Volgograd State University

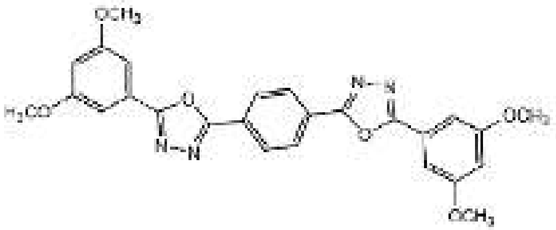
ANATOLY IVANOV

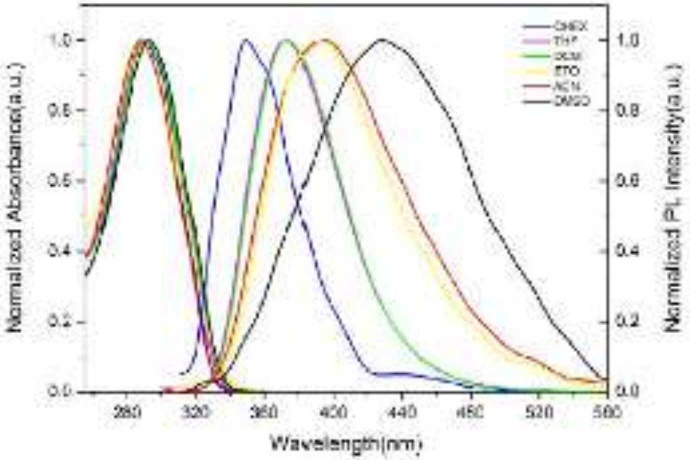
Charge Transfer Symmetry Breaking in Excited Quadrupolar Molecules in Protic Solvents

X INTERNATIONAL VOEVODSKY CONFERENCE «PHYSICS AND CHEMISTRY OF ELEMENTARY CHEMICAL PROCESSES»

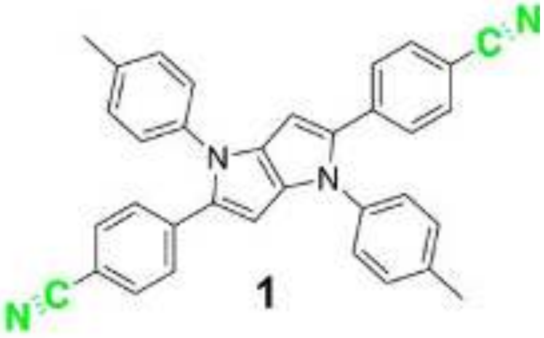
Novosibirsk, 06.09.2022

Excited state charge transfer symmetry breaking





Lingyan Meng [a], Fangyi Chen [a], Fu-Quan Bai [b], Binglian Bai [c], Haitao Wang [a,*], and Min Li [a]
J. Photochem. Photobiol. A, 2019



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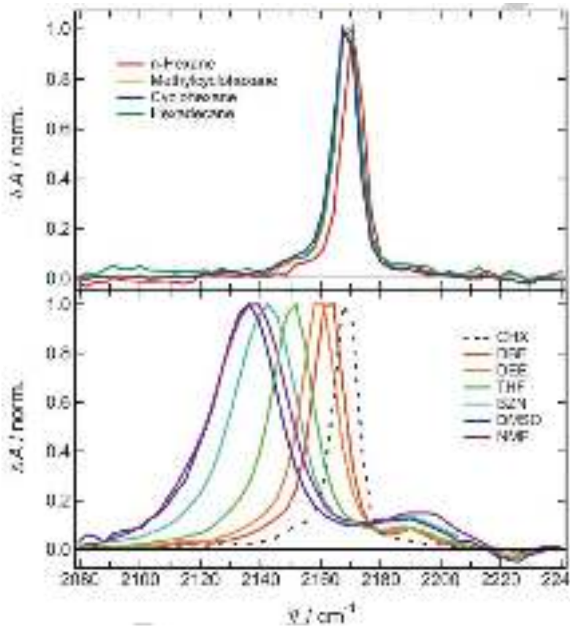


B. Dereka, A. Rosspeintner, M. Krzeszewski, D. T. Gryko, E. Vauthey. Angew. Chem., Int. Ed. 55, 15624 (2016).

The model of charge transfer symmetry breaking

$$A_L - D - A_R \xrightarrow{h\nu} A_L^{-1/2} - D^{+1} - A_R^{-1/2} \xrightarrow{SB} A_L^{\delta_L} - D^{+} - A_R^{\delta_R}.$$

$$\Psi = a_L\varphi_L + a_R\varphi_R$$

$$A_L^{-1} - D^{+1} - A_R^{0} \rightarrow \varphi_L$$

$$A_L^{0} - D^{+} - A_R^{-1} \rightarrow \varphi_R$$

$$H_0 = \begin{pmatrix} E_L & V \\ V & E_R \end{pmatrix}$$

$$K = a_L^2 a_R^2 \frac{e^2}{\varepsilon_{im} R_{LR}} \qquad H_C = \gamma \left[\langle\Psi|\hat{P}_L|\Psi\rangle\hat{P}_R + \langle\Psi|\hat{P}_R|\Psi\rangle\hat{P}_L \right] \qquad \gamma = \frac{e^2}{2\varepsilon_{im} R_{LR}}.$$

$$W = -\frac{D^2\mu^2\Delta f}{r_d^3} \qquad H_S = -\lambda \left[\langle\Psi|\hat{P}_L|\Psi\rangle\hat{P}_L + \langle\Psi|\hat{P}_R|\Psi\rangle\hat{P}_R \right] \qquad \lambda = \frac{2\mu^2\Delta f}{r_d^3} = \lambda_1\Delta f$$

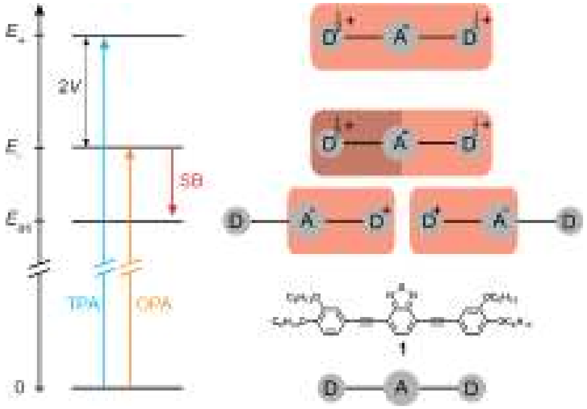
$\Delta f = f(\varepsilon_s) - f(n^2)$ with $f(x) = 2(x-1)/(2x+1)$

