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Picosecond time-dependent Stokes shift studies of fluoroprobe in liquid solution

E.R. Middelhoek^a, P. van der Meulen^a, J.W. Verhoeven^b, M. Glasbeek^a

^a *Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam, The Netherlands*

^b *Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands*

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Abstract

We report on a picosecond spectroscopic study of the dynamical Stokes shift of fluoroprobe in the lowest excited state in the solvents diethylether and ethylacetate. Time-resolved emission spectra with a time-resolution of approximately 10 ps are presented. The spectra reflect dynamical Stokes shifts of a few thousand wave numbers within 10–100 ps after the pulsed laser excitation. The time-dependent shifts are representative of the solvation dynamics of fluoroprobe in diethylether and ethylacetate.

1. Introduction

It has long been recognized that the solvent influences the dynamics of a chemical reaction in solution not only by modifying the free energy surface on which the reaction takes place, but also by exerting a frictional force on the system while it is moving along the reaction coordinate [1,2]. In polar solvents this frictional force originates, at least in part, from the solvent polarization which is unable to keep up with a sudden change in the charge distribution of the reactants (dielectric friction) [3,4]. The solvent induced friction may greatly influence the dynamics of the reaction [5–7] and it appears that a thorough knowledge of the dynamics of the solvent is a prerequisite for a detailed understanding of chemical reaction dynamics in solution.

As shown by Ware et al. [8], the kinetics of the solvation process can be studied by monitoring the red shift of the fluorescence spectrum of a probe molecule following pulsed excitation. The time-de-

pendent fluorescence Stokes shift provides a direct measure of the time scale of the orientational relaxation of the solvent molecules [9–11]. In a number of recent studies the organic donor-acceptor compound fluoroprobe (1-phenyl-4-((4-cyano-1-naphthyl)methylene)piperidine, see inset of Fig. 1) [12–14] has been reported and it has also already been used as a probe molecule to examine the solvation process in a number of polymer matrices and organic glasses [15–17]. The solvation times for these highly viscous and slowly relaxing ‘solvents’ are on the order of tens of nanoseconds, and these systems could be conveniently studied at relatively low time resolution (approximately 10 ns) in an experiment in which the sample was excited by a nanosecond laser pulse and the emission was detected by a synchronized electronically gated optical multichannel analyser [15–17]. In the present work we use the same probe molecule, but now applying fluorescence spectroscopy with a time resolution of approximately 10 ps, in an attempt to elucidate dynamics of two

ordinary solvents, viz. diethylether and ethylacetate, at reduced temperatures. For these liquids, as for many other non-alcoholic solvents, few low-temperature solvation data are available [18–25].

Upon photoexcitation, fluoroprobe gives rise to an intramolecular charge separation reaction leading to a difference between the dipole moments of the ground state and the excited (charge transfer) state of approximately 30 D [12–14]. The large change in dipole moment produced in the charge separation reaction makes fluoroprobe extraordinarily sensitive towards solvent polarity. In addition, the fluoroprobe molecule shows a high fluorescence quantum yield. As a result, fluoroprobe is an attractive candidate for time-dependent Stokes shift studies. However, as far as the study of solvation dynamics is concerned, an excited state chemical reaction, such as charge separation, may lead to non-ideal probe behavior and can be a complicating factor in interpreting the experimental results [10]. Especially at early times, the charge separation and solvation processes may interfere, thereby making it more difficult to extract meaningful solvation times. In this respect a detailed understanding of both the mechanism and the time scale of the charge separation reaction in fluoroprobe is highly desirable.

Unfortunately, little is known about the charge separation dynamics of fluoroprobe. The conjecture that this reaction takes place in the strongly adiabatic limit [26–28] has partly motivated us to undertake this research. For jet-cooled derivative compounds of fluoroprobe, the excitation spectra have recently been published [29]. From the line widths of the spectral transitions it can be concluded that in the gas phase the rate constant for the charge-separation reaction is smaller than 0.1 ps^{-1} . In solution, the absence of a second (non-charge-separation) emission band in the steady-state fluorescence spectra, even at low temperatures, as well as a linear Lippert–Mataga plot [12–14] suggest that the charge separation is completed on a picosecond time scale. In a time-dependent Stokes shift experiment spectral features may be observed that provide an indication for the occurrence of an excited state charge separation reaction. In particular, any deviation from the expected $\langle \nu \rangle^3$ dependence [30] for the integrated emission intensity may very well occur due to a charge separation reaction [10,31–33]. Hence, a careful analysis of the

time evolution of the fluorescence spectrum does not only yield information about the solvent dynamics, but may also provide a clue to the presence of a charge separation process.

