

relaxation of electronically excited $[\text{Co}(\text{NH}_3)_6]^{3+}$. In the related d^6 complex $[\text{Rh}(\text{NH}_3)_6]^{3+}$, a large decrease in the ${}^3\text{T}_{1g} \rightarrow {}^1\text{A}_{1g}$ radiationless relaxation rate was observed on deuteration, implicating the NH_3 groups in the vibronic coupling which promotes nonradiative relaxation.³⁸

From the absorption coefficients at 1064 nm (Table I) it can be seen that one third of the absorbed photons cause direct excitation into N-H ($\nu = 3$). In order to compete with this direct pathway of state-selective excitation of a mode linked to the proton-transfer reaction coordinate, an indirect route to a hot ground state via radiationless relaxation from an electronically excited state would have to be highly efficient and selective.

In summary, the evidence supports a mechanism for enhanced H/D exchange of $[\text{Co}(\text{NH}_3)_6]^{3+}$ involving direct vibrational excitation in the electronic ground state. A single-photon process is indicated because of the low power density used (kW cm^{-2}) and the small absorption coefficients for vibrational overtone excitation (cf. ref 7). To clarify whether there is any indirect excitation via radiationless relaxation from an excited electronic state it would be of interest to examine the wavelength dependence of the H/D exchange, tuning both within the N-H vibrational overtone band centered at 1052 nm and at higher energies where purely electronic excitation occurs.

This is the third example of vibrational photochemistry involving laser-enhanced proton transfers in the liquid state. All three reactants H_2O ,^{6,7} CH_3NO_2 ,⁹ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ have quantum yields of 10^{-4} or below. The reason for a low value of $\phi(\nu)$ for $[\text{Co}(\text{NH}_3)_6]^{3+}$ is most likely to be the competition between (1) cleavage of the $-\text{NH}_2\cdots\text{H-O}$ hydrogen bond in the ion pair formed by laser-driven proton transfer, which must be followed by rotational or translational diffusion to generate $-\text{NH}_2\cdots\text{D-O}$ in order to give H/D exchange^{39,40} and (2) intramolecular vi-

brational relaxation (IVR)^{5,41} and intermolecular vibrational relaxation,⁴² both processes leading to dissipative relaxation of energy away from the $-\text{NH}_2\cdots\text{H-O}$ bond and favoring the lower energy $-\text{NH}_3\cdots\text{O}$ structure of the relaxed reactant.

IVR from high levels of vibrational excitation occurs in femtoseconds,⁴¹ whereas the rotational reorientational time for D_2O is 5 ps at 10 °C.⁴³ This could lead to an upper limit of 10^{-3} – 10^{-2} for $\phi(\nu)$ in H/D exchange reactions. In considering ion pair return, Coulomb interactions in the intermediate $[\text{Co}(\text{NH}_3)_5(\text{NH}_2^-)]^{2+}\cdots\text{HOD}_2$ should be more favorable for proton release from the ion pair into the bulk solution than in the case of $\text{OH}^-\cdots\text{HOH}_2$, the intermediate in the vibrational photochemistry of water. At 1064 nm and 25 °C, $\phi(\nu)$ in the well-documented water photoionization^{6,7} is 4×10^{-7} , three orders of magnitude lower than $\phi(\nu)$ for $[\text{Co}(\text{NH}_3)_6]^{3+}$.

The lack of any indication of vibrational photochemistry for $[\text{Coen}_3]^{3+}$ ($\phi(\nu) < 7 \times 10^{-5}$) may be a consequence of the greater number of vibrational modes over which to unproductively delocalize the energy in the $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ unit than in NH_3 .

$[\text{Co}(\text{NH}_3)_5\text{Me}_2\text{SO}]^{3+}$ was chosen in our search for mode-selective chemistry as an example of a compound with two reaction channels. We have characterized the competition in the thermal reaction between H/D exchange in the trans NH_3 group and Me_2SO loss to give $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$. The overlap of electronic and vibrational absorption bands at 1064 nm with $\epsilon(\text{e}) \gg \epsilon(\nu)$ explains why ligand loss, the reaction pathway favored by electronic excitation, was observed to be dominant.

Acknowledgment. Acknowledgment is made to the Science and Engineering Research Council (Grant GR/B/6405.5) for support of this research.

Registry No. $[\text{Co}(\text{NH}_3)_6]^{3+}$, 14695-95-5; $[\text{Coen}_3]^{3+}$, 14878-41-2; $[\text{Co}(\text{NH}_3)_5\text{Me}_2\text{SO}]^{3+}$, 44915-85-7.

(39) Anderson, J. S.; Briscoe, H. V. A.; Spoor, N. L. *J. Chem. Soc.* **1943**, 361.