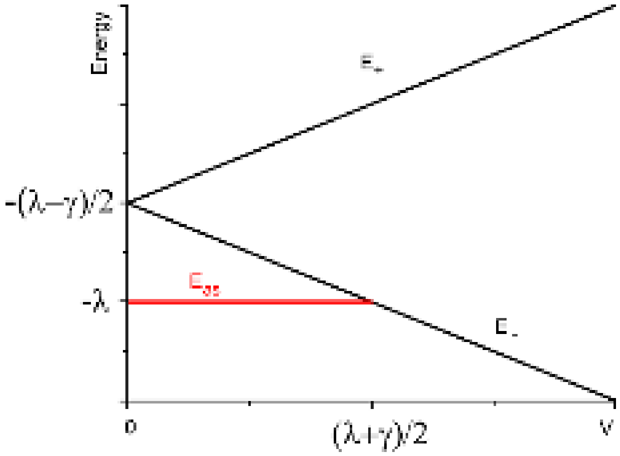
$$D = a_L^2 - a_R^2, \; H\Psi = E\Psi, \; H = H_0 + H_C + H_S$$

A.I. Ivanov, B. Dereka, E. Vauthey. J. Chem. Phys. **146**, 164306 (2017)

A.I. Ivanov, V.G. Tkachev. J. Chem. Phys. 151, 124309 (2019)

The model of charge transfer symmetry breaking





$$(a_L - a_R)[(\lambda+\gamma)a_R a_L + V + \lambda + E] = 0,$$

$$(a_L + a_R)[-(\lambda+\gamma)a_R a_L - V + \lambda + E] = 0.$$

$$a_L = a_R \qquad E_+ = V - (\lambda-\gamma)/2;$$

$$a_L = -a_R \qquad E_- = -V - (\lambda-\gamma)/2$$

$$a_L^2 = \frac{1}{2} \pm \sqrt{\frac{1}{4} - \frac{V^2}{(\lambda+\gamma)^2}}$$

$$D = a_{\mathrm{L}}^2 - a_{\mathrm{R}}^2 = 2a_{\mathrm{L}}^2 - 1$$

$$D = 2a_L^2 - 1 = \sqrt{1 - \frac{4V^2}{(\lambda+\gamma)^2}}.$$

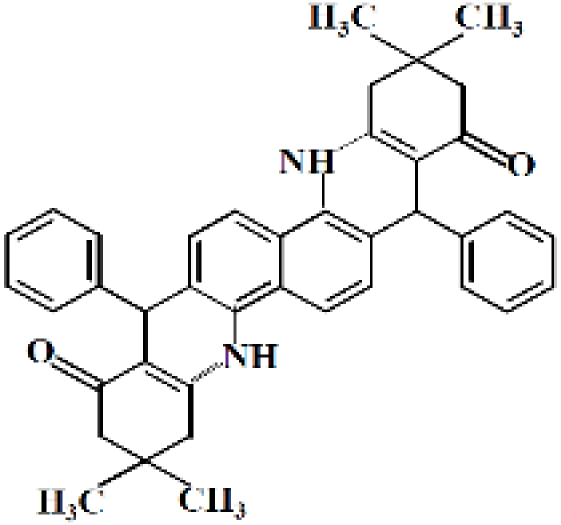
$$E_{as} = -\lambda$$

Асимметричное решение существует при условии $2V < \lambda+\gamma$

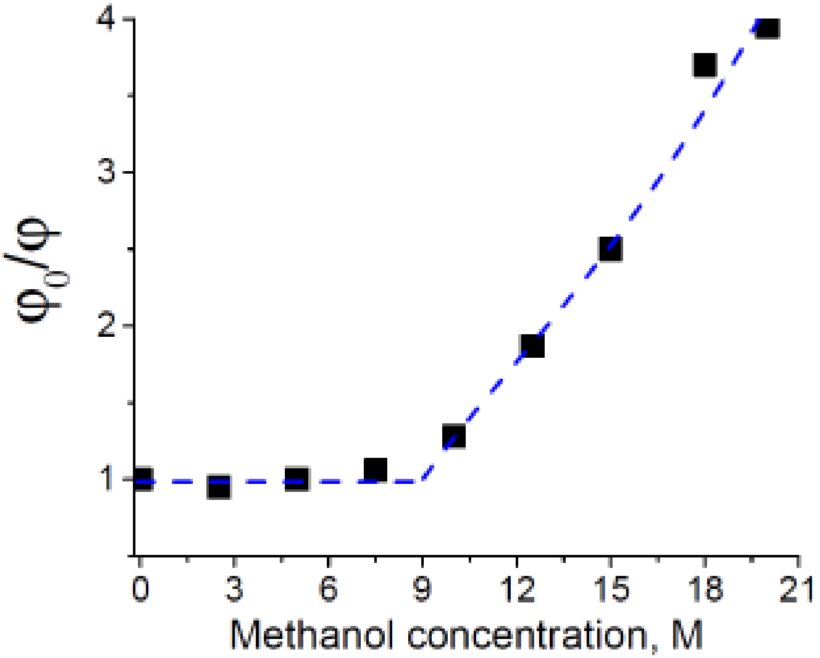
Экспериментальные свидетельства нарушения симметрии в возбужденном состоянии.