In this paper we aim at the investigation of the low temperature charge separation and solvation dynamics of fluoroprobe in diethylether and ethylacetate using picosecond time-resolved fluorescence spectroscopy. Dynamical Stokes shifts on the order of a few thousand wave numbers are obtained on a time scale of several tens of picoseconds. However, on a picosecond time scale, a substantial fraction of the overall photo-induced dynamics is not resolved. It appears that the effect of an excited state charge separation reaction on the measured dynamics is fairly small and it seems that fluoroprobe does indeed behave as an ideal solvation probe (on a picosecond time scale). Details of the effects of temperature and concomitant solvent polarity changes are also presented.

2. Experimental

Fluoroprobe was synthesized as described elsewhere [12–14]. Diethylether (Fluka) was carefully purified and dried before use [34]. Ethylacetate (Merck Uvasol) was used as received. Fluoroprobe was dissolved in a concentration of about 10^{-5} M . The solution was de-aired by bubbling with dry nitrogen and was transferred to a quartz cuvette which was then hermetically sealed. All sample manipulations were carried out in a glove box to exclude oxygen and moisture. Two adjacent side walls of the cuvette were blackened to avoid unwanted reflections. The sample cuvette was mounted inside a home-built liquid nitrogen flow cryostat. The temperature was varied in the range 190–290 K (ethylacetate) and 160–290 K (diethylether) by means of a Cryoson 17-90B/1 temperature regulator, attached to the liquid nitrogen supply. The temperature was measured with a thermocouple attached to the copper cuvette holder. After equilibration, the temperature reading is accurate to about 3 K.

Fluorescence intensity decay curves were obtained using picosecond laser excitation combined with single photon counting detection. Briefly, a mode-locked Coherent Innova 200-15 Ar^+ ion laser

synchronously pumped a Coherent 702-3 dye laser. The dye laser was operated at 634 nm employing DCM-spezial (Radiant Dyes Chemie) as a dye. No saturable absorber was used. A Coherent 7200 cavity dumper reduced the repetition rate to 3.7 MHz. The cavity-dumped dye laser generated nearly transform limited pulses with an autocorrelation trace of about 7 ps FWHM and an energy of approximately 25 nJ. The dye laser output was frequency doubled in a 6 mm BBO crystal to yield light at the excitation wavelength of 317 nm with an average power of 3 mW. Fluorescence emitted in a direction perpendicular to the excitation beam was focused onto the entrance slit of a Zeiss M20 monochromator outfitted with a Hamamatsu R3809U microchannel plate photomultiplier. To circumvent contributions to the fluorescence decays arising from reorientational motions of the probe, the decays were measured under magic angle conditions, i.e., only fluorescence polarized at the magic angle of $54^{\circ}44'$ with respect to the vertically polarized excitation beam was detected. Any scattered excitation light was removed by inserting a 345 nm cut-off filter in the optical path.

The single photon counting set-up was operated in reverse mode. The output of the photomultiplier tube was amplified using a Hewlett Packard 8347A 3 GHz amplifier, sent to a (modified) Tennelec TC 455 constant fraction discriminator and finally acted as the start pulse for the Tennelec TC 864 time-to-amplitude converter. The undoubled dye laser pulse was monitored by an Antel FS1010 photodiode. The photodiode signal was sent directly to a Tennelec TC 454 constant fraction discriminator and was then used as the stop pulse for the TC 864. A Tennelec TC 412A delay generator served to shift the photodiode signal into the active time window of the TC 864. The output of the TC 864 was fed into an EG & G Ortec 918 multichannel buffer. The timebase of the TC 864 was calibrated to an accuracy of 1% by optically delaying the arrival of the visible dye laser pulse at the photodiode with respect to the arrival of the UV excitation pulse at the sample.

