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Ultrafast Excited-State Proton Transfer in 1-Naphthol¹

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Abstract

The first direct observation of the excited-state proton-transfer reaction of 1-naphthol in aqueous solution is reported. Using picosecond, time-resolved emission spectroscopy, the lifetime of 1-naphthol at pH = 7 is found to be 33 ± 5 psec, one to three orders of magnitude faster than previous determinations. Coupled with steady-state techniques, direct, time-resolved measurements provide a generally applicable method for the accurate determination of the numerous rate constants required for a complete description of the kinetics of electronically excited 1-naphthol in water. Comparison of the present results on 1-naphthol with previous work on 2-naphthol reveals striking differences in the excited-state reaction dynamics of these seemingly similar molecules.

Proton-transfer reactions provide the fundamental basis for all acid-base chemistry in protic solvents. Literally hundreds of examples of excited-state proton-transfer reactions are known.² In nearly all these systems, large changes in pK_a occur upon electronic excitation. Picosecond laser sources can thus be used to effect the sudden introduction of a strong acid or base into an otherwise unchanged solution.³ The ensuing reaction dynamics reflect the influence of electronic structure, solute-solvent interactions, and solvent organization on proton-transfer reactions. As previously demonstrated,³⁻⁵ time-resolved measurements are often required for the correct determination of the kinetic and thermodynamic parameters necessary for the complete characterization of excited-state proton-transfer reactions.

In this communication, we present the results of picosecond, time-resolved emission spectroscopy of electronically excited 1-naphthol in aqueous solution. In the past, excited-state proton transfer in 1-naphthol has been studied using both steady-state⁶⁻⁹ and nanosecond time-resolved⁹⁻¹¹ emission spectroscopy. These previous results predicted excited-state proton-transfer rates one to three orders of magnitude slower than the rate presented here. Analysis of the results reported here show that previous values for other parameters describing excited-state proton transfer in 1-naphthol are also in error, including the excited-state acid dissociation constant, pK_a^* .^{10,12-14} Perhaps most importantly, the earlier results obscured the processes responsible for the substantial differences between the excited-state proton-transfer dynamics of 1-naphthol and 2-naphthol.¹⁵

The experimental method and kinetic analysis used in these measurements can be explained using the generalized excited-state proton-transfer reaction diagram shown in Fig. 1. Since 1-naphthol has a pK_a of 9.2,¹⁶ essentially all ground-state 1-naphthol molecules will be fully protonated for a solution $pH < 7$. Irradiation of such a solution will produce the substantially more acidic,² electronically excited

1-naphthol (ROH^*), which can adiabatically transfer a proton to water to produce an electronically excited 1-naphtholate anion (RO^{-*}). As expected from simple thermodynamic arguments such as the Förster cycle,⁶ the emission from RO^{-*} is at lower energies than that of ROH^* . This spectral difference allows the two species to be distinguished and independently monitored.¹³ The reaction scheme of Fig. 1 predicts that both the decay time of the ROH^* emission and the risetime of the RO^{-*} emission will be equal to the total rate of decay of the ROH^* population.

The picosecond, time-resolved emission spectroscopy apparatus used for these experiments will be described in detail elsewhere.¹⁷ Briefly, 20-ps, fourth harmonic (266 nm) pulses derived from a passively mode-locked Nd:YAG oscillator-amplifier system (Quantel, YG400) were used to excite the sample. The resulting emission was spectrally filtered with appropriate narrow-band (~ 10 nm FWHM) interference filters and imaged onto the entrance slit of an ultrafast streak camera (Hadland-Photonics, Imacon 500). The streak records were digitized with an intensified photodiode array (Tracor-Northern, IDARSS) and transferred to a microcomputer (DEC, LSI 11/73) for signal averaging. The data presented here represent the average of the signal from 500 laser pulses. Samples consisted of 10^{-3} to 10^{-4} M aqueous solutions of HPLC-purified 1-naphthol prepared and maintained under oxygen-free conditions. All experiments were carried out at ambient temperature.