(40) Lin, A. C.; Chiang, Y.; Dahlberg, D. H.; Kresge, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 5380. Kresge, A. J. *Acc. Chem. Res.* **1975**, *8*, 354.

(41) Jortner, J.; Levine, R. D. *Adv. Chem. Phys.* **1981**, *47*, 1. Bondybey, V. E. *Annu. Rev. Phys. Chem.* **1984**, *35*, 591.

(42) Laubereau, A.; Kaiser, W. *Rev. Mod. Phys.* **1978**, *50*, 608.

(43) Jones, J.; DeFries, T.; Wilbur, D. J. *J. Chem. Phys.* **1976**, *65*, 582.

Excited-State Intramolecular Proton Transfer in 3-Hydroxyflavone Isolated in Solid Argon: Fluorescence and Fluorescence-Excitation Spectra and Tautomer Fluorescence Rise Time

Bernhard Dick* and Niko P. Ernsting

Max-Planck-Institut für biophysikalische Chemie, Abteilung Laserphysik, Am Fassberg, D-3400 Göttingen, Federal Republic of Germany (Received: November 20, 1986; In Final Form: April 1, 1987)

The fluorescence properties of 3-hydroxyflavone isolated in solid argon at 15 K have been investigated. Upon electronic excitation the molecules undergo rapid intramolecular proton transfer. No fluorescence from the excited state of the normal form of the molecule could be detected. Perturbations due to hydrogen-bonding impurities which produce serious experimental problems in hydrocarbon glasses are largely suppressed in argon matrices. The rise of the green fluorescence of the tautomer was studied with excitation pulses of 230-fs duration and streak camera detection. An apparent tautomer fluorescence rise time of 2.7 ps was obtained by deconvolution. A comparative measurement of the dye coumarin 6 yielded an apparent fluorescence rise time of 2.5 ps, which can be entirely attributed to the group velocity dispersion of the streak camera optics. This indicates a rate constant for excited-state intramolecular proton transfer in 3-hydroxyflavone of greater than 10^{12} s^{-1} .

Introduction

Excited-state intramolecular proton transfer (ESIPT) is a fast reaction occurring in many organic molecules of biological or technical interest.^{1,2} Typically, these molecules possess a phenolic

hydroxyl group close to a heteroatom of the same chromophore. After electronic excitation of such a molecule to the excited state of its normal form (A), the phenolic proton jumps to the opposite heteroatom, usually along a hydrogen bond, to form the tautomer

(1) Klöpffer, W. *Adv. Photochem.* **1977**, *10*, 311.

(2) Huppert, D.; Gutman, M.; Kaufmann, K. J. *Adv. Chem. Phys.* **1981**, *47*, 643.

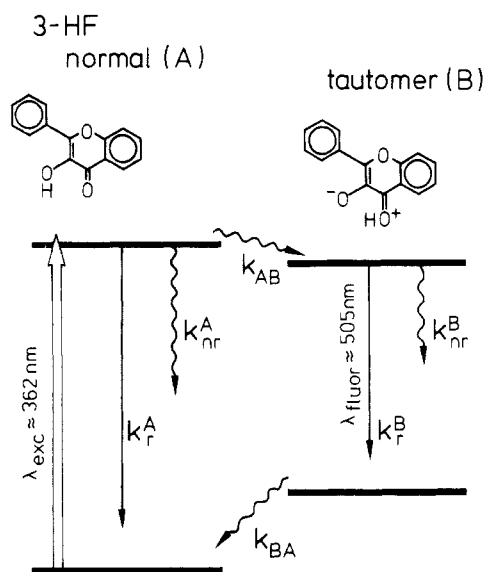


Figure 1. Schematic energy level diagram for ES IPT in 3-hydroxyflavone indicating radiative (k_r) and nonradiative (k_{nr}) decay processes of the normal form (A) and the tautomer (B). Proton transfer is assumed to be irreversible with constants k_{AB} and k_{BA} in the excited state and the ground state, respectively.

(B) in its lowest excited singlet state. Figure 1 shows the structural formulas of both forms of 3-hydroxyflavone (3-HF) and a schematic diagram indicating the various decay paths and rate constants involved. When the tautomer undergoes fast internal conversion ($k_{nr}^B \gg k_r^B$, and no intersystem crossing) followed by rapid back-transfer of the proton in the electronic ground state, such molecules are effective UV stabilizers. On the other hand, when the tautomer excited state has long lifetime ($k_r^B \geq k_{nr}^B$), these molecules are potential laser dyes since the tautomer B is generated within picoseconds in complete inversion. Laser action has already been reported for 3-HF.^{3,4} It is therefore of particular interest to obtain detailed knowledge of ES IPT as a function of structural and environmental parameters. Especially the existence of intrinsic energy barriers to ES IPT and their heights are still a matter of controversy.

