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Excited-State Intramolecular Proton Transfer in 3-Hydroxyflavone: Comparison of Time- and Frequency-Domain Spectroscopy

Abstract

We report (I) the spectral evolution of transient absorption and gain for 3-hydroxyflavone (3-HF) in dry methyl cyclohexane, (II) the fluorescence excitation spectrum of the deuterated compound isolated in a supersonic jet. A comparison suggests that jet spectroscopy interrogates a metastable isomer of 3-HF in the electronic ground state. Semiempirical calculations support this hypothesis.

Introduction

Ever since Sengupta and Kasha (1979) reported dual fluorescence from 3-hydroxyflavone, this compound has kept spectroscopists busy — and often frustrated — by its rich pathology. The characteristic photochemical reaction following optical $\pi\pi^*$ excitation of 3-HF is excited-state intramolecular proton transfer (ESIPT) in the singlet manifold (cf. Fig. 1), after which green fluores-

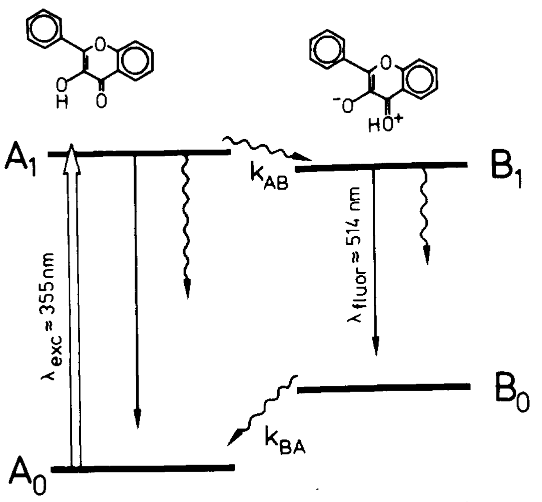

Fig. 1. Förster cycle for intramolecular proton transfer in 3-hydroxyflavone.

cence may be observed. A large part of previous work was aimed at establishing whether a barrier to this reaction exists. The pathology which has emerged so far may be grouped into two areas: extreme sensitivity to solvent perturbation (Mc Morrow and Kasha, 1984), and even to jet conditions (Ito et al., 1992), and a low-lying triplet state for the proton-transferred tautomer (Chou, 1990; Dick, 1989). Here we add a third: the hypothesis that the normal form of isolated 3-HF in its electronic ground-state possesses an isomer in which the hydroxyl group is oriented towards the phenyl ring. This hypothesis will be developed here in order to account for completely different behaviour of the isolated compound, as compared to a solution in dry, aliphatic solvents.

Transient Absorption in Solution

The latest time-resolved measurement of ESIPT in 3-HF was reported by Harris and coworkers (Schwartz et al., 1992; they also summarize the extensive earlier work). At room temperature in methyl cyclohexane, three kinetic contributions were observed. A time constant of 240 fs was attributed to the intrinsic process and a component with 80 fs could clearly be assigned to a cyclic monosolvate with hydroxyl-containing impurities. A long kinetic component, with time constant of 10.5 ps, was attributed to 3-HF which is H-bonded to at least two hydroxylic impurities in an external fashion without a cyclic structure.

We have repeated the transient absorption measurement, however with an extremely dry sample solution (solvent repeatedly dried over K/Na, transferred and used in a sealed quartz line) using broadband detection. Fig. 2 shows some of the transient absorption spectra at various delay times. They consist predominantly of excited-state absorption onto which the tautomer gain has been overlaid. At later times, there is net gain at 500 nm which has been used for stimulated emission (Chou and Aartsma, 1986; Parthenopoulus and Kasha, 1988). The time resolution of our experiments is limited by an optical path length of 1 mm (needed to achieve sample flow by using a closed gravity-flow system). The rise of absorption at 603 nm is shown in Fig. 3. It contains two kinetic components, with time constants of 160 fs and 10.5 ps. The observed short risetime is consistent with the earlier report (Schwartz et al., 1992) for internally H-bonded 3-HF, given an experimental error in determining time-zero for our setup. It is interesting to compare the spectral shape of the transient spectra at $t < 1$ ps and $t > 5$ ps in Fig. 2. One observes the slow rise of excited-state absorption around 610 nm (with time constant of 10.5 ps, as mentioned above) and some change in the shape of the gain band. Now the slow rise component can no longer be attributed to externally H-bonded 3-HF because of our stringent sample purity. We conclude that intramolecular vibrational redistribution and relaxation of excess vibrational energy must be responsible for the slow rise of absorption near 610 nm. This observation already points to a capacious potential energy surface for 3-HF in the S_1-state.

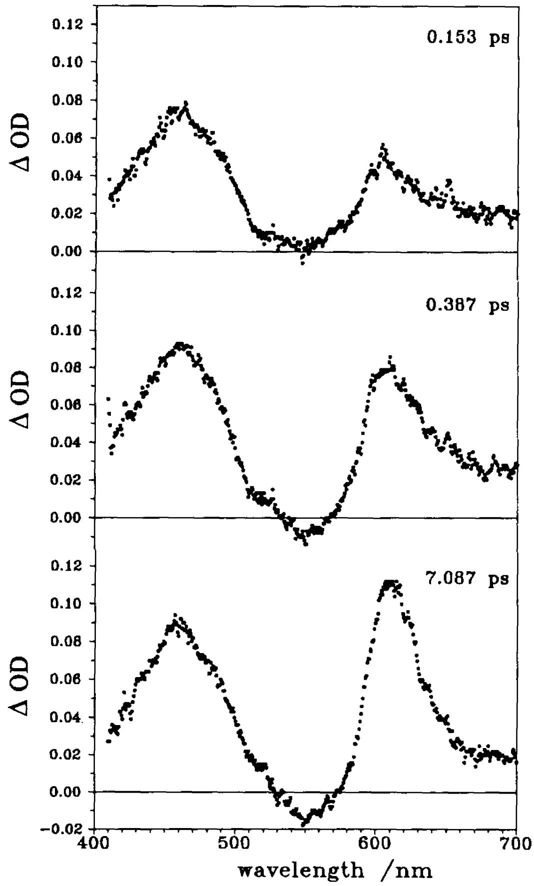

Fig. 2. Transient absorption spectra of 3-HF in dry methyl cyclohexane.