The first time-resolved observation of excited-state proton transfer in 1-naphthol is presented in Fig. 2. At a solution pH of 12, >99.8% of ground state species present is RO^- . Laser excitation produces RO^{-*} emission with an instrument-limited risetime (< 6 ps) and an 8.0 ± 0.4 ns fluorescence lifetime, as expected for direct excitation of RO^{-*} . At a solution pH of 7, >99.4% of the ground-state species present is ROH . Laser excitation produces a RO^{-*} time-resolved emission profile with a distinct, 31 ± 5 ps risetime and a 7.5 ± 0.4 ns decay, proof that RO^{-*} is indirectly produced via excited-state proton transfer from ROH^* . The

validity of the reaction scheme of Fig. 1 is confirmed by the results shown in Fig. 3. The average decay time of the ROH* emission, measured at wavelengths between 350 and 370 nm, is 35 ± 5 ps. Within experimental error, this is identical with the 31 ± 5 ps average risetime of the RO^{-*} emission at wavelengths >500 nm. Further evidence that the reaction scheme of Fig. 1 is correct is provided by the observation of an isosbestic point in the picosecond, time-resolved emission spectrum of 1-naphthol.¹⁸

Kinetic expressions for the temporal dependence of the emission intensity from the protonated, I_(ROH*), and anionic, I_(RO^{-*}), species, as derived from the model of Fig. 1, have the general form:^{2,15}

$$I_{(\text{ROH}^*)} = A_1 e^{-\gamma_1 t} + A_2 e^{-\gamma_2 t} \quad (1)$$

$$I_{(\text{RO}^{-*})} = B(e^{-\gamma_2 t} - e^{-\gamma_1 t}). \quad (2)$$

All the excited-state rate constants can, in principle, be extracted by measuring γ_1, γ_2 , and the ratio A_1/A_2 as a function of hydronium ion concentration.^{2,9,15} Such an analysis is difficult due to the complex relationship between the various kinetic parameters and the double exponential temporal profile of the emission. Given the uncertainties in the experimental results, it has thus far been impossible to obtain all of the necessary rate constants with high accuracy solely on the basis of the time-resolved data.

Combination of the results of steady-state measurements with direct, time-resolved measurements yields the most accurate determination of the desired rates. For example, the constants τ_0 ($1/\tau_0 = k_r + k_{nr}$) and k^*_{dp} (see Fig. 1) can be readily determined from

$$\phi'/\phi'_0 = k^*_{dp}/\gamma_1 = k^*_{dp}/(k^*_{dp} + 1/\tau_0), \quad (3)$$

where ϕ'/ϕ'_0 is the quantum yield of fluorescence of the anion at neutral pH relative to that at high pH, and γ_1 is obtained from the neutral fall time and/or the anion risetime at pH 7. A complete kinetic analysis will be presented

in a subsequent paper.¹⁹ A short summary of representative results from this analysis is given in Table 1.

Perhaps the most striking result revealed by this work is the contrast between the excited-state reaction dynamics of 1-naphthol and those of 2-naphthol²⁰ (see Table 1). For 2-naphthol, nanosecond time resolution is sufficient for direct observation of the excited-state processes. In 1-naphthol, excited-state proton transfer (k_{dp}^*) is ~280 times faster and solvent quenching (as manifested by τ_0) is ~80 times faster than in 2-naphthol. Proton-induced quenching of RO^-* is found to be substantial in 1-naphthol¹⁹ compared to 2-naphthol, direct confirmation of the results of previous indirect studies.^{7,9,20} Such results demonstrate that changes in electronic structure as subtle as those expected for two such similar isomers can have dramatic effects on excited-state proton-transfer dynamics. The observed effects can be explained by the difference in the charge-transfer character of the lowest excited singlet states of 1-naphthol and 2-naphthol.¹⁹ The present results suggest that direct, time-resolved measurements provide a generally applicable experimental method for determining the role of electronic structure and solvent organization in acid-base chemistry. The measurements reported here are currently being extended by the systematic study of excited-state proton-transfer dynamics in naphthols and substituted naphthols as a function of solvent, temperature, and pressure.

References and Notes

- (1) This work was supported by the Research Corporation and by the Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.
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Figure Captions

Fig. 1. Kinetic scheme for excited-state dynamics of 1-naphthol in aqueous solution: k_{dp} , k^*_{dp} , k_p , and k^*_p represent the ground and excited state deprotonation and protonation rate constants, respectively; k_{nr} , k'_{nr} , k_r , k'_r , k_q , and k'_q are the rate constants for non-radiative decay, radiative decay, and proton-induced quenching for the neutral and anionic species, respectively.

Fig. 2. Time-resolved 550 ± 5 nm emission from electronically excited 1-naphtholate ions in pH 12 and pH 7 aqueous solutions. The smooth curves are computer-generated fits to the data with risetimes of 5.6 ps (pH 12) and 30 ps (pH 7).