A personal computer was used for data acquisition, storage and analysis. All fluorescence decay curves were recorded at a spectral resolution of 5 nm. Typically, 30 decay curves, at 10 nm intervals, were obtained for each sample. A set of neutral density filters was used to adjust the count rate to

about 5 kHz, irrespective of the detection wavelength. To suppress photodecomposition of fluoroprobe the excitation beam has in all cases been attenuated by at least a factor of ten, i.e., the laser power incident on the sample never exceeded 0.3 mW. The instrumental time response function was obtained by monitoring the Raman scattered light at 356 nm of a water cell. Care was taken to measure the response function with the same spectral resolution and count rate as the fluorescence decay curves. The instrumental time resolution was about 20 ps (FWHM); the final experimental time resolution was improved to about 10 ps after deconvolution of the transients with the instrumental response function (see also Section 3). Steady state absorption spectra were recorded with a Shimadzu spectrophotometer UV240. The emission spectra have been corrected for the wavelength dependent sensitivity of the monochromator and the photomultiplier by standard calibration procedures [35].

3. Results and discussion

3.1. Steady state spectra

Fig. 1 displays the steady-state absorption and emission spectra of fluoroprobe dissolved in diethylether at room temperature. The long wavelength absorption spectrum ($\lambda > 300$ nm) is dominated by the 1-vinyl-4-cyano-naphthalene acceptor chro-

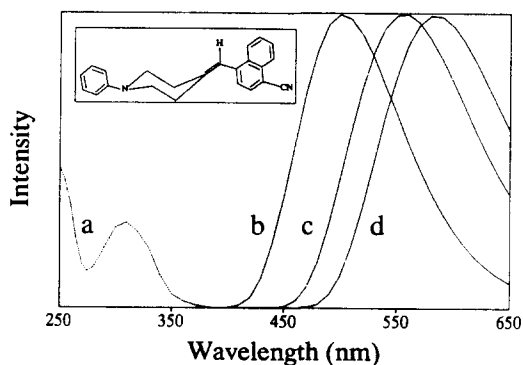


Fig. 1. (a) Steady-state absorption spectrum of fluoroprobe (see inset) in diethylether at room temperature (dashed line); (b), (c) and (d) corrected emission spectra of fluoroprobe in diethylether at 294, 202 and 162 K, respectively (solid lines).

mophore ($\lambda_{\max} \approx 310$ nm) [12–14]. Whereas the absorption spectrum does not change with the solvent used [12–14], the cw emission spectrum is known to exhibit a large solvatochromic effect: in the non-polar solvent *n*-hexane the wavelength of the emission band maximum, λ_{\max} , lies near 407 nm, while in the extremely polar solvent acetonitrile the maximum is near 694 nm [12–14]. The broad and structureless emission band and the solvatochromism are typical for an excited charge transfer state.

Fig. 1 shows the emission spectra of fluoroprobe in diethylether at three different temperatures. Clearly, the emission band shows a shift to the red upon lowering the temperature. On the other hand, the absorption spectrum is hardly affected when the temperature is decreased [12–14]. In Table 1 we have collected the experimentally determined values for the fluorescence band maximum (ν_{\max}) of fluoroprobe in both diethylether and ethylacetate at a number of different temperatures. In diethylether, cooling the solution from room temperature down to 162 K leads to a frequency shift of $\Delta\nu_{\max} \approx 2800$ cm^{-1} . The maximum observed shift in ethylacetate is about 1400 cm^{-1} . These red shifts are due to an increase in solvent polarity as the temperature is reduced. A more polar solvent decreases the (vertical) transition energies by lowering the minimum of the excited (charge transfer) state free energy surface, and, at the same time, increasing the slope of the ground state free energy surface [10].

