of a continuous set of vibrational sublevels in each electronic state. In addition, the spectroscopic properties of dye molecules in solution are influenced by the surrounding medium even when specific interactions or chemical bonds are absent. The theory of spectral shifts of solute spectra owing to intermolecular interaction in solution was developed in papers [1–3].

In 1970, it was shown [4–6] for the first time that apart from molecular vibrations there is another cause of the substantial broadening of electronic spectra of organic molecules in solution, namely, the fluctuations of the structure of the solvation shell surrounding the molecule. The variations of the local

electric field caused by the thermal fluctuations of the shell structure and interaction of this field with a solute dipole lead to a statistical distribution of the frequencies of the electronic transitions and, therefore, to inhomogeneous broadening (IB) of the solute spectrum. To take into account the IB factor the spectroscopic properties of a dye solution may be analysed by treating its elementary cell (solvate), which includes a fluorescent organic molecule and its immediate surroundings [7]. Solvates have different local electric fields due to the statistical variations of the cell structure, hence, electronic transitions of the same solutes in a set of solvates are accomplished in different fields. To describe this situation, a solvate field diagram (representing the potential energy of the solvate versus the reaction field strength R) was introduced phenomenologically [8] and supported by both the statistical approach [9] and the classical treatment of the solution solvates [7]. In the last approach the luminophor was supposed to have constant dipole electric moments in the ground and the excited states and appropriate expressions were derived for this case in [7–9].

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Later, such diagrams were considered by many authors; sometimes, instead of the field coordinate an indefinite general configurational coordinate of reaction was employed. The exploration of similar schemes makes it easier to present inhomogeneous broadening of electronic spectra of polar molecules in solution and to understand its various spectroscopic and luminescent manifestations, especially, a possibility of selective excitation and registration of individual states of inhomogeneous ensemble. The last fact directly creates conditions for the observation of a number of spectroscopic effects arising upon the red-edge excitation (REE), so-called, the REE effects [6,7,10].

In this paper, employing a classical model of a solvate, we present an energy field diagram for a description of inhomogeneous spectra characteristics of solutes with changeable in the S_1 state electric dipole moment. The model could be applied for a study of photophysics of the solutes appearing in charge transfer (CT) excited states and explains spectroscopic effects emerging at wavelength selective excitation and registration of luminescence of such solutes.

2. Model of a solution containing molecules with changeable dipole moment in the excited state

Let us consider a solvate of polar solution containing a solute molecule (dye, organic molecule, luminophor, itd), as an elementary cell of solution. Firstly, we shall follow the approach suggested for a solute molecule with a rigid skeleton, which possesses a stable geometrical configuration in the ground (g) and the excited (e) states and, hence, has the constant dipole moments.

In each elementary cell of such a solution the near surrounding is polarised due to the dipole moment, μ_g , of the solute, thus giving rise to a reaction field, R_1 , in the cell:

$$R_1 = f\mu_g, \quad (1)$$

where f is a factor of reaction field.

Inhomogeneous broadening occurs because, as a result of the thermal motion of molecules in a solution, a set of cells has different solvate shells and, therefore, different reaction fields R , which fluctuate somewhat relative to the mean value of R_1 (Eq. (1)). As the 0–0 transition frequency of the solute depends on the reaction field intensity, this means that in the solution there is an inhomogeneous set of solvates with solutes distributed in frequencies of the 0–0 transitions.

In the simplified model under consideration it was assumed [7] that two forces are responsible for the elementary cell state:

- i the polarising force which is caused by the presence of a constant dipole moment in the solute molecule and induces the reaction field R in the cell;
- ii the restoring force which is caused by the action of the reaction field on the dipole molecules of solvent forming the solvate shell.

The cell is in its equilibrium state when the two forces compensate each other. This state is the most stable one, and it is characterised by the reaction field R_1 .

A configuration dependent energy of the cell versus its reaction field R can be determined as the work required to restructure the solvate from its equilibrium state with the field R_1 to the state with the field R and, as was shown in [7], this work is equal to

$$E_g(R) = \frac{(R - R_1)^2}{2f}. \quad (2)$$

As it can be seen from Eq. (2), a plot of the potential energy of the solvate configurational interactions versus the internal reaction field have a parabolic shape with its minimum at the equilibrium, where $R = R_1$ takes place.