A barrier to ES IPT would manifest itself in the occurrence of dual fluorescence from the normal form (A) and the tautomeric form (B) of the molecule. Integration of the kinetic system sketched in Figure 1 with all initial excited-state population in the normal form A leads to the following ratio of quantum yields for both emissions:

$$\frac{F_A}{F_B} = \frac{k_r^A}{k_r^B} \frac{k_r^B + k_{nr}^B}{k_{AB}} \quad (1)$$

Hence, when the radiative rate constants k_r^A and k_r^B as well as the total lifetime of the tautomer excited-state $\tau_B = 1/(k_r^B + k_{nr}^B)$ are known, the rate constant for ES IPT, k_{AB} , can be calculated. A temperature dependence of the ratio F_A/F_B is thus an indication of a barrier to ES IPT.

However, in many cases a temperature dependence of dual-fluorescence quantum efficiencies was later found to originate from a varying degree of complexation with hydrogen-bonding impurities. A much-discussed example is 3-HF: solutions in hydrocarbon solvents at 298 K show only the green tautomer fluorescence; glasses made with commercial solvents at 77 K, on the other hand, displayed mainly violet fluorescence which was attributed to the normal form of the molecule.⁵ The temperature dependence was interpreted with a model of a viscosity-dependent barrier height associated with phenyl-ring torsion.⁵ However, pressure- and viscosity-dependent measurements at room tem-

perature showed that the rigidity of the medium had no effect on the tautomerization process.⁶ Time-resolved measurements revealed a fast (≤ 30 ps, unresolved) and a slow, temperature-dependent reaction.⁷⁻¹⁰ It was subsequently shown¹¹ that the violet emission in hydrocarbon glasses is due to complexes of 3-HF with hydrogen-bonding impurities and is absent when extensively purified and dried solvents are used. The slow reaction was assigned to a rearrangement of the excited complex leading to the internally hydrogen-bonded molecule which subsequently undergoes ES IPT.

McMorrow, Dzuga, and Aartsma have studied the rise time of the tautomer fluorescence from 3-HF in the absence of hydrogen-bonding perturbers.¹² They report a rise time of less than 8 ps at 298 K which increases to ca. 40 ps at 77 K, apparently indicating an intrinsic though small energy barrier to ES IPT. Hence it seemed worthwhile to study the fluorescence of 3-HF at very low temperatures, since the low barrier height should become most effective below 20 K.¹¹ All previous measurements of 3-HF were performed at temperatures of 77 K or higher. We choose argon matrices for a medium to minimize solvent interactions. Furthermore, we found it easy to prevent the formation of hydrogen-bonded complexes with water. After deposition of the matrix at 15 K no diffusion occurs. Rare gas matrices have been used successfully in the study of degenerate or near-degenerate proton-transfer reactions in hydroxyphenalenones¹³⁻¹⁸ and tropolone,¹⁹ where the barrier height could be inferred from the measured tunneling splitting. We also measured the rise time of the tautomer fluorescence from 3-HF with a streak camera.

Experimental Section

Compound and Matrix Deposition. 3-Hydroxyflavone (Eastman) was purified by recrystallization from methanol (3X) followed by vacuum sublimation (mp 171.5 °C). Matrices were deposited on a sapphire substrate kept at 15 K by a closed-cycle refrigerator (Leybold ROK 10-300). A glass tube containing 3-HF dispersed over glass wool served as the inlet for the argon gas. Deposition was controlled through regulating the argon flux in the range 1–3 mmol/h and heating the sample to 40 °C. After deposition (2–4 h) the exit of the glass tube was closed with a shutter to prevent further sublimation.

Fluorescence and Excitation Spectra were excited with light of a 75-W xenon arc lamp dispersed through a monochromator (Spex 1780, $f = 50$ cm). Fluorescence was detected at an angle of 90° through a glass filter and a small monochromator (Jarrell Ash) with ca. 4 nm bandpass. Part of the excitation light was split off and directed into a quantum counter (Rhodamine B in glycol) to provide a reference signal. Red-sensitive photomultipliers (EMI 9659Q and EMI 9558Q) were used for photon counting. Fluorescence photons were counted by a multichannel analyzer (Canberra 8100). The monochromator and the multichannel analyzer were advanced to the next position when a preset number of reference photons had been counted. For fluorescence excitation spectra, the excitation monochromator was stepped in 1.5-Å increments with a bandwidth of 2.5 Å.