Проявление нарушения симметрии в оптических спектрах

- octahydroacridino[4,3-c]acridine-1,9 (2H, 5H) dione



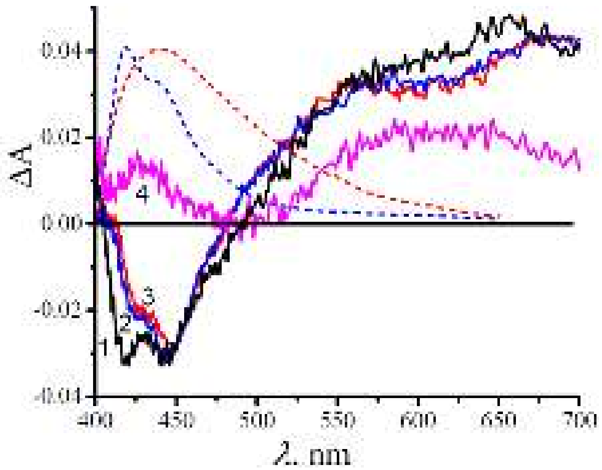
DMF - Methanol mixtures

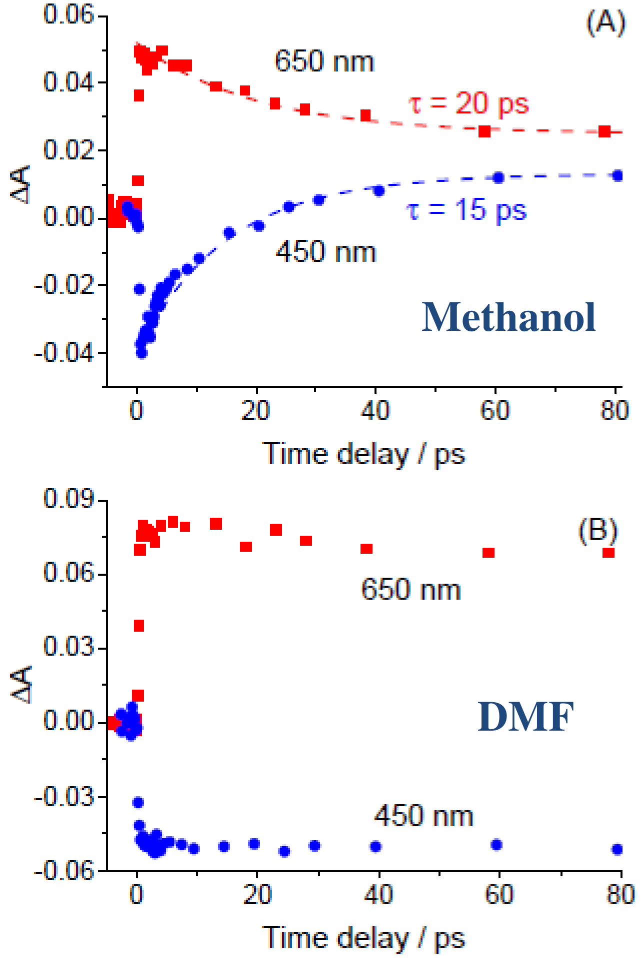


S. L. Bondarev, T. F. Raichenok, S. A. Tikhomirov, N. G. Kozlov, T. V. Mikhailova, A. I. Ivanov. J. Phys. Chem. B 2021, 125, P. 8117

Экспериментальные свидетельства нарушения симметрии в возбужденном состоянии.

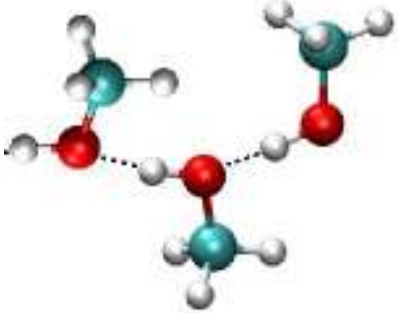
Проявление нарушения симметрии в оптических спектрах





S. L. Bondarev, T. F. Raichenok, S. A. Tikhomirov, N. G. Kozlov, T. V. Mikhailova, A. I. Ivanov. J. Phys. Chem. B 2021, 125, P. 8117