A quantitative estimate of the effect of the solvent polarity on the position of the fluorescence spectrum can be obtained from the Lippert–Mataga equation [36–38]. In the Lippert–Mataga model the frequency of the emission band maximum varies linearly with the solvent polarity parameter Δf :

$$\nu_{\max} = a - b\Delta f, \quad (1a)$$

$$\Delta f = \frac{\epsilon_0 - 1}{2\epsilon_0 + 1} - \frac{n^2 - 1}{4n^2 + 2}, \quad (1b)$$

where ϵ_0 is the static dielectric constant and n is the refractive index of the solvent, respectively. The variation of Δf with temperature can be readily calculated from ϵ_0 and n values available in the literature [39–43]. Using $a = 27.9$ kK and $b = 33.9$ kK [13], we obtain shifts of 2200 and 1400 cm^{-1} for diethylether and ethylacetate, respectively. Taking

into account the approximations in the Lippert–Mataga model as well as the uncertainties in the values of ϵ_0 and n , the agreement is considered satisfactory. However, the experimentally observed shifts appear to be slightly larger than the calculated ones, which indicates that the slope b in Eq. (1a) is too small. This may be due to the fact that Hermant et al. [13] inadvertently omitted the λ^2 correction in transferring the fluorescence spectra from a wavelength to a wavenumber scale [35]. It is estimated that the application of this correction factor will increase the slope by about 10% which brings the calculated and experimental shifts in even better agreement.

3.2. Picosecond transients

Picosecond fluorescence intensity decays were measured for fluoroprobe at a series of wavelengths and temperatures. It was verified that the decay transients were not affected when changing the incident laser power from 0.3 up to 1 mW. Thus the transient spectral effects discussed hereafter are not due to sample heating phenomena. Typical results for the changes in the emission transient as a function of detection wavelength are presented in Fig. 2 for the fluoroprobe/diethylether solution at a temperature of 162 K. As is seen from the figure, on the blue edge of the spectrum the transient contains a picosecond decay component, at longer wavelengths this component becomes slower and of smaller rela-

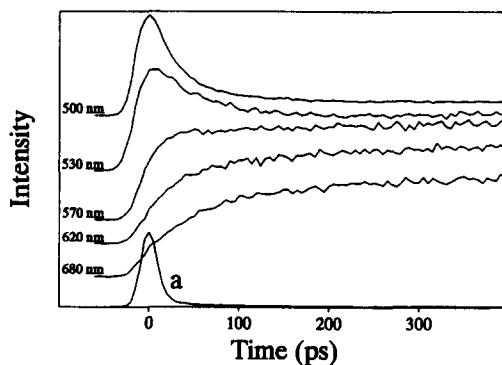


Fig. 2. Fluorescence transients of fluoroprobe in diethylether at 162 K at the detection wavelengths as indicated. The transients have been rescaled to the same maximum intensity change; (a) the instrumental response function.

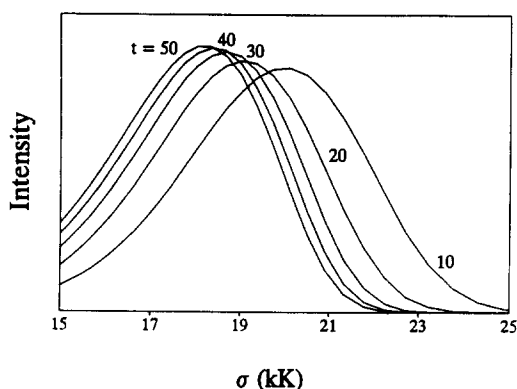


Fig. 3. Time resolved emission spectra of fluoroprobe in diethylether at 162 K; the delay times of the deconvoluted spectra (in picoseconds) with respect to the pulsed excitation are as indicated. The spectra shown are lognormal function fits to experimental data points.

tive amplitude, whereas finally, at the red side of the spectrum, an initial rise of the fluorescence intensity is observed.

By means of the method of spectral reconstruction [9] we evaluated the time evolution of the fluorescence spectrum of fluoroprobe. In this procedure the transients were first fit to a function which is a convolution of the response function (see inset in Fig. 2) with a sum of three exponentials using a nonlinear least squares fitting technique [44]. The deconvoluted fluorescence decay curves were then normalized by equating the area under each fluorescence decay curve to the intensity of the steady state fluorescence spectrum at the same wavelength. From