- (6) Salman, O. A.; Drickamer, H. G. *J. Chem. Phys.* **1981**, *75*, 572.
- (7) Woolfe, G. J.; Thistlethwaite, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 6916.
- (8) Itoh, M.; Tokumura, K.; Tanimoto, Y.; Okada, Y.; Takeuchi, H.; Obi, K.; Tanaka, I. *J. Am. Chem. Soc.* **1982**, *104*, 4146.
- (9) Strandjord, A. J. G.; Barbara, P. F. *Chem. Phys. Lett.* **1983**, *98*, 21.
- (10) Strandjord, A. J. G.; Courtney, S. H.; Friedrich, D. M.; Barbara, P. F. *J. Phys. Chem.* **1983**, *87*, 1125.
- (11) McMorrow, D.; Kasha, M. *J. Phys. Chem.* **1984**, *88*, 2235.
- (12) McMorrow, D.; Dzuga, T. P.; Aartsma, T. J. *Chem. Phys. Lett.* **1984**, *103*, 492.
- (13) Rossetti, R.; Haddon, R. C.; Brus, L. E. *J. Am. Chem. Soc.* **1980**, *102*, 1546.
- (14) Rossetti, R.; Rayford, R.; Haddon, R. C.; Brus, L. E. *J. Am. Chem. Soc.* **1981**, *103*, 4303.
- (15) Van Benthem, M. H.; Gillispie, G. D.; Haddon, R. C. *J. Phys. Chem.* **1982**, *86*, 4281.
- (16) Bondybey, V. E.; Haddon, R. C.; English, J. H. *J. Chem. Phys.* **1984**, *80*, 5432.
- (17) Bondybey, V. E.; Haddon, R. C.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5969.
- (18) Gillispie, G. D.; Van Benthem, M. H.; Vangness, M. J. *J. Phys. Chem.* **1986**, *90*, 2596.
- (19) Rossetti, R.; Brus, L. E. *J. Chem. Phys.* **1980**, *73*, 1546.

(3) Chou, P.; McMorrow, D.; Aartsma, T. J.; Kasha, M. *J. Phys. Chem.* **1984**, *88*, 4596.

(4) Chou, P.; Aartsma, T. J. *J. Phys. Chem.* **1986**, *90*, 721.

(5) Sengupta, P. K.; Kasha, M. *Chem. Phys. Lett.* **1979**, *68*, 382.

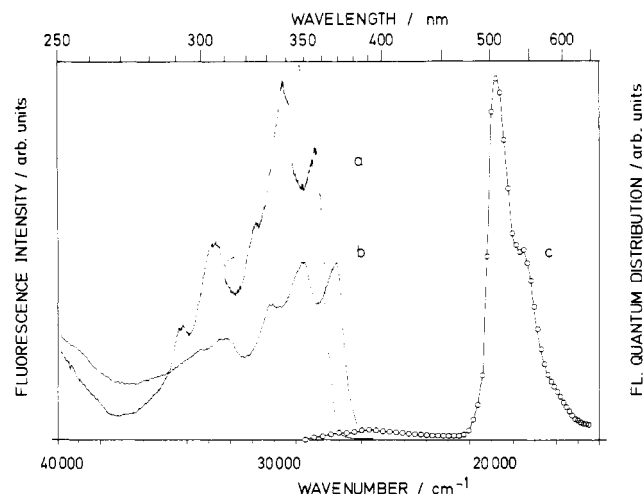


Figure 2. Spectra of 3-hydroxyflavone isolated in solid argon at 15 K: (a) excitation spectrum of the green fluorescence of the tautomer, monitored at 505 nm; (b) excitation spectrum of the residual violet fluorescence monitored at 410 nm; (c) corrected fluorescence spectrum (relative number of quanta per wavenumber interval) excited at 305 nm.

Fluorescence spectra were obtained in a point-by-point fashion by scanning the detection monochromator manually in 5-nm steps. The spectral sensitivity of the detection system was calibrated with a tungsten-halogen standard lamp (Optronic).

Temporal Resolution of Tautomer Fluorescence. Two sets of time-resolved fluorescence measurements were performed, with excitation pulses of different wavelength and pulse duration. In the first experiment the sample was excited with light pulses of 10-ps duration at 362 nm with a pulse energy of ca. 4 μ J which were generated by an excimer-pumped dye laser.²⁰ The first stage of this simple system consists of a *p*-terphenyl dye laser in a quenched-cavity configuration. Its output, after one-stage amplification, pumps a short-cavity dye laser operating with a solution of Bu-PBD in methanol. The resulting pulse is amplified in two further stages. A second short-cavity dye laser with dichroic mirrors, and using a methanolic BBOT solution as lasing medium, is used between the last amplifiers as a saturable absorber with a fast trailing gate due to stimulated emission.

