Self-quenching of azulene fluorescence in cyclohexane

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Abstract

The self-quenching of azulene fluorescence in cyclohexane was studied by steady-state and time resolved fluorescence measurements. The quenching proceeds by a short-range exchange type non-radiative energy transfer from S\textsubscript{2} to S\textsubscript{1}, owing to a substantial overlap between the S\textsubscript{2}–S\textsubscript{1} fluorescence and the S\textsubscript{2}→S\textsubscript{1} absorption spectra of azulene. At room temperature the quenching occurs on the encounter of an excited azulene molecule with a ground state molecule with a diffusion-controlled rate constant, \( k_0 = 1.4 \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1} \).

1. Introduction

Fluorescence quenching in fluid solutions can occur either by a long range and/or a collisional quenching mechanism [1]. The long range mechanism is due to dipole–dipole energy transfer, while the collisional quenching in many cases involves the formation of new excited species, an excimer or an exciplex. Nevertheless, collisional quenching without formation of new excited species can still occur by multipole–multipole or an exchange type energy transfer mechanisms. However, these mechanisms cannot explain self-quenching in cases where energy is transferred to the same excited state (energy migration). Indeed, the number of excited species remain constant in the presence or absence of energy migration and only the spatial distribution of excited species and its polarization are modified [2,3].

Azulene is a special molecule with substantial self-quenching, first observed by Stevens and Dubois [4] from fluorescence spectra measurements. The main fluorescence emission comes from the second excited singlet state as observed by Longuet-Higgins [5] a long time ago. Since then, S\textsubscript{1}→S\textsubscript{0} and S\textsubscript{2}→S\textsubscript{1} emissions were detected, with very low quantum yields, in fluid solution at room temperature and in hydrocarbon glasses at 77 K [6–10]. However, the effect of concentration quenching on fluorescence lifetimes was not studied, although the fluorescence lifetimes of dilute solutions of azulene and several of its derivatives have been reported [11–13].

Here, the self-quenching of the fluorescence from the second excited singlet state of azulene is studied in cyclohexane at room temperature. The quenching is diffusion-controlled (rate constant, \( k_0 = 1.4 \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1} \)), and occurs probably by a short range energy transfer mechanism. This phenomenon takes place on the encounter of an excited molecule with a ground state molecule and leads to energy transfer from S\textsubscript{2} to S\textsubscript{1}, owing to a substantial overlap between the azulene fluorescence from S\textsubscript{2} and the absorption to high vibrational excited states of S\textsubscript{1}. This homotransfer is peculiar since the final excited state is different from the initial one, explaining therefore fluorescence quenching of the initial state. Consequently, the S\textsubscript{1} fluorescence quantum yield should increase.

2. Experimental details

Azulene (Az) Koch–Light puriss. and cyclohexane (Cx) Merck–Uvasol were used without further purification. Fluorescence spectra at front-face viewing were obtained on a home-built spectrofluorometer previously described [14]. Decay curves were obtained by single-photon timing technique using picosecond excitation light from a cavity dumped Kiton Red dye laser synchronously pumped by an Argon ion laser (Spectra Physics model 2020). The emission
of the dye was frequency doubled with a KDP crystal to obtain excitation light of 322 nm. The fluorescence emission (\(\lambda = 375\) nm) was selected with a Jobin-Yvon (model H-20) monochromator and detected by a Philips (XP 2020) photomultiplier.

Experiments were performed at room temperature (22 °C). Samples were degassed from oxygen either by the freeze-pump-thaw technique, 3 cycles (lifetime measurements) or by N₂ bubbling, 5 min (fluorescence spectra).

Diffusion coefficients were measured by Taylor’s method [15] using a fluorescence detector.

3. Data and data analysis

The fluorescence intensities of azulene solutions, corrected for dilution effects, decrease with azulene concentration (Fig. 1). These effects were corrected using a calibration curve (intensity vs. optical density) obtained from the fluorescence spectra of 9,10-diphenylanthracene solutions in cyclohexane. The radiative transport (self-absorption) is negligible, even at high concentrations, owing to a very small overlap between the S₂ → S₀ fluorescence and the corresponding absorption spectra.