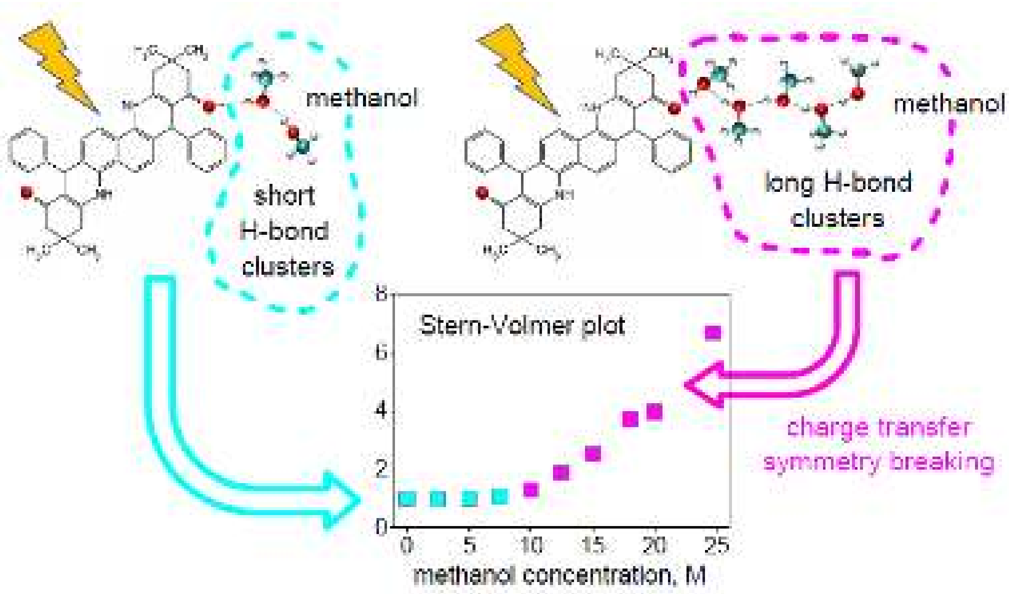
Clustering of methanol



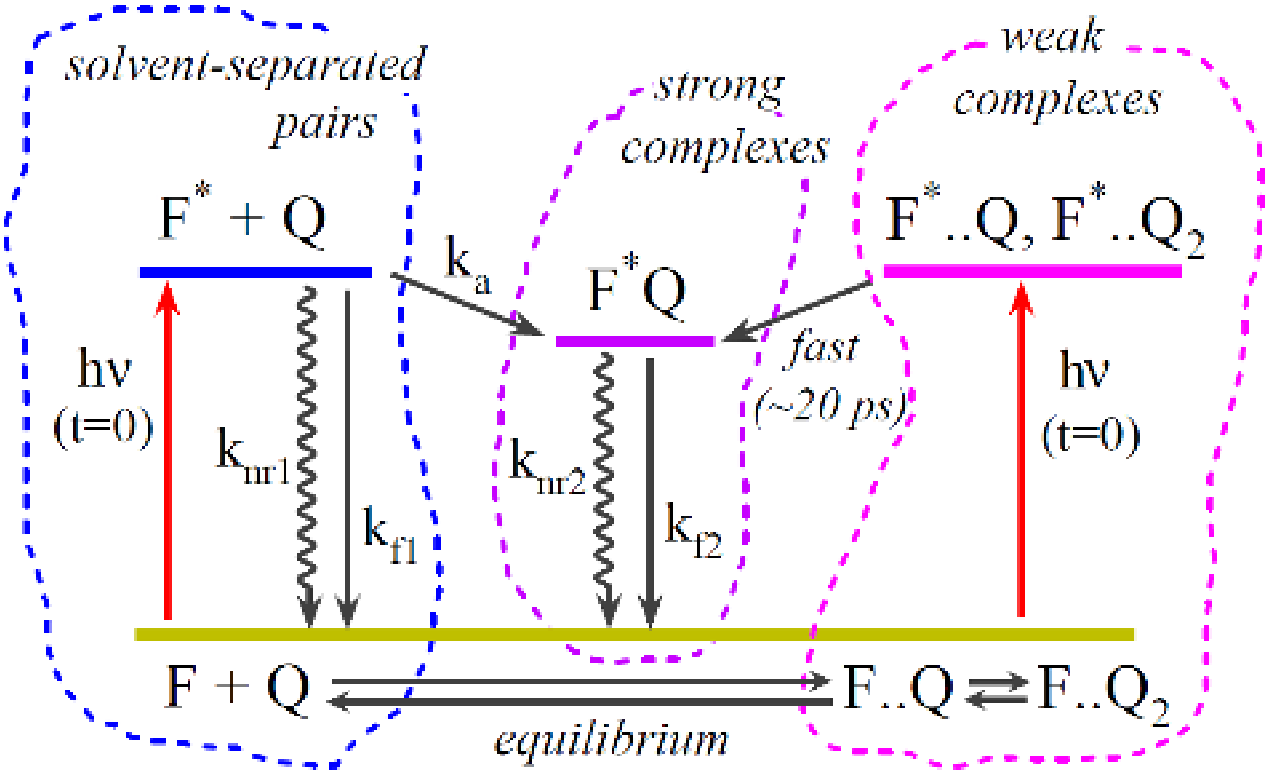
- Some facts known from the literature:
- Methanol molecules form chains.
- There are practically no branches.
- There are closed structures (loops).
- Cooperative effect - the longer the chain, the stronger the hydrogen bonds.
- The lifetime of a hydrogen bond in methanol is 5 – 7 ps.
- The average number of molecules in a methanol cluster is 5.9 (pure methanol, simulation results).
- The formation of a loop is possible only in long clusters.

Clustering of alcohol molecules and its role in the quenching of acredinedione fluorescence

1. In the ground state, short and long chains of methanol form weak hydrogen bonds with the acredine dione molecule. (The absorption spectra in protic and aprotic solvents are almost the same.)
2. Hypothesis: in the excited state, only sufficiently long clusters form strong hydrogen bonds with methanol, leading to symmetry breaking and fluorescence quenching.
3. Sufficiently long clusters appear only in mixtures with a high concentration of alcohol.



Mechanism of Acredine Dione Fluorescence Quenching with Methanol



Fluorescence quenching kinetics

$$\begin{aligned}\frac{d[F^*]}{dt} &= -k_1[F^*] \\ \frac{d[F^*Q]}{dt} &= k_a[Q][F^*] - k_2[F^*Q]\end{aligned}$$

$$F + Q \overset{K}{\rightleftharpoons} F..Q$$

$$F..Q + Q \overset{K/2}{\rightleftharpoons} F..Q_2$$

$$[F..Q] = K[F][Q], \quad [F..Q_2] = 0.5K[F..Q][Q]$$

$$[F] = \frac{[F]_0}{W}, \quad [F..Q] + [F..Q_2] = \frac{[F]_0(W-1)}{W}$$

$$W = 1 + K[Q] + 0.5K^2[Q]^2.$$

$$[F^*](0) = \frac{1}{W}, \quad [F^*Q](0) = \frac{W-1}{W}$$

$$k_1 = k_{f1} + k_{nr1} + k_a[Q]$$

$$k_2 = k_{f2} + k_{nr2},$$

$$\begin{aligned}[F^*](t) &= \frac{1}{W}\exp(-k_1 t) \\ [F^*Q](t) &= \frac{1}{W}\left[\frac{k_a[Q]}{k_2 - k_1}(\exp(-k_1 t) - \exp(-k_2 t)) + (W-1)\exp(-k_2 t)\right]\end{aligned}$$

$$I(t) = k_{f1}[F^*](t) + k_{f2}[F^*Q](t)$$

$$\varphi = \frac{1}{W}\left[\frac{k_{f1}}{k_1} + \frac{k_{f2}}{k_2}\left(\frac{k_a}{k_1}[Q] + W - 1\right)\right]$$

It is necessary to determine the concentration of the quencher [Q] and its dependence on methanol concentration.

Anderson-Schulz-Flory model

$$r(n) = P_{\mathrm{b}}^{n-1}\left(1 - P_{\mathrm{b}}\right)$$

$$\langle n \rangle = \frac{1}{1 - P_{\mathrm{b}}}$$

$$\Psi_s = \sum_{n \geq s} r(n) = P_{\mathrm{b}}^{s-1}$$

$$C_{\mathrm{all}} = \frac{C}{\langle n \rangle}$$

$$C_s = \frac{C \Psi_s}{\langle n \rangle}$$

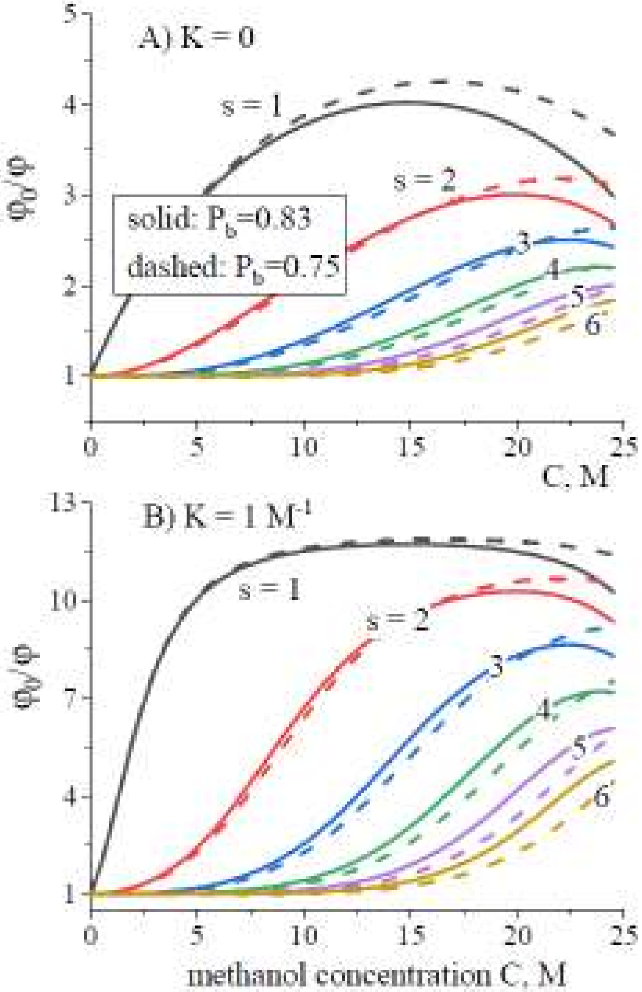
$$P_{\mathrm{b}} = \bar{P}_{\mathrm{b}} \frac{C}{\bar{C}}$$