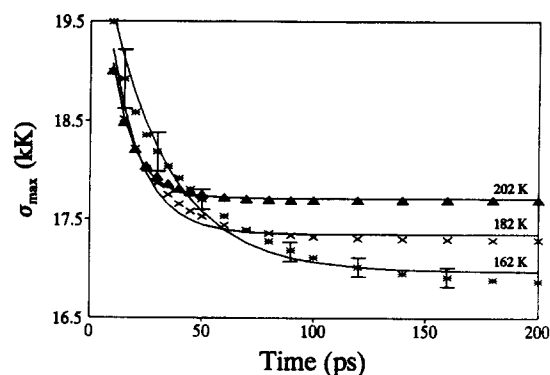


Fig. 4. Time dependent behavior of the peak position (σ_{\max}) at the indicated temperatures. Solid lines are best monoexponential fits to data points. Typical error bars are as indicated for a few data points.

these normalized transients the spectrum at a certain time following excitation was readily obtained. As usual [9], the reconstructed fluorescence spectra were subsequently fitted to a lognormal distribution function in order to extract the peak position, $\nu_{\max}(t)$, and the integrated emission intensity, $A(t)$. Fig. 3 shows the reconstructed emission spectra for fluoroprobe in diethylether at a temperature of 162 K at various times after excitation. From Fig. 3, an emission band red shift of a few thousand wave numbers within the first several tens of picoseconds can be easily inferred. Similar results are obtained for fluoroprobe dissolved in ethylacetate.

The temporal behavior of $\nu_{\max}(t)$ (which represents the dynamical Stokes shift) as determined for

Table 1

Emission characteristics of fluoroprobe in ethylacetate and diethylether at various temperatures

	Temperature (K)	ν_{\max} (kK) (exp)	τ_s (ps) (exp)	τ_s^a (ps) (litt)	τ_{lifetime} (ns) (exp)	τ_D^b (ps)	τ_1^c (ps)
diethylether	294	19.7			13.0	2.4	1.2
	201	17.8	10		15.9	9.1	2.9
	182	17.5	14	390	16.7	14	4.1
	162	17.0	27	270	17.8	26	6.5
ethylacetate	294	16.7			7.0	3.1	1.1
	205	15.5	16		3.3	16	4.2
	196	15.3	28		3.1	21	5.3

^a Solvation relaxation times as taken from Ref. [18].

^b The Debye relaxation times (τ_D) are from Ref. [42] (diethylether) and Ref. [43] (ethylacetate).

^c The longitudinal relaxation times (τ_1) are calculated by means of $\tau_1 = [(2n^2 + \epsilon_c)/(2\epsilon_0 + \epsilon_c)] \tau_D$. (n and ϵ_0 data are from Refs. [39–42] (diethylether) and Refs. [41,43] (ethylacetate) and $\epsilon_c = 1$).

fluoroprobe in diethylether in the picosecond range, at temperatures of 162, 182 and 202 K, is shown in Fig. 4. The decay curves are fitted to a monoexponential function (see drawn curves in Fig. 4). Note that the data points in Fig. 4 do not completely follow the calculated monoexponential decay curve. The apparent time constants, τ_s , of the fitted exponential curves are collected in Table 1.

In agreement with the results of the steady state experiments discussed above, it follows from Fig. 4 that $\nu_{\max}(\infty)$ is decreased as the temperature is lowered. This is obviously related to the fact that the polarity of the solvent is increased as the temperature is decreased. It can also be seen from Fig. 4 that the observed dynamical Stokes shift, i.e. the total shift of the emission band from 10 ps onwards, is increased upon reducing the temperature. This is, of course, due to an increase in solvent polarity as well. Moreover, the dynamics slows down at lower temperature (see Table 1) and, given the time resolution in the present experiments, a progressively larger fraction of the total dynamical Stokes shift becomes accessible experimentally as the temperature is reduced. An estimate of the influence of our limited time resolution on the magnitude of the observed total dynamical Stokes shift may be obtained as follows [45,46]. The solvent's contribution to the total dynamical Stokes shift can be calculated by comparing the energy difference between the maxima of the (steady state) absorption and emission spectra in the solvent under investigation with that obtained in a very apolar solvent such as *n*-hexane [45,46]. In this way, we find that the dynamical Stokes shift in diethylether amounts to about 7000 to 8000 cm^{-1} , depending on the temperature. Even in the most favorable case, diethylether at 162 K, the experimental Stokes shift in the time interval from $t = 10$ ps to $t = \infty$ is only about 2700 cm^{-1} . This means that in the current experiments we probably trace less than 50% of the actual dynamical Stokes shift. Most of the Stokes shift dynamics apparently occurs on a time scale of a few picoseconds, or faster, and is not resolved. Fortunately, although a large fraction of the dynamics cannot be monitored, the remaining experimental Stokes shift is still quite large and exceeds that of many other common solvation probes, e.g. the coumarine dyes, notwithstanding the fact that the latter probes were studied in more polar solvents and

at much higher time resolution [11,47,48]. This clearly illustrates that fluoroprobe is an exceptionally good solvation probe [12–17].