These results are similar to the ones obtained by Stevens and Dubois [4] and indicate that S₂ → S₀ azulene fluorescence is self-quenched. The shape of the fluorescence spectra of azulene solutions does not change with concentration, even at longer wavelengths, which excludes the possibility of formation of other excited fluorescent species. The UV-Vis absorption and fluorescence excitation spectra show no evidence for ground state aggregation.

In order to further study the quenching phenomenon, decay curve measurements of azulene solutions with different concentrations were performed. The decays can be reasonably well fitted by a single exponential in the full range of concentrations used. The lifetime decreases with azulene concentration in agreement with fluorescence spectra measurements.

The fluorescence quenching of azulene (Az) was described by Stevens and Dubois [4] using Scheme I

\[
\begin{align*}
\text{hv} & \quad \text{Az}^{**} + \text{Az} \quad \xrightarrow{k_Q} \quad \text{Az} + \text{Az}^{*} \\
& \quad \downarrow \tau_0 \\
\text{Scheme I}
\end{align*}
\]

where \(\text{Az}^{**}\) and \(\text{Az}^{*}\) mean the azulene molecules in the second and first singlet excited states, respectively, \(\tau_0\) is the intrinsic lifetime of \(\text{Az}^{**}\) and \(k_Q\) is the rate constant for the irreversible fluorescence self-quenching of azulene. The Stern-Volmer equation (eqn. (1)) should be followed, once \(k_Q\) can be considered time-independent.

\[
\frac{\tau_0}{\tau} = 1 + k_Q[\text{Az}]
\]

Figure 2 shows that eqn. (1) is obeyed which allows the calculation of the quenching rate constant, \(k_Q = 1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}\), which indicates that the reaction is diffusion-controlled [16]. Indeed, the long time limit for diffusion-controlled reactions is given by

\[
k_Q = \frac{4\pi D_{\text{Az}} R_e}{1000}
\]

where \(D\) is the mutual diffusion coefficient, \((D = 2D_{\text{Az}})\), \(R_e\) the encounter radius of the reaction \((R_e = 2r_{\text{Az}})\) and \(N_A\) is Avogadro’s number. Assuming that the diffusion coefficient of azulene is given by [17]

\[
D_{\text{Az}} = \frac{kT}{6\pi \eta r_{\text{Az}} f_l}
\]

where \(k\) is the Boltzmann constant, \(r_{\text{Az}}\) the radius of a azulene molecule, \(\eta\) the solvent viscosity and \(f_l\), the friction coefficient

\[
f_l = 0.16 + 0.41 \frac{r_{\text{Az}}}{r_{\text{C6}}}
\]
equation (2) can be rewritten in the form
\[ k_{Qm} = \frac{8k_{TN_A}}{3000\eta f_i} \] (5)

In cyclohexane at 22 °C (\( \eta = 1.03 \) cP, \( f_i = 0.6 \) \( r_{Ae} = 3.3 \) Å, \( r_{Ce} = 2.90 \) Å from van der Waals molar volumes [18]), \( k_{Qm} = 1.1 \times 10^{10} \) M\(^{-1}\) s\(^{-1}\), which is close to the experimental value obtained from the lifetime measurements. Nevertheless, it is well known that the quenching rate coefficient for a diffusion-controlled process is time-dependent [16].

\[ k_{Q} = \frac{4\pi D N_A R_e}{1000} \left[ 1 + \frac{R_e}{\sqrt{\pi D t}} \right] \] (6)

attaining at long times (\( t \gg R_e^2/\pi D \)) the constant value \( k_{Qm} \). This time-dependence is not perceptible in decay curve analysis in the range of concentrations used, as confirmed by simulation of azulene fluorescence decay curves in the presence of self-quenching with rate coefficient given by eqn. (6).