$$\bar{C} = 24.75\ \mathrm{M}$$

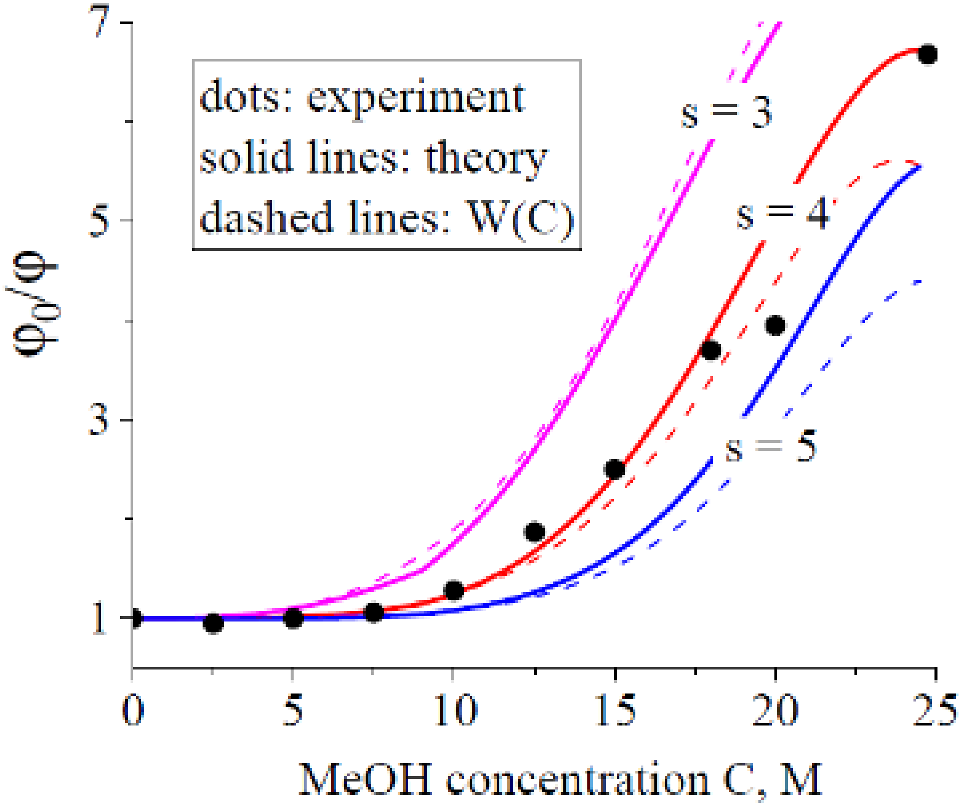
$$[Q] = C_s = C \left(\bar{P}_{\mathrm{b}} \frac{C}{\bar{C}} \right)^{s-1} \left(1 - \bar{P}_{\mathrm{b}} \frac{C}{\bar{C}} \right)$$