Fig. 3. Time-resolved emission from the protonated (ROH^* , 370 ± 6 nm) and anionic (RO^{-*} , 540 ± 5 nm) forms of electronically excited 1-naphthol in pH 7 aqueous solution. Smooth curves show computer-generated fits to the data with a ROH^* decay time of 34 ps and a RO^{-*} risetime of 31 ps.

Table 1. Measured rates, lifetimes, and relative fluorescence quantum yields for 1-naphthol (present work) and 2-naphthol²⁰ in aqueous solution.

$$1/\tau'_0 = k'_r + k'_{nr}$$

Solute	ϕ'/ϕ'_0	γ_1^{-1} (ps)	k^*_{dp} (s^{-1})	τ_0 (ps)	τ'_0 (ns)
1-naphthol	0.66	33	2.1×10^{10}	100	8.0
2-naphthol	0.64	5.0×10^3	7.5×10^7	8.0×10^3	9.0

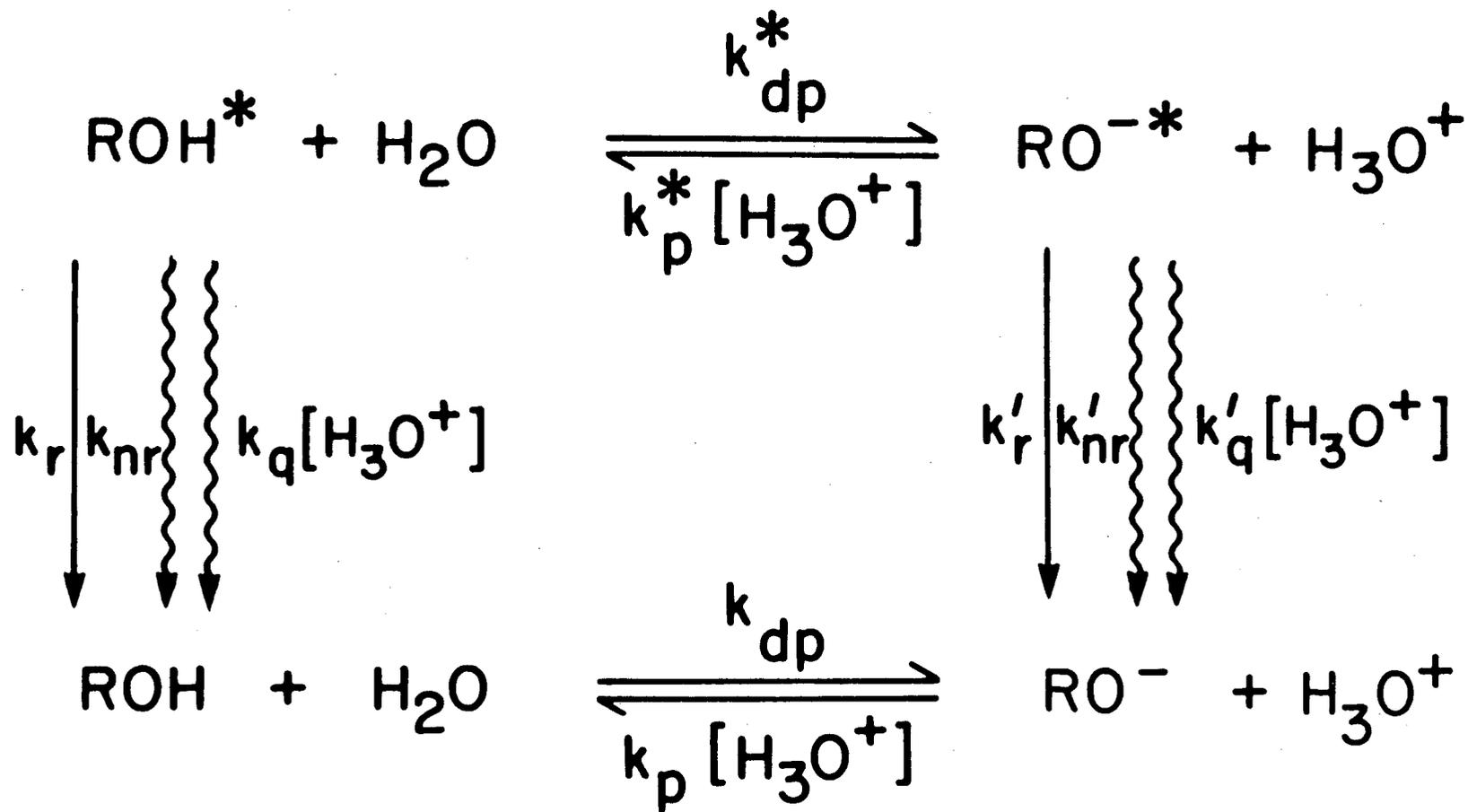


Fig. 1

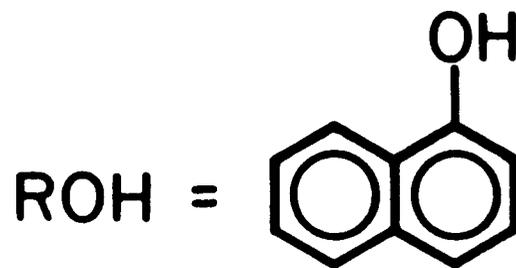


Fig. 2

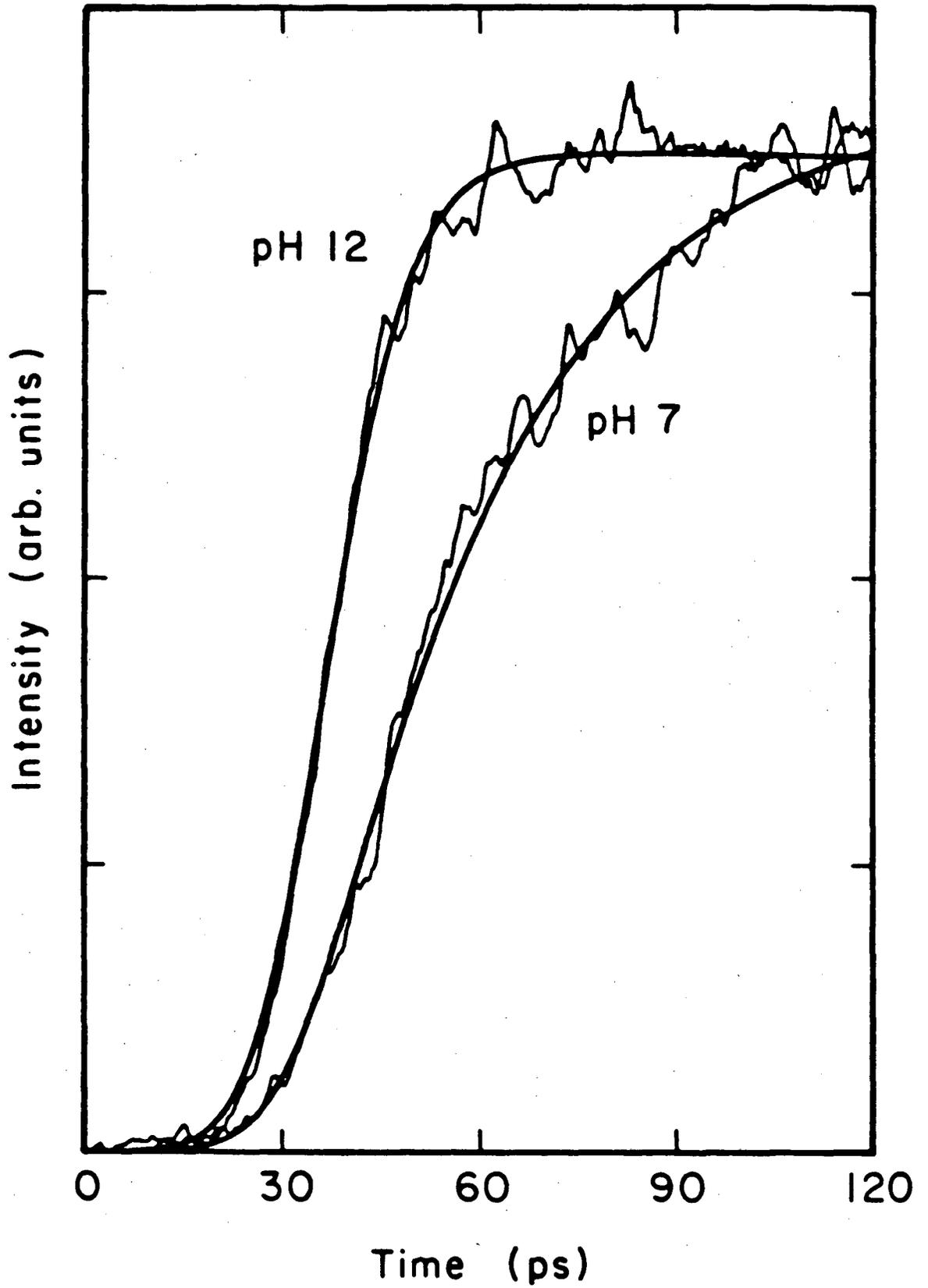
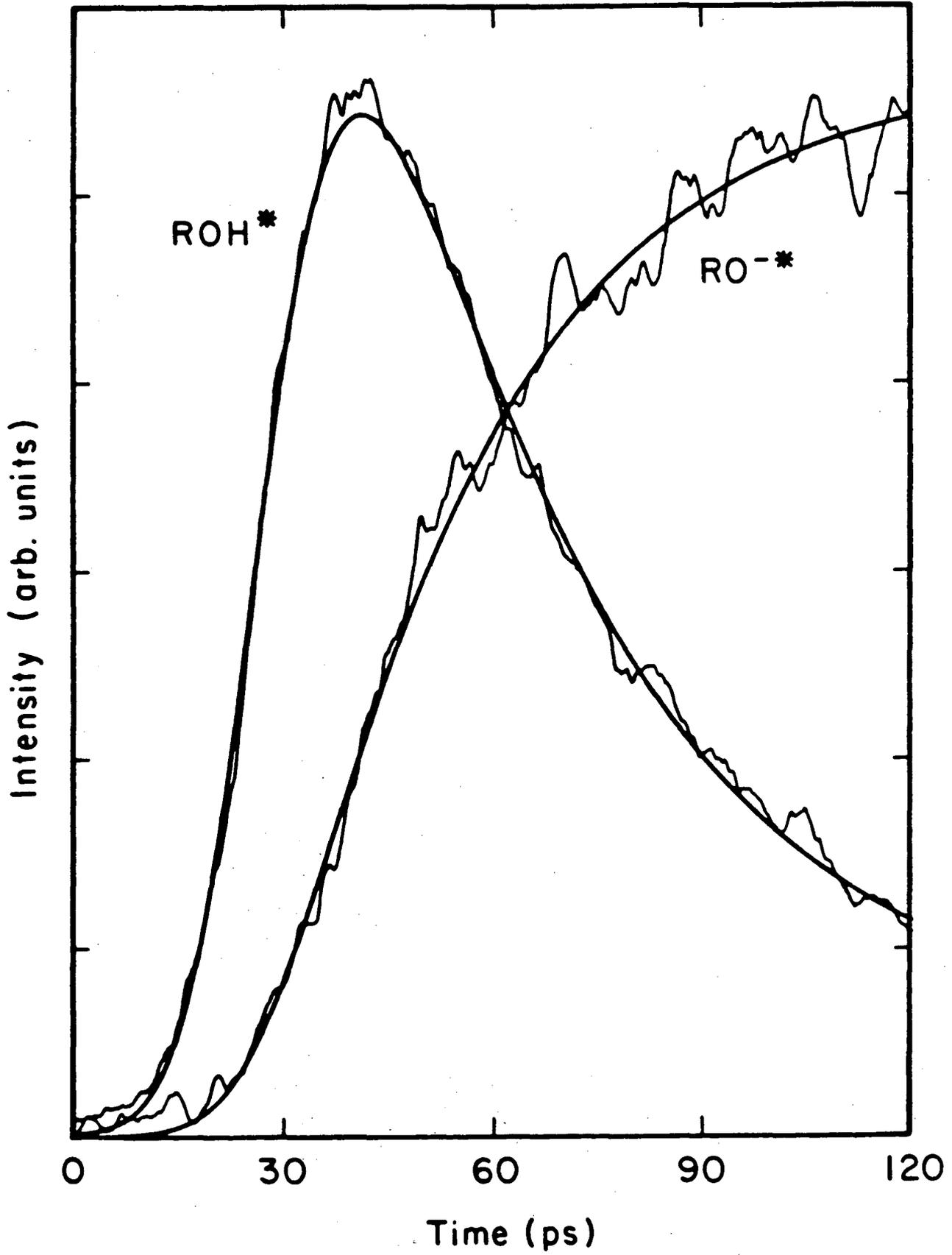


Fig. 3



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