Figure 3 shows the Stern–Volmer plot of the ratio of fluorescence quantum yields of a diluted (10\(^{-4}\) M) and several concentrated solutions vs. azulene concentration. For high concentrations the plot shows an upward curvature, characteristic of the time dependence of the rate coefficient.

The ratio of quantum yields for low azulene concentrations (\( \Phi_0 \)) and for concentrations high enough to have self-quenching (\( \Phi \)) is given by ref. 19

\[ \Phi = \frac{1 + k_{Qm} \tau_0 [Az]}{I(\lambda)} \] (7)

where
\[ I(\lambda) = 1 - \frac{1}{2} \lambda \sqrt{\pi} \exp\left(\frac{\lambda^2}{2}\right) \text{erfc}\left(\frac{\lambda}{2}\right) \] (8)

with
\[ \lambda = \frac{2}{\sqrt{\tau}} \frac{k_{Qm} \tau_0 [Az]}{\sqrt{1 + k_{Qm} \tau_0 [Az]}} \frac{R_e}{\sqrt{D \tau_0}} \] (9)

\[ \text{erfc}(x) = 1 - \text{erf}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp(-z^2) \, dz \] (10)

The fit of values \( \Phi_0/\Phi \) with eqn. (7), with \( \tau_0 = 1.4 \) ns, gives \( R_e = 6.7 \) Å and \( D = 3.0 \times 10^{-5} \) cm\(^2\) s\(^{-1}\). These values allow the calculation of the long time limit of the self-quenching rate coefficient, \( k_{Qm} = 1.5 \times 10^{10} \) M\(^{-1}\) s\(^{-1}\), which is in agreement with the value obtained from decay curve measurements. The diffusion coefficient of azulene, \( D_{Az} = 1.5 \times 10^{-5} \) cm\(^2\) s\(^{-1}\), is close to the value calculated from eqn. (3), \( 1.1 \times 10^{-5} \) cm\(^2\) s\(^{-1}\), and is (within the experimental error) equal to the diffusion coefficient of azulene in cyclohexane measured by Taylor's method [15]. The radius of
3. Discussion and conclusion

The self-quenching of azulene fluorescence occurs on the encounter of an azulene molecule in its second excited state with another one in the ground state. In cyclohexane, at room temperature, the process is diffusion-controlled, which implies a very efficient quenching on the encounter of the excited and ground state molecules. As no other species are formed in the ground or excited state, we should invoke an energy transfer process as the quenching mechanism on the encounter. Figure 4 shows the \( S_2 \rightarrow S_0 \) fluorescence and absorption spectra of azulene.

The overlap integral of the fluorescence spectrum with highly vibrationally excited \( S_0 \rightarrow S_1 \) absorption is substantial, although with very low values of the molar absorptivity. This implies a Förster's \( R_0 \) value for a dipole–dipole interaction of \( \sim 8 \, \text{Å} \) [20], which is very low to ensure an efficient energy transfer on the encounter [21]. The high efficiency of quenching on the encounter is due to a short-range exchange type energy transfer from \( S_2 \) to \( S_1 \). Indeed, the rate constant for an exchange mechanism depends on the overlap integral between the fluorescence and absorption spectra but not on the absolute values of the molar absorptivity as in the dipole–dipole type mechanism [22]. The possibility of cross-relaxation (\( \text{Az}^{**} + \text{Az} \rightarrow 2\text{Az}^{*} \)) is unimportant since the \( S_2 \rightarrow S_1 \) transition occurs at lower energies than the \( S_0 \rightarrow S_1 \) absorption [7,8]. Existence of significant energy migration would delocalize the excitation thus increasing the self-quenching rate constant. However, its contribution to the overall quenching rate constant is negligible in this system, owing to the very small overlap integral between \( S_2 \rightarrow S_0 \) fluorescence and \( S_0 \rightarrow S_2 \) absorption spectra.

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References