P_b=0.83

Влияние параметров s и K на график Штерна-Фольмера

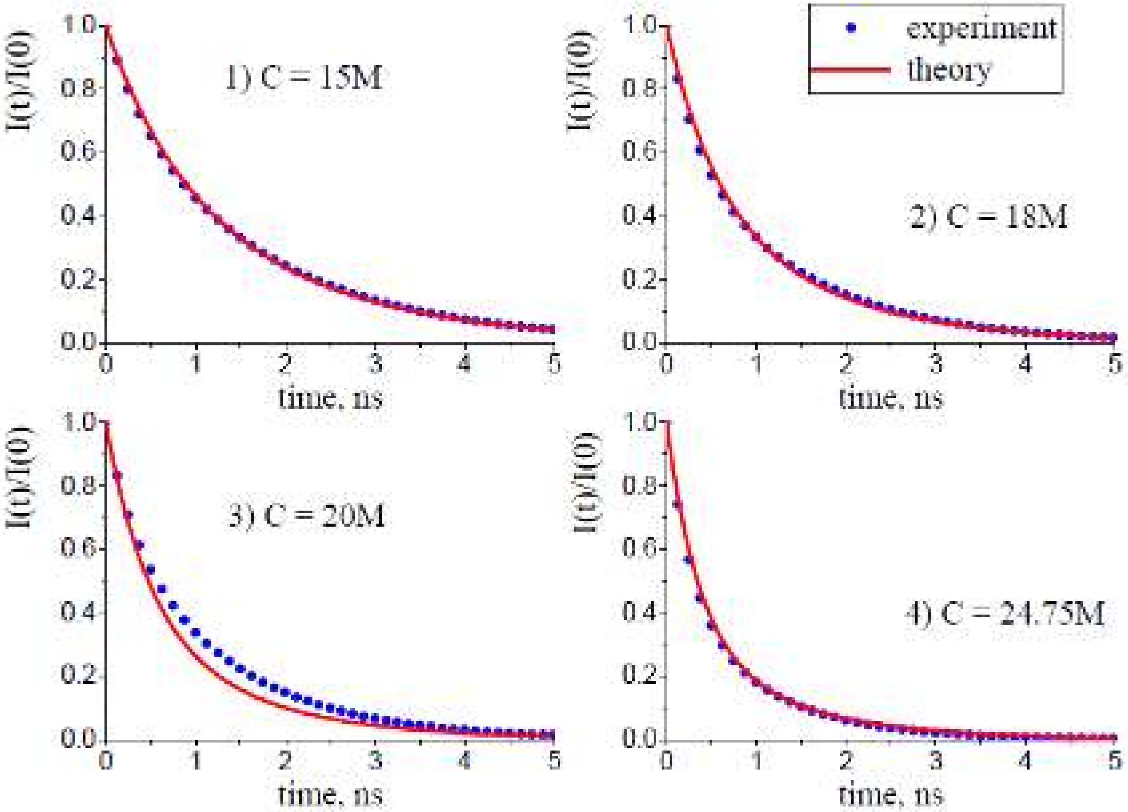


Fitting Stern-Volmer dependence



k_a = 0.18 M^{-1} ns^{-1} , K = 0.9 M^{-1}.
k_{nr2} = =8 k_{fl}

Фитинг кинетики затухания флуоресценции

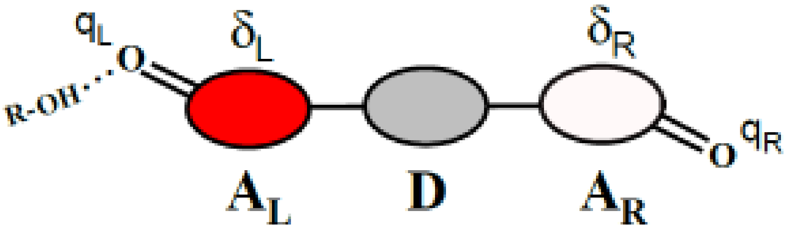


Conclusions

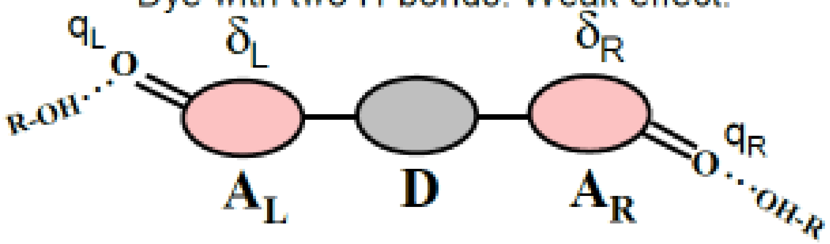
1. The proposed model of fluorescence quenching by methanol gives a quantitative description of the kinetics and quantum yield of fluorescence in mixtures of methanol and DMF.
2. The threshold value of the concentration at which quenching occurs depends critically on the minimum length of a cluster capable of inducing symmetry breaking in acridine dione.
3. The degree of symmetry breaking in molecules depends on the interaction energy that causes the symmetry breaking. This opens up a fundamentally new possibility for the experimental study of hydrogen bond clustering in alcohols and their mixtures with aprotic solvents.

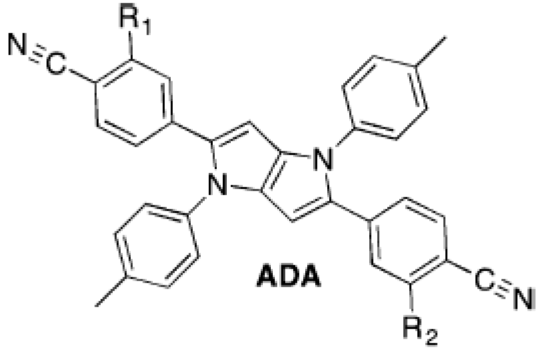
A simple model of H-bond effect on excited-state charge transfer symmetry breaking in quadrupolar molecules

Dye with one H-bond. Strong effect.



Dye with two H-bonds. Weak effect.





ADA

$$\delta q_L = \alpha(a_L^2 - 1/2) = \alpha D/2$$

$$\delta q_R = -\delta q_L.$$

$$G_{HB}^{L} = G_{HB}(0) + a\delta q_L + b(\delta q_L)^2 + \ldots = G_{HB}(0) - AD + \lambda_{HB}D^2/2 + \ldots,$$

$$G_{HB}^{R} = G_{HB}(0) - a\delta q_L + b(\delta q_L)^2 + \ldots = G_{HB}(0) + AD + \lambda_{HB}D^2/2 + \ldots,$$

$$G_1 = G_0 + G_{HB}^{L},$$

$$G_2 = G_0 + G_{HB}^{L} + G_{HB}^{R}.$$

$$G_0 = -V\sqrt{1-D^2} - \lambda_0 D^2/2$$

Influence of H-bonds on symmetry breaking

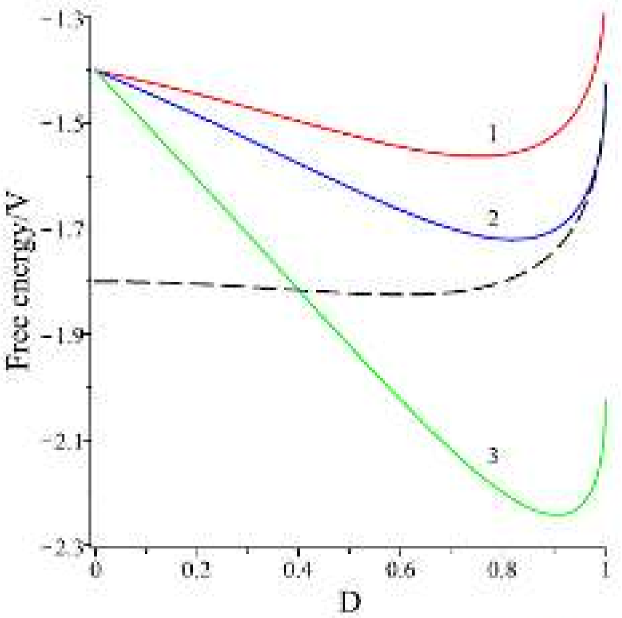


FIG. 2. Dependence of the free energies G_1 (solid lines) and G_2 (dashed line) on the dissymmetry degree for three values of the parameter A: $A = 0.2$ (1, red), $A = 0.4$ (2, blue), $A = 1.0$ (3, green). $\Delta f = 0.5$, other parameters in V units are: $\lambda_{\rm fL} = 0.85$, $\lambda_{\rm or} = 0.8$, and $G_{\rm HB}(0) = -0.4$.