A conclusion similar to that of the preceding paragraph can be reached from the solvation times τ_s compiled in Table 1. In a simple Debye continuum model [49], one predicts a single exponential decay with a time constant $\tau_s \approx \tau_1 = \tau_D \cdot \epsilon_\infty / \epsilon_0$, where τ_D is the (transverse) Debye relaxation time, τ_1 is the longitudinal relaxation time and ϵ_∞ and ϵ_0 are the dielectric constants at infinite and zero frequency, respectively. In more sophisticated models the solvation dynamics can be highly nonexponential, but, especially when the translation of the solvent molecules is included, the magnitude of the average relaxation time approaches that for τ_1 [50]. Experimentally, one indeed often finds nonexponential behaviour, but in many cases the average relaxation time is remarkably close to τ_1 [10,11]. From the data collected in Table 1, a comparison of our experimental τ_s values with the τ_D and τ_1 values for diethylether and ethylacetate can be made. It should be kept in mind that the quality of the dielectric data [39–43] used in the construction of Table 1 is rather poor (typically two or three points in a Debye semicircle) and that sometimes values for τ_D , ϵ_∞ and ϵ_0 had to be extrapolated because they were not available from the literature. Nevertheless, the solvation times of this work seem to be comparable to the Debye relaxation times and much longer than the expected longitudinal relaxation times. This result need not surprise us since, as noted above, on the picosecond time scale of our experiments we are able to resolve only the trailing edge of the solvation decay. Hence the experimentally determined effective decay time constant will appear longer than the actual decay time.

The experimental solvation times are apparently severely dependent on the instrumental time resolution. However, they do show the qualitatively expected temperature dependence: the rotational diffusional motion of the solvent molecules slows down as the temperature decreases. Furthermore, our solvation times in diethylether in the temperature range 160–180 K are considerably shorter than those obtained by Lessing and Reichert [18] in a time-resolved fluorescence experiment with nanosecond resolution (cf. Table 1).

Normally, the integrated emission intensity should vary as ν_{\max}^3 [30] and therefore as $\nu_{\max}(t)$ is red-shifted as the solvation progresses, one anticipates a decrease in the integrated fluorescence intensity. For the spectral region of concern here the estimated total change in the integrated intensity would approximately amount to a 30% decrease. According to the model developed by Bixon et al. [51], a somewhat larger decrease may be expected if intensity borrowing from a locally excited state plays a significant role. As deduced from the areas $A(t)$ covered by the lognormal spectra in Fig. 3, however, we find very little dependence of the emission intensity with time. Probably, the accuracy of our spectral reconstruction analysis is not sufficient to reliably determine rather small intensity changes during the picosecond time evolution of the fluorescence spectra and thus more definite conclusions regarding the dynamics of the charge transfer process in photoexcited fluoroprobe cannot be discerned from our integrated intensity studies.

In summary, we used picosecond time-resolved fluorescence spectroscopy to study the low temperature charge separation and solvation dynamics of fluoroprobe in diethylether and ethylacetate. Dynamical Stokes shifts of a few thousand wave numbers on a time scale of about 10–30 ps, depending on solvent and temperature, have been reported. A major result is that on a picosecond time scale only the (slower) trailing edge of the solvation decay of photoexcited fluoroprobe could be probed. With regard to the dynamics of the charge separation reaction in the excited state our experiments remained rather inconclusive, but most likely the charge separation process is not seriously affecting the measured solvation dynamics. Hence, fluoroprobe forms a convenient and highly sensitive solvation probe, at least on a picosecond time scale. Currently, experiments with femtosecond time resolution are in progress in this laboratory in order to improve our understanding of solvation and charge transfer dynamics of fluoroprobe in ordinary solvents.

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