relaxation of electronically excited [Co(NH₃)₆]³⁺. In the related d⁶ complex [Rh(NH₃)₆]³', a large decrease in the T_{1g} \rightarrow A_{1g} radiationless relaxation rate was observed on deuteration, implicating the NH₃ groups in the vibronic coupling which promotes nonradiative relaxation.¹³ 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 (v = 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 [Co(NH₃)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 excitation 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 H₂O,¹⁰ CH₃NO₂,³ and [Co(NH₃)₆]³⁺ have quantum yields of 10⁻⁴ or below. The reason for a low value of φ(v) for [Co(NH₃)₆]³⁺ is most likely to be the competition between (1) cleavage of the -NH₃+-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 -NH₃+-D-O in order to give H/D exchange³⁹,⁴⁰ and (2) intramolecular vibrational relaxation (IVR)³⁴ and intermolecular vibrational relaxation,³² both processes leading to dissipative relaxation of energy away from the -NH₃+-H-O bond and favoring the lower energy -NH₂+-O structure of the relaxed reactant.

IVR from high levels of vibrational excitation occurs in femtoseconds,⁴¹ whereas the rotational reorientational time for D₂O is 5 ps at 10 °C.⁴² This could lead to an upper limit of 10⁻³-10⁻⁴ for φ(v) in H/D exchange reactions. In considering ion pair return, Coulomb interactions in the intermediate [Co(NH₃)₅(NH₂)]²⁺*HOD₂ should be more favorable for proton release from the ion pair into the bulk solution than in the case of OH⁺*HOH₂, the intermediate in the vibrational photochemistry of water. At 1064 nm and 25 °C, φ(v) in the well-documented water photoionization⁶⁷ is 4 × 10⁻⁷, three orders of magnitude lower than φ(v) for [Co(NH₃)₆]³⁺. The lack of any indication of vibrational photochemistry for [Coen₃]³⁺ (φ(v) < 7 × 10⁻⁸) may be a consequence of the greater number of vibrational modes over which to unproductively de-localize the energy in the NH₂CH₃CH₃NH₂ unit than in NH₃.

[Co(NH₃)₆]Me₂SO⁺⁺ 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 NH₃ group and Me₂SO loss to give [Co(NH₃)₂H₂O]⁺⁺. The overlap of electronic and vibrational absorption bands at 1064 nm with ε(e) > ε(v) explains why ligand loss, the reaction pathway favored by electronic excitation, was observed to be dominant.

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Registry No. [Co(NH₃)₆]¹⁺, 14695-95-5; [Coen₃]³⁺, 14878-41-2; [Co(NH₃)₆]Me₂SO⁺⁺, 44915-85-7.

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

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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 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 form of the molecule could be detected.

**Introduction**

Excited-state intramolecular proton transfer (ESIPT) is a fast reaction occurring in many organic molecules of biological or technical interest.¹² 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 (B) in the excited state. In general, the tautomer is more stable than the normal form. The tautomer isomerizes back into the normal form via an intermediate C. The intermediate C is formed by the reaction of the excited normal form A with the ground state (ground state) tautomer B.

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controversy. The normal form A leads to the following ratio of quantum yields of dual fluorescence from the normal form (A) and the tautomeric form (B) of the molecule. 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 ($k_B^P \gg k_B^A$, and no inter-system 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 ($k_B^A \gg k_B^P$), these molecules are potential laser dyes since the tautomer is the ground state, respectively.

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

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, display mainly violet fluorescence which was attributed to the normal form of the molecule. The temperature dependence was interpreted with a model of a viscosity-dependent barrier height associated with phenyl-ring torsion. However, pressure- and viscosity-dependent measurements at room temperature showed that the rigidity of the medium had no effect on the tautomerization process. Time-resolved measurements revealed a fast ($\leq 30$ ps, unresolved) and a slow, temperature-dependent reaction. It was subsequently shown 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 ESPT.

Mc Morrow, Dzugen, and Aartsma have studied the rise time of the tautomer fluorescence from 3-HF in the absence of hydrogen-bonding perturbers. 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 ESPT. 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. 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 hydroxypylenones and tropolone, 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.

The 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 (Spx 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 bandwidth. 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.

Figure 1. Schematic energy level diagram for ESPT 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.

Proton Transfer in 3-Hydroxyflavone


**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 μJ which were generated by an excimer-pumped dye laser. 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. 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). A small portion containing 38 μJ 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.** 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 McMorrow and Kasha in highly purified and dried methycyclohexane (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 McMorrow 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 ESIP/PT 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 ESIP/PT. 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 us conclude 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 10³ 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 the diffusion of water and formation of the hydrogen-bonded complex occurs only at the surface of the argon matrices at temperatures above 30 K.

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

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 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.4 14 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 the molecular response function of eq 4 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

(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.
average decomposition is well-known and has had an inhibiting effect
with the exception of
variation of
time origin. From this observation
of the streak is too short to allow a meaningful fit. However,
excitation pulses of 10-ps duration. In this case the simulated
simulated curves for various rise times
was fixed to 540 ps, the fast decay component mentioned above.
The decay time
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and occurs on the time scale of vibrational relaxation in the excited
state. That the reaction has no intrinsic energy barrier
proton transfer: that the reaction has no intrinsic energy barrier
measured by
McMorrow, Dzugan, and Aartsema (MDA) in several alkanes. 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
ESIPT 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.

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

**Photolysis of Nitrogen Trichloride**

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Spectra and time profiles of the emission resulting from pulsed irradiation of NCI₃ at 248 and 308 nm were collected and analyzed. Two distinct spectral features were observed, one a long series of bands separated by 320 ± 30 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 NCI₃.

**Introduction**

The halogen amines are in general thermodynamically unstable with the exception of NF₃. The explosive nature of the spontaneous decomposition is well-known and has had an inhibiting effect on the scientific research of these interesting compounds. NCI₃ has been studied more than most of the other members of the...