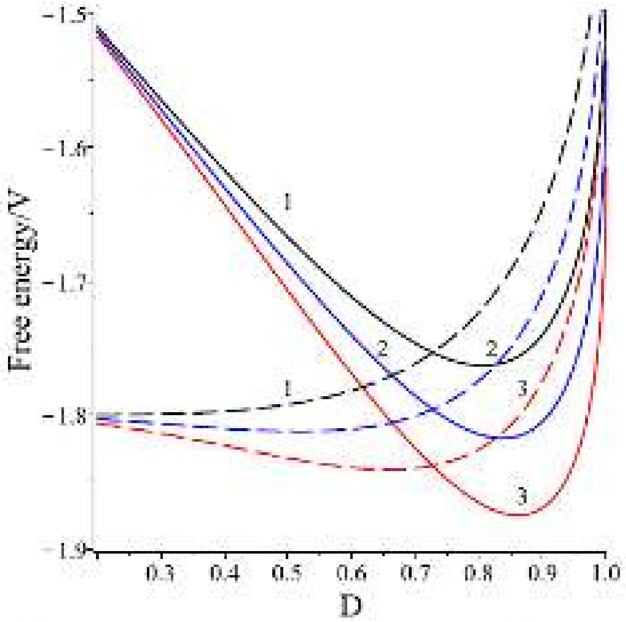


FIG. 3. Dependence of the free energies G_1 (solid lines) and G_2 (dashed lines) on the dissymmetry degree for three values of the solvent polarity $\Delta f = 0.2$ (1, black), $\Delta f = 0.4$ (2, blue), $\Delta f = 0.6$ (3, red). Parameters in V units are: $\lambda_{\rm fL} = 0.85$, $\lambda_{\rm or} = 0.8$, $G_{\rm HB}(0) = -0.4$, $A = 0.55$.

Influence of H-bonds on symmetry breaking

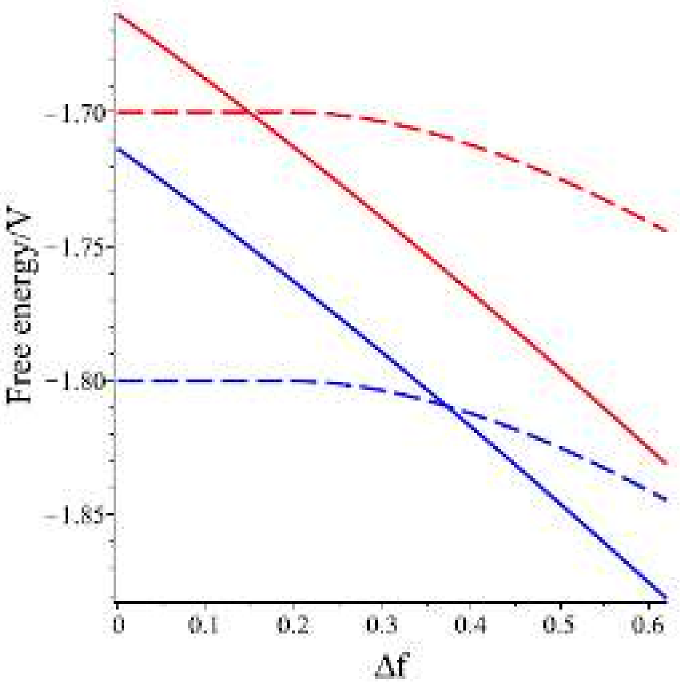


FIG. 4. Dependence of the equilibrium values of free energies $G_1^{(\min)}$ (solid lines) and $G_2^{(\min)}$ (dashed lines) on the solvent polarity for $G_{\mathrm{HB}}(0) = -0.35V$ (red lines) and $G_{\mathrm{HB}}(0) = -0.4V$ (blue lines). Parameters in V units are: $\lambda_{\mathrm{IL}} = 0.85$, $\lambda_{\mathrm{or}} = 0.8$, $A = 0.55$.

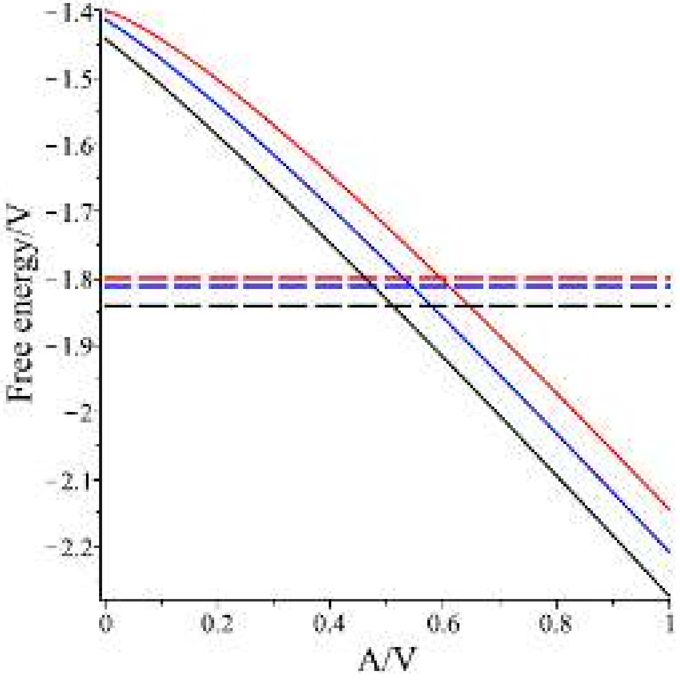


FIG. 5. Dependence of the equilibrium values of the free energies $G_1^{(\min)}$ (solid lines) and $G_2^{(\min)}$ (dashed lines) on the parameter A for three values of the solvent polarity $\Delta f = 0.2$ (red lines), $\Delta f = 0.4$ (blue lines), $\Delta f = 0.6$ (black lines). Other parameters in V units are: $\lambda_{\mathrm{IL}} = 0.85$, $\lambda_{\mathrm{or}} = 0.8$, $G_{\mathrm{HB}}(0) = -0.4$.