It is convenient to introduce the total solvate energy, which is the sum of the configurational and electronic energies of the solvate molecules. In thermodynamics it may be called the free energy of the system. Since we are considering electronic transitions only of the solute, the electronic energy of all the solute shell molecules can be assumed invariable and equal to zero. We will call the elementary cells of solution with the solute in its ground and excited states unexcited and excited solvates, respectively. Assuming the electronic energy of the ground state of the solute to be equal to zero, the total unexcited solvate energy will be described by Eq. (2).

The electronic transition frequency of the solute as a function of the reaction field can be written [3,7] as

$$h\nu = h\nu_0 - \Delta\mu R, \quad (3)$$

where $\Delta\mu = \mu_e - \mu_g$, μ_g and μ_e are the dipole moments of the solute in the ground and the excited states, respectively, and ν_0 is the 0–0 transition frequency of the free (non-interacting) molecule. Here, in Eq. (3) we will treat only the strongest dipole–dipole orientational interactions which play the most important role in the IB of electronic spectra.

Upon absorption of a quantum $h\nu$ and the transition of the solvate to the excited state, the energy of the solvate, becomes equal to

$$E_e(R) = E_g + h\nu. \quad (4)$$

Now replasing $h\nu$ by expression (3) and E_g by expression (2) in the last formula we get

$$E_e(R) = E_g + h\nu = h\nu_0 + \frac{(R - R_2)^2}{2f} - \frac{\Delta R(R_2 + R_1)}{2f}, \quad (5)$$

where

$$\Delta R = R_2 - R_1 = f(\mu_e - \mu_g) = f\Delta\mu, \quad (6)$$

and R_2 is the equilibrium value of the reaction field in the excited state of our solvate.

As follows from the last expression, the $E_e(R)$ curve represents the parabola centred at $R = R_2$.

Let us consider the most common case corresponding to increasing of a dipole moment while excitation, i.e. when inequality $\mu_e > \mu_g$ holds. Then from Eq. (1) follows that $R_2 > R_1$, and the upper parabola is shifted to the stronger field intensities R and lifted up by the value

$$h\nu_0 - \frac{\Delta R(R_2 + R_1)}{2f}. \quad (7)$$

Obviously, for molecules with the constant dipoles μ_e and μ_g , ΔR will be constant and we obtain the well-known case for the description of inhomogeneous broadening [7,8].

However, this is not the case for the CT states as they are characterised by a dipole moment growth in the excited state from $\mu_e^{(1)}$ up to $\mu_e^{(2)}$ value, the latter one may be several times larger than $\mu_e^{(1)}$ [11]. Therefore, the charge transfer process can mathematically be accounted as a function of $\Delta\mu(R)$, because it is an adiabatic reaction along the configurational coordinate R which can be treated as natural coordinate of the CT process. Hence, suppose, that for treating CT molecules one can formally introduce a dependence of the excited dipole μ_e on the intensity of the electric field R . Let this function for the fields range $R \leq R_2$ be given as

$$\Delta\mu(R) = \Delta\mu^{(0)} + (\mu_e^{(2)} - \mu_e^{(1)}) \exp\left(C \frac{R - R_2}{R - R_1}\right), \quad (8)$$

where

$$\Delta\mu^{(0)} = \mu_e^{(1)} - \mu_g, \quad (9)$$

and presents the Franck–Condon difference between the dipole moments in the ground μ_g and the local-excited (LE) states, $\mu_e^{(1)}$. For the sake of simplicity we assume that the dipole moment of the ground state is constant, i.e. μ_g is the constant, and then the $E_g(R)$ function may be described by (2). Constant C allows us to change the shape of $\Delta\mu(R)$ function in a broad scale.