The fluorescence emitted from the sample was filtered through a yellow glass filter (Schott GG475/3 mm) and imaged onto the entrance slit of a streak camera (Hamamatsu C1370). A portion of the excitation pulse was split off and also brought to the entrance slit of the streak camera to provide each streak with a time reference. Individual streaks were digitized and stored. Up to 251 streaks were subsequently averaged, with the center of the excitation pulse taken as the time reference.

In the second experiment the sample was excited with light pulses of ca. 230-fs duration at 308 nm. The pulses were generated by a XeCl excimer laser system which includes the above-mentioned short-cavity dye laser and a distributed feedback dye laser (DFDL) operating at 616 nm with pulse duration of 350 fs.²¹ After amplification the red pulses were frequency-doubled, and the resulting pulses at 308 nm were amplified in the second discharge channel of the excimer laser (Lambda Physik EMG 150).²² A small portion containing 38 μ J of the total pulse energy was used for fluorescence excitation. Part of the red fundamental pulse was split off and used as a preceding time marker for streak-camera measurements.

Results and Discussion

Steady-State Spectra. Figure 2 shows the corrected fluorescence spectrum and the fluorescence excitation spectra of 3-HF in an argon matrix at 15 K. The fluorescence (curve c) is almost entirely due to the tautomer emission with a maximum at 505

nm. The residual emission in the range of the normal fluorescence, 360–470 nm, accounts for less than 3% of the total fluorescence emission. This is similar to the behavior found by McMorro and Kasha in highly purified and dried methylcyclohexane (MCH)¹¹ or *n*-alkanes²³ at 77 K. Hence the matrix isolation technique produces samples that are essentially of the same quality as those obtained in extensively purified solvents.

The excitation spectrum of the tautomer emission (curve a in Figure 2) has its first peak at 356 nm, only slightly blue-shifted from the position at 361 nm in a MCH glass at 77 K.¹¹ However, it displays more vibrational structure with higher intensities for the higher energy bands, resembling more the absorption spectrum. This indicates that in the argon matrix the fluorescence quantum yield is nearly constant over the excitation spectrum. In hydrocarbon matrices at 77 K the fluorescence quantum yield decreases with increasing excess energy. This hints at a nonradiative decay channel that is not active in solid argon at 15 K.

The peak of the tautomer fluorescence occurs at 505 nm compared to 523 nm in a MCH glass. This stronger blue-shift with respect to the excitation spectrum can be explained by the lower polarizability of argon compared to hydrocarbons and the higher polarity of the tautomer compared to the normal form of 3-HF.

The excitation spectrum of the violet emission at 410 nm (curve b in Figure 2) shows that this emission is not due to unperturbed 3-HF molecules in their normal form. Instead it has its first peak at 368 nm, red-shifted from the excitation spectrum of the tautomer fluorescence. This red-shift of 12 nm was also found by McMorro and Kasha¹¹ for the excitation spectrum of 3-HF in solvents contaminated with hydrogen-bonding impurities. From the bandshape of the excitation spectrum of the violet fluorescence we estimate that less than 1% of the excited unperturbed 3-HF molecules fluoresce from their normal form. Hence we conclude that even at 15 K no intrinsic barrier for ESIPT is effective in isolated 3-HF.

The violet emitting species could be an impurity, a water complex, a dimer, or a conformer of 3-HF with a high barrier to ESIPT. We believe that an impurity can be excluded as the source of violet emission since essentially the same spectra are obtained when 3-HF purified only by recrystallization from methanol, or even not purified at all, was used. However, the relative contribution of violet emission increased to about 6% when the matrix was annealed at ca. 30 K for 1–2 h. A possible explanation for the latter effect is diffusion of water molecules in the matrix to form hydrogen-bonded complexes. Since purification of the argon gas by a liquid nitrogen trap filled with molecular sieve (4Å) did not alter the results, the contaminating water could only come from the sample itself, from the vaporization oven, or from the cryostat walls. However, adding 4% water vapor to the argon before deposition of the matrix increased the violet emission only to about 4.5%, which further increased to 7.5% through annealing. Thus even a large excess of water does not produce large amounts of hydrogen-bonded complexes, and this lets it seem unlikely that the violet emission in the “dry” matrices is due to small amounts of water from residual contamination of the sample or the apparatus.