Influence of H-bonds on symmetry breaking

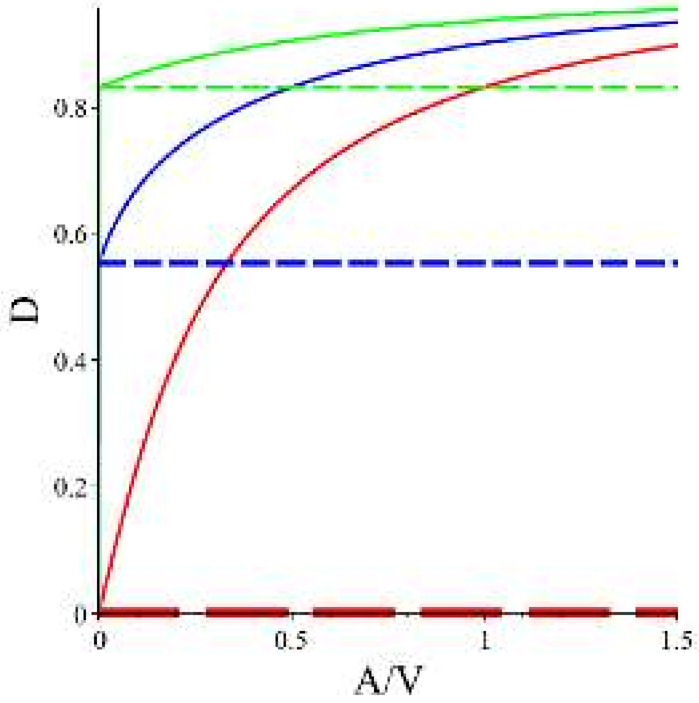


FIG. 6. Dependence of the minimum location of the free energy G_1 (solid lines) and G_2 (dashed lines), D, on the parameter A for $\lambda = 0.6V$ (red line), $\lambda = 1.2V$ (blue line), and $\lambda = 1.8V$ (green line). There is no dependence on $G_{\mathrm{HB}}(0)$.

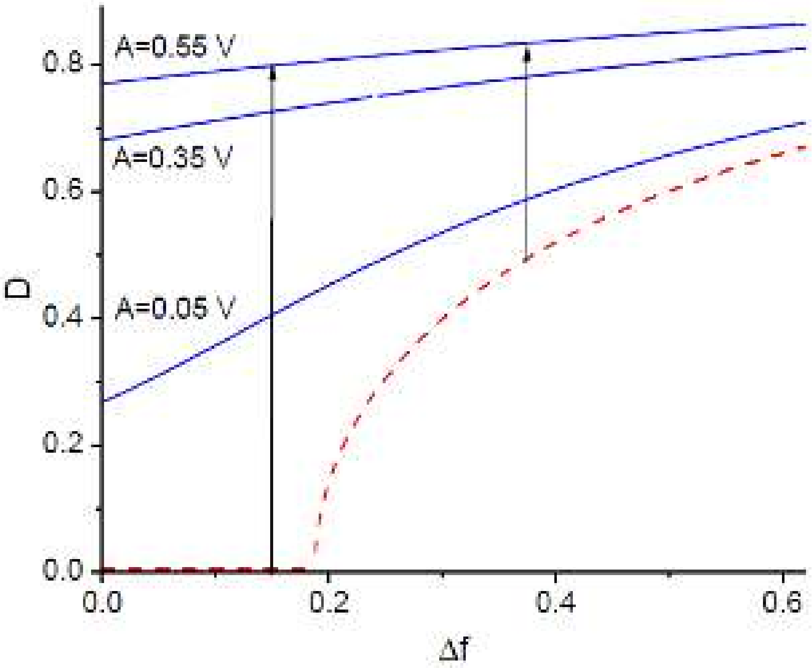
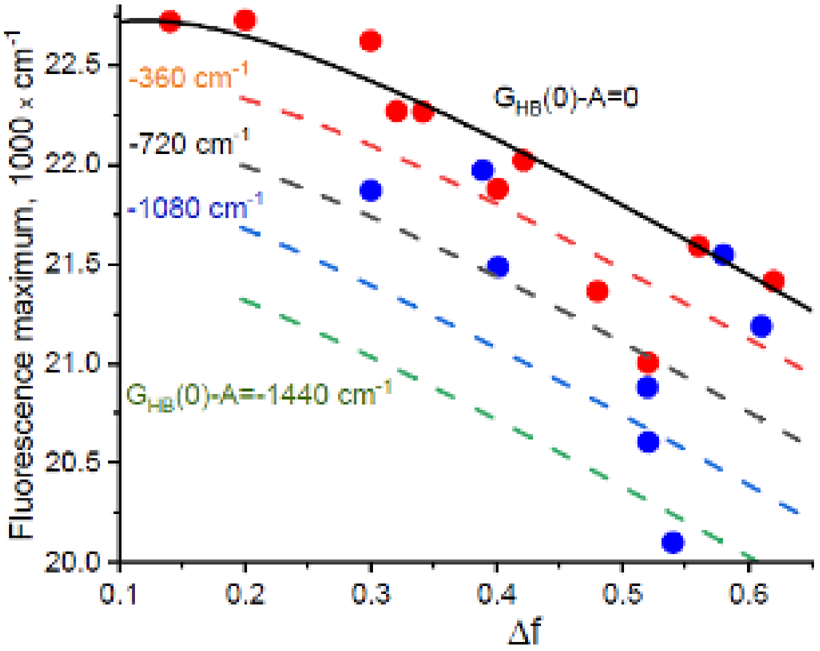


FIG. 7. Dependence of the minimum location of the free energies G_2 (red dashed line) and G_1 (blue lines) on the solvent polarity. Parameters in V units are: $\lambda_{\mathrm{IL}} = 0.85$, $\lambda_{\mathrm{or}} = 0.8$. The values of A are listed in the Figure.

Influence of H-bonds on symmetry breaking. Shift of the fluorescence band due to the formation of H-bonds

$$\begin{aligned} h\Delta\nu_0 &= \min(G_0) + V - \frac{\lambda_{or}}{2} D_0^2 \\ &= V - \frac{1}{2}\left(\lambda_0 + \frac{V^2}{\lambda_0}\right) - \frac{\lambda_{or}}{2}\left(1 - \frac{V^2}{\lambda_0^2}\right), \\ h\Delta\nu_1 &= \min(G_1) + V - \frac{\lambda_{or}}{2} D_1^2, \end{aligned}$$



B. Dereka, A. Rosspeintner, M. Krzeszewski, D. T. Gryko, and E. Vauthey, *Angew. Chem. Int. Ed.* **2016**, 55, 1–6

Conclusions

1. The H-bond has little effect on the magnitude of the asymmetry if complexes with two H-bonds are more stable.
2. The H-bond strongly affects the magnitude of the asymmetry if complexes with one H-bond are more stable.
3. The G_HB(0) value does not affect the degree of symmetry breaking in complexes with one and two H-bonds, but if its increase makes complexes with one H-bond more stable, then this leads to a sharp increase in asymmetry.
4. Conditions are revealed when an increase in the strength of the H-bond G_HB(0) leads to a decrease in the degree of asymmetry.
5. An increase in the parameter A does not affect the magnitude of the asymmetry as long as complexes with two H-bonds are more stable.

Thank you for your attention!

Работа поддержана Российским научным фондом, проект № 122-13-00180, https://rscf.ru/en/project/22-13-00180/.