On the basis of the experimental data on kinetics of instant spectra of dimethylaminobenzonitrile (DMABN) emission, one may assume that the growth of the excited dipole may be in many cases approximated with (8) at $C > 1$. This dependence will be close to that given in [12] and showing the relation of dipole moment and twisting angle θ as the coordinate of reaction (θ is a mutual orientation of dimethyl groups and organic moiety planes)

$$\mu_e(\theta) = \mu_{LE} + (\mu_{CT} - \mu_{LE}) \sin^2 \theta.$$

Now we will calculate the shape of the potential curve $E_e(R)$ in the excited S_1 state taking into account $\Delta\mu(R)$ function in Eq. (3). If we put Eq. (8) into Eq. (3), we obtain the following formula from Eq. (4)

$$E_e(R) = E_g + h\nu = h\nu_0 + \frac{(R - R_1)^2}{2f} - (\mu_e^{(2)} - \mu_e^{(1)}) \exp\left[C \frac{R - R_2}{R - R_1}\right] R. \quad (10)$$

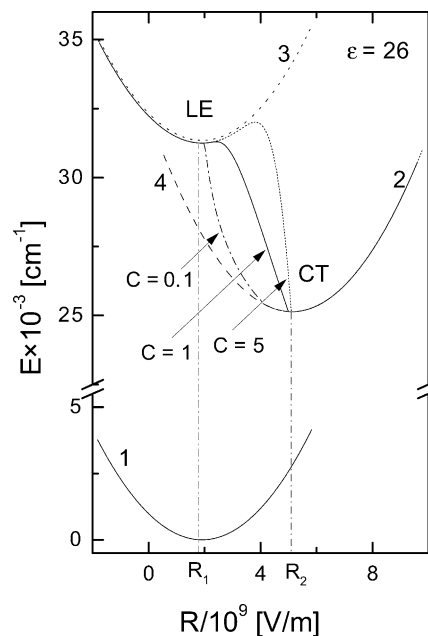


Fig. 1. The potential energies of DMABN molecules in solution in the ground (1) and the excited (2–4) states vs. the local electric field intensity R ; solutes in the CT state (2) and for the same solutes, but assuming constant dipoles corresponding to $\mu_e^{(1)} = 6D$ (3) and $\mu_e^{(2)} = 16D$ (4) values. Dielectric constant of solvent is $\epsilon = 26$.

This function is a parabola of the second-order of the value and from (10) we have

$$E_e = h\nu_0 - \Delta\mu^{(0)} R_1 \quad \text{at} \quad R = R_1,$$

and

$$E_e = h\nu_0 - \Delta\mu^{(0)} R_2 - (\mu_e^{(2)} - \mu_e^{(1)}) R_2 \quad \text{at} \quad R = R_2.$$

The function (10) is valid for the R values in the range $R \leq R_2$. For the larger intensities, i.e. $R \geq R_2$, the change of the dipole moment $\Delta\mu = \mu_e^{(2)} - \mu_g$ is maximal (see (8)) and may be treated as a constant. This situation presents the full charge separation and, therefore, we can use Eq. (5) assuming $\mu_e(R) = \mu_e$ for this case. Both solutions (5) and (10) must be launched at the point where $R = R_2$ and, in fact, it takes place.

In Fig. 1 the potential curves for both the ground, the $E_g(R)$, and the excited, the $E_e(R)$, states calculated with the help of Eqs. (2)–(10) are shown. The Onsager's model [3,7] for calculation of the factor of reaction f was applied. The following parameters of solution, which are valid for DMABN molecules [13], were taken: $\mu_g \approx \mu_e^{(1)} \approx 6D$, $\mu_e^{(2)} = 16.5D$, $a = 0.45$ nm, where a is the Onsager's radius. The potential curves are given in Fig. 1, for DMABN molecules in polar solvent, with dielectric constant $\epsilon = 26$, and with various values of C constant from (8). We can use here, as in the previous papers [7,8], the term field diagram presenting the dependence of potential energy of solvate on the electric field intensity R .

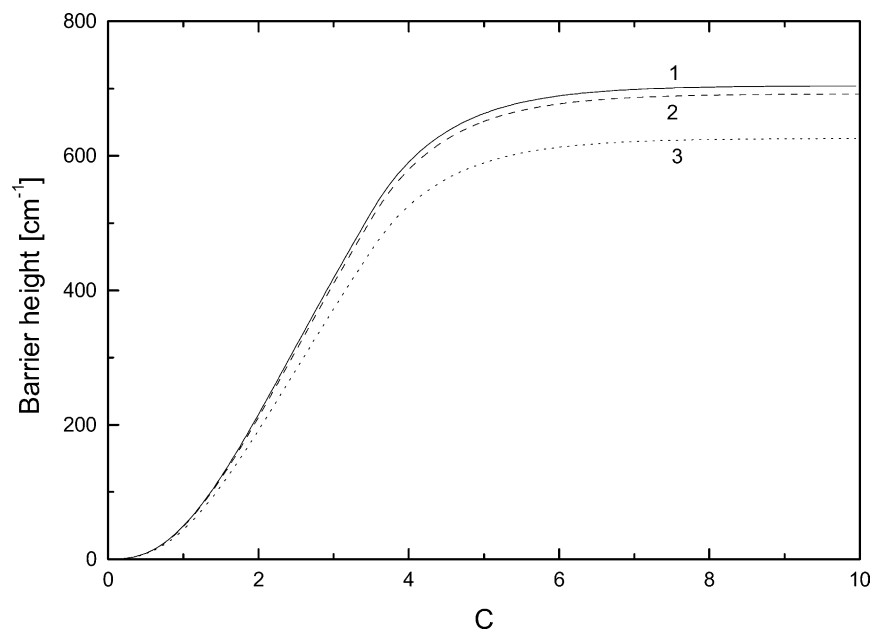


Fig. 2. The height of the barrier between the LE and the CT states vs. constant C for different dielectric constants: (1) $\epsilon = 10$, (2) 26 and (3) 40.

3. Discussion

We can see in Fig. 1, that the curve $E_g(R)$ is a parabola centred at $R = R_1$ (equilibrium configuration of solvate dipoles) because we have taken electric moment μ_g unchangeable. For comparison we also present in the same figure two other curves 3 and 4 in the S_1 state. The curve 3 corresponds to the case when $\Delta\mu(R) = \Delta\mu^{(0)}$ constant, as if we have a system without charge transfer, and this case is well known and described [7–9] for the solutes with a rigid skeleton. The curve 4, in turn, presents the case of the same rigid molecules but with larger dipole moment differences $\Delta\mu = \mu_e^{(2)} - \mu_g$. The curves $E_e(R)$ in the excited state are more complicated. The left branch of the $E_e(R)$ may have local minima and barriers for parameters $C > 1$. The appropriate dependencies are noted in Fig. 2 and show that the height of the barrier grows with the constant C from $\sim 200 \text{ cm}^{-1}$ at $C = 2$ up to $\sim 800 \text{ cm}^{-1}$ for $C = 10$ and further the curves reach saturation. The barriers in all cases show a growth depending on polarity of the solvents. Here, it is worth pointing out that independent phenomenological study [14] based on high pressure measurements allow note for DMABN the barriers of the same value between the LE and the CT states (Fig. 2).

The character of the $E_e(R)$ curve strongly depends on the dielectric properties of a solution. The appropriate curves for the same solute molecules DMABN in nonpolar solvent, e.g. $\epsilon = 2$ and in highly polar, $\epsilon = 40$, are presented for a comparison in Fig. 3 and they illustrate the last statement. As seen from this figure all processes of solvation and charge transfer should take place at lower reaction fields, the R_1 and R_2 intensities are equal $0.7 \times 10^9 \text{ V/m}$ and $2 \times 10^9 \text{ V/m}$ in hexane against $2.5 \times 10^9 \text{ V/m}$ and $5 \times 10^9 \text{ V/m}$ in glycerol. This circumstance allows to understand

quantitatively the well-known fact of more effective charge separation in the excited state in well polar environment. Obviously, broadening of electronic spectra in nonpolar solvent is absent. This fact was established experimentally, for instance, for DMABN in hexane and cyclohexane [15,16] (Fig. 3).

We can show the interpretation of some important photoprocesses in solutions containing CT molecules using the

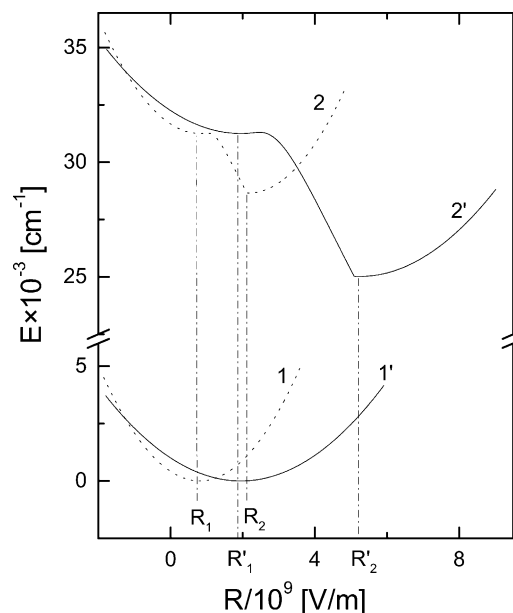


Fig. 3. The potential energies of DMABN molecules in the ground (1 and 1') and the excited (2 and 2') states vs. the local electric field intensity R in nonpolar solvent (2') with dielectric constant $\epsilon = 2$ and in high polar solvent (2') having $\epsilon = 40$.

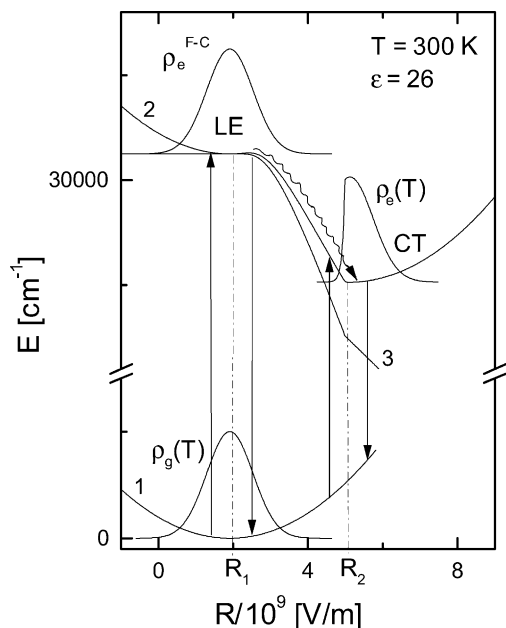


Fig. 4. The potential energies of DMABN molecules in solution in the ground (1) and the excited (2) states, the 0–0 transition wavenumbers (3), the distributions of equilibrium unexcited, the $\rho_g(T)$, and excited, the $\rho_e(T)$, and initial Franck–Condon, μ_e^{FC} , solvates vs. the local electric field intensity R . Dielectric constant of solvent is $\epsilon = 26$.

field diagram presented in Fig. 4 for DMABN molecules in solvents like ethanol with dielectric constant $\epsilon = 26$.

The absorption and luminescence transitions of the LE and the CT bands are shown by the vertical arrows in Fig. 4 in agreement with the Franck–Condon principle which is in force here. The relative position of the $E_g(R)$ and $E_e(R)$ curves in the field diagram is such that their difference, i.e. the 0–0 frequency for the definite diapason of fields, permanently drops (see curve 3) with an increase of the field intensity R . As seen, the 0–0 frequency change in the range of $R_1 < R < R_2$ is as large as $\sim 9000 \text{ cm}^{-1}$ for solvents having dielectric constant $\epsilon \sim 26$. This fact creates the principal groundation for a spectral broadening mechanism, if to take into consideration simultaneous existence of the solvates with various reaction fields in a solution. For equilibrium conditions the solvate distributions can be written with the help of the Boltzmann law over potential energies of the ground and the excited states presented by the formulas (2) and (10). The results of such calculations shown by the curves $\rho_g(T)$ and $\rho_e(T)$ are given in Fig. 4. As seen from the figure the thermal factor is very essential and leads to a quite broad distribution over the fields R or the wavenumbers of the 0–0 transitions in different solvates. The halfwidth of the $\rho_g(T)$ function depends on the temperature and reaches $\sim 420 \text{ cm}^{-1}$ at the room temperature. The equilibrium distribution of the CT excited state, $\rho_e(T)$, is also broad and for our field diagram has the halfwidth $\sim 300 \text{ cm}^{-1}$ (Fig. 4).

It is obvious that the modelling of absorption and emission of solution should account for such distributions for the following reasons:

- i they provide significant broadening of both the absorption and emission spectra comparable with vibrational one;
- ii the character of this broadening may be inhomogeneous.

It is essential to note the significant concentrations of the unexcited solvates with lower 0–0 transition frequencies in the field range between the R_1 and the R_2 (interval $3\text{--}4 \times 10^9 \text{ V/m}$ for ethanol). In other words, there are the solvates structures which could upon the proper excitation to populate the states close to the CT states. Therefore, it means that it is possible that the direct excitation and further registration of longwavelength emission of the CT states and their intensity may be high enough. The selective spectroscopy methods enable us to excite and observe in emission at appropriate physical conditions various separate states, i.e. states with different local fields along the horizontal axis R in Fig. 4 if conditions of inhomogeneous broadening are valid.

The standard Stokes excitation at the maximum of absorption band populates the LE configurations of the solutes creating the inequilibrium distribution, ρ_e^{FC} , in the excited state and initiates two important processes responsible for appearing of dual luminescence:

- i emission from the LE states and
- ii non-radiative process of the charge transfer (or transformation of the LE configuration to the CT ones) populating the CT states; the latter could be treated as energy relaxation (wave arrow in Fig. 4) along the left branch of the $E_e(R)$ curve. The relative intensities of the LE and the CT bands of emission are controlled by relaxation process constants, which, in turn, are influenced by both intramolecular and intermolecular factors.

The REE effects are caused by the excitation of ‘the red’ solvates with a higher electric strength $R \sim R_2$ and could be observed, if relaxation processes within the excited state are slow, in comparison with their lifetime. The spectra of such solvates characterise a ‘redder’ location in the scale of wavelengths. Cutting off relaxation process upon the long-wavelength excitation provides the conditions for emission only from the CT band. Thus, instead of dual emission at the Stokes excitation, we will observe only luminescence of the CT band. This interesting consequence of the presented diagrams of potential energies was recently supported experimentally in our papers [15,16], where an anomalous inhomogeneous broadening of DMABN molecules was found and studied in detail. In polar solvents, at excitation at the maximum of the absorption band, $\lambda_{ex} \sim 270 \text{ nm}$, both the LE and the CT bands was monitored. Subsequent decrease of the excitation wavelength noted the drops of the LE band participation and the growth of the CT relative contribution in luminescence. Lastly, at the far Antistokes excitation, $\lambda_{ex} \sim 410\text{--}440 \text{ nm}$, only the broad band of emission in the red part of the spectrum, near the CT band localisation, was observed.

4. Conclusion

Accounting for the CT processes results in a considerable change of the potential energy curve of the excited state, namely, it appears that the left branch is with the faster decrease, and with the deeper minimum shifted to the higher values of the electric field intensities R . The barriers for LE \rightarrow CT reactions are noted as well. The height of the ones grows with the constant C and depends on the polarity of the solvent. The value of dielectric constant of solvent drastically changes the shape of potential energy curves, and, therefore, the CT process and the dual luminescence characteristics.

The presented field diagrams may be used for an explanation of various features of the CT reactions, such as the rate constants of relaxation LE \rightarrow CT, the absorption and the emission spectra, the REE effects and some others. In particular, due to the field diagram one can easily interpret the effect of 'disappearing' of the LE contribution to the total dual emission of DMABN in polar solvents with shifting the excitation towards the red part of spectra [13,14].

Choosing the reaction field R as the coordinate of the CT reaction is convenient and allows to evaluate the electric reaction fields in different stages of these processes.

A more detailed treatment of polar solution photophysics using the suggested approach will be presented soon.

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