3-HF could be forced to produce the hydrogen-bonded water complex only when argon containing 4% water was deposited onto the sapphire substrate at temperatures between 30 and 35 K (at 35 K the vapor pressure of Ar increases to 10^{-3} mbar). In these samples 55% of the fluorescence quanta were emitted in the violet region (see Figure 3, curve c). The excitation spectrum of the green tautomer fluorescence is still shifted 10 nm to shorter wavelengths from the excitation spectrum of the violet fluorescence. The vibrational structure in both excitation spectra appears smoothed with respect to the spectra of the “dry” matrices and resembles that found in MCH glass at 77 K. We conclude that diffusion of water and formation of the hydrogen-bonded complex occurs only at the surface of the argon matrices at temperatures above 30 K.

(20) Szatmari, S.; Racz, B. *Opt. Quantum Electron.* in press.

(21) Szatmari, S.; Racz, B. *Appl. Phys. B* **1987**, *43*, 93.

(22) Szatmari, S.; Racz, B.; Schäfer, F. P. *Opt. Commun.* **1987**, *62*, 271.

(23) McMorro, D.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 3375.

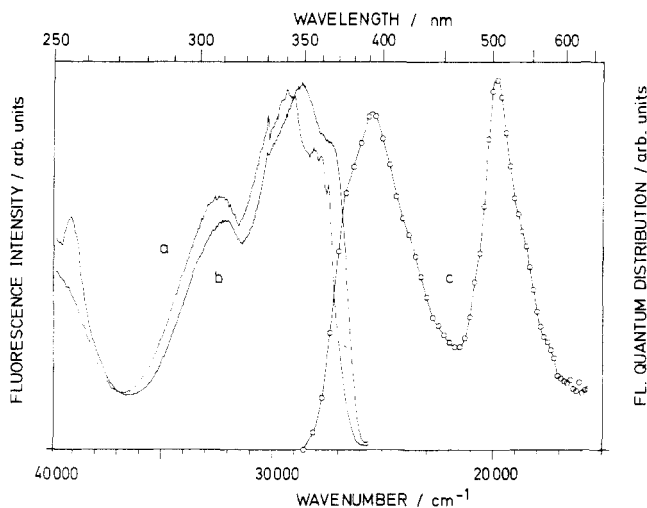


Figure 3. Same as Figure 2, but with 4% water added to the argon prior to matrix deposition at temperatures of 30–35 K.

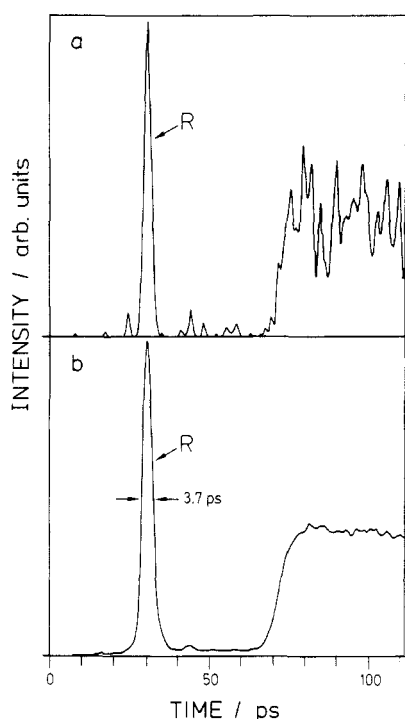


Figure 4. (a) Example of a single streak measured with the fastest streak speed (111 ps/256 channels) of the streak camera. The red DFDL pulse at 616 nm produces the sharp peak marked "R" which was used as the time reference for averaging. (b) Average of 251 single streak records.

The residual violet emission in the "dry" argon matrices at 15 K could be explained by the existence of a conformer or a dimer of 3-HF with a high energy barrier to ESIPT. If the site for these conformers or dimers is thermodynamically more stable than the site for the green emitting species, annealing of the matrix would account for the increase in violet emission. Adding water to the matrix could also increase the number of favorable sites for the conformer or the dimer.

Streak Camera Measurements. For time-resolved measurements of the green tautomer fluorescence only "dry" matrices were used and the residual violet fluorescence was cut off by a glass filter.

First, we discuss the results obtained with 10-ps excitation at 362 nm. With the slowest streak speed of the streak camera we followed the decay of the fluorescence over a period of 5.5 ns. A numerical fit to the experimental data within this limited range yields a lifetime of 8.6 ± 0.2 ns for the exponential decay of the tautomer fluorescence. Strandjord and Barbara obtained a lifetime of 7.7 ns for their samples in alkane glass at 77 K.¹⁶ In faster

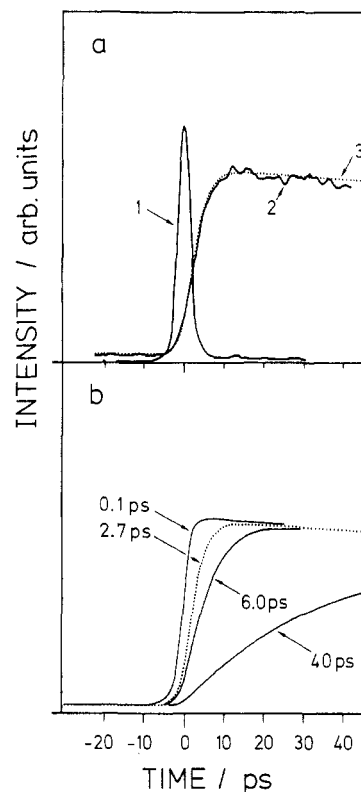


Figure 5. (a) Streak camera measurements of green tautomer fluorescence of 3-hydroxyflavone isolated in solid argon at 15 K. 251 streaks have been averaged: Curve 1, reference pulse section of the averaged streaks giving the instrument function of our apparatus; curve 2, fluorescence section of the streak, scaled by a factor of 2 relative to the reference pulse and shifted to the same time origin with the reference pulse; curve 3, least-squares fit with an apparent rise time τ_R of 2.7 ps. (b) Simulations of the temporal fluorescence profile obtained by convolution of the experimentally determined instrument function with the molecular response function of eq 4 for several rise times τ_R .

streak modes we observed a small component with an approximate decay time constant of 540 ps. This fast decay component might be due to inhomogeneous site effects. It could also be caused by stimulated emission, since the tautomer is formed in complete population inversion resulting in a high gain for amplification of spontaneous emission. Laser action of the tautomer form of 3-HF has already been reported.^{3,4} When stimulated emission contributes to the decay of the tautomer excited state the decay should not be strictly exponential, at least during the initial phase. However, observation over a longer period with higher signal-to-noise ratio would be required to measure a significant deviation from exponential behavior.

The second experiment employed 230-fs excitation pulses at 308 nm for the measurement of the tautomer fluorescence rise time. Here, the fastest speed of the streak camera (111 ps/256 channels) was used. Light levels were kept low in order to keep within the dynamic range of the streak camera,²⁴ and many streaks were averaged on a computer. Figure 4a shows a typical example of a single streak: the streak-camera is operated almost on a single-photon-counting level with low signal-to-noise ratio. Figure 4b shows the result of averaging 251 streaks. The center of the red DFDL pulse at 616 nm was used as a time reference for the averaging procedure to compensate for the time jitter in the trigger of the streak camera. The averaged streak consists of two regions containing the averaged reference pulses and the averaged fluorescence signal, respectively.

In Figure 5 these two parts are plotted on the same absolute time axis, i.e. the fluorescence part was shifted back in time by the duration of the optical delay employed in the experiment. The

(24) Campillo, A. J.; Shapiro, S. L. *IEEE J. Quantum Electron.* **1983**, *QE-19*, 585.

averaged reference peak (curve 1 in Figure 5a) has a full-width at half-maximum of 3.7 ps. Autocorrelation measurements of the DF DL pulses yield a much shorter pulsewidth of ca. 350 fs.²¹ Hence the measured shape of the reference pulse is dominated by the instrument function of our apparatus. Its width is determined by the temporal resolution of the streak camera and the uncertainty in the determination of the center of the reference pulse in each streak.

The measured temporal profile of the fluorescence $F(t)$ is the convolution of a molecular response function $R(t)$ with the temporal profile of the excitation pulse $P(t)$ and an instrument function $Q(t)$:

$$F(t) = \int_{-\infty}^{+\infty} dt' R(t-t') S(t'-t_0) \quad (2)$$

$$S(t) = \int_{-\infty}^{+\infty} dt' Q(t-t') P(t') \quad (3)$$

The response function for the rise and decay of the tautomer fluorescence is

$$R(t) = A(\exp(-t/\tau_D) - \exp(-t/\tau_R)); \quad t > 0 \\ = 0; \quad t < 0 \quad (4)$$

The temporal profile of the reference pulse is also described by 2 and 3, setting $R(t) = \delta(t)$. This suggests that we may identify $S(t)$ with the measured pulse shape of the reference pulse. We performed several numerical simulations and a least-squares fit to the experimental temporal profile of the tautomer fluorescence using the experimentally determined $S(t)$. Figure 5b shows a few simulated curves for various rise times τ_R . The decay time τ_D was fixed to 540 ps, the fast decay component mentioned above. The least-squares fit to the experimental data yielded $\tau_R = 2.7 \pm 0.2$ ps. In this fit the rise time τ_R , the amplitude A , the time origin t_0 , and a constant background were simultaneously optimized. The decay time τ_D was kept fixed since the decay portion of the streak is too short to allow a meaningful fit. However, variation of τ_D in the range 540 ps to 8 ns affected the calculated τ_R only by ± 0.1 ps. The simulated curve corresponding to the best fit is superimposed as a dotted line on the experimental curve in Figure 5a. It is also shown as a dotted line in Figure 5b in comparison to other simulated fluorescence rise curves.

The value of 2.7 ps for the deconvoluted rise time is comparable to the experimental time resolution of 3.7 ps. In the preceding experiment we performed essentially the same measurement with excitation pulses of 10-ps duration. In this case the simulated fluorescence time profile with $\tau_R = 5$ ps could not be distinguished from the simulation with $\tau_R = 0.1$ ps, and both simulations could be made to coincide almost perfectly with the experimental curve through a small shift of the time origin. From this observation

we conclude that deconvoluted rise times smaller than the time resolution of the experiment (i.e. the width of the function $S(t)$ in eq 3) must be interpreted with caution. The simulated curves in Figure 5b show, however, that in the present experiment a rise time of 2.7 ps can be clearly distinguished from the case of an instantaneous rise, i.e. the instrument-limited rise (approximated by $\tau_R = 0.1$ ps).

The data analysis presented above is valid for a streak camera which has the same transit time for all wavelength components of the fluorescence. If this is not the case, the rise time measurement of a spectrally broad emission will yield a slower apparent rise time. To estimate the contribution of this effect we repeated the experiment with the dye coumarin 6, which has a fluorescence spectrum similar to that of 3-HF. The apparent rise time of this fluorescence, which is expected to rise instantaneously, was found to be 2.5 ps. This is not significantly shorter than the apparent rise time observed for 3-HF. Hence we must conclude that the true rise time of the tautomer fluorescence of 3-HF is faster than the time resolution of our apparatus, which is approximately 1 ps. This leads to an estimate of $k_{AB} \geq 10^{12} \text{ s}^{-1}$ for the rate constant of ES IPT in 3-HF.

This rise time must be compared to the rise time measured by Mc Morrow, Dzugan, and Aartsma (MDA) in several alkanes.¹² They find a rise time of 8 ps at room temperature which increases to ca. 40 ps at 77 K. Such an increase of the rise time with decreasing temperature would indicate an effective barrier to ES IPT and would predict even longer rise times for the low temperatures in argon matrices. We have reasons to question the results of MDA. They use a Kerr-shutter method with light pulses for excitation and gating of 33-ps duration. This corresponds to a time resolution of 46 ps when Gaussian pulse shapes are assumed. Hence, in view of our own experience with deconvolution and the similar noise level in our and their data, a deconvoluted rise time of less than 40 ps should be interpreted very cautiously.

In summary it appears that 3-HF in the condensed phase is no exception to the rule of exothermic excited-state intramolecular proton transfer: that the reaction has no intrinsic energy barrier and occurs on the time scale of vibrational relaxation in the excited state.

Acknowledgment. We are indebted to Dr. B. Nickel for the loan of the photon-counting equipment and helpful discussions concerning its use, and to Dr. Staerk who brought to our attention the group velocity dispersion he observed with a streak camera similar to ours. We thank Dr. S. Szatmari and Dr. B. Racz for kindly permitting us to use the 230-fs pulses from their laser system. We also thank Prof. Alexander Müller for a loan of the streak camera, and Prof. F. P. Schäfer for support.

Registry No. 3-HF, 577-85-5; Ar, 7440-37-1; coumarin 6, 38215-36-0.

Photolysis of Nitrogen Trichloride

J. V. Gilbert,* X. L. Wu, D. H. Stedman, and R. D. Coombe

Department of Chemistry, University of Denver, Denver, Colorado 80208 (Received: December 29, 1986; In Final Form: March 13, 1987)

Spectra and time profiles of the emission resulting from pulsed irradiation of NCl_3 at 248 and 308 nm were collected and analyzed. Two distinct spectral features were observed, one a long series of bands separated by $320 \pm 30 \text{ cm}^{-1}$, the second an unresolved emission underlying the bands. The two features exhibit different time behavior and lifetimes in the limit of zero pressure. The photochemistry is interpreted via a model which involves the interaction of three electronic states of NCl_3 .

Introduction

The halogen amines are in general thermodynamically unstable with the exception of NF_3 . The explosive nature of the spontaneous decomposition is well-known and has had an inhibiting effect

on the scientific research of these interesting compounds.^{1,2} NCl_3 has been studied more than most of the other members of the

(1) Davy, H. *Philos. Trans. R. Soc.* **1813**, 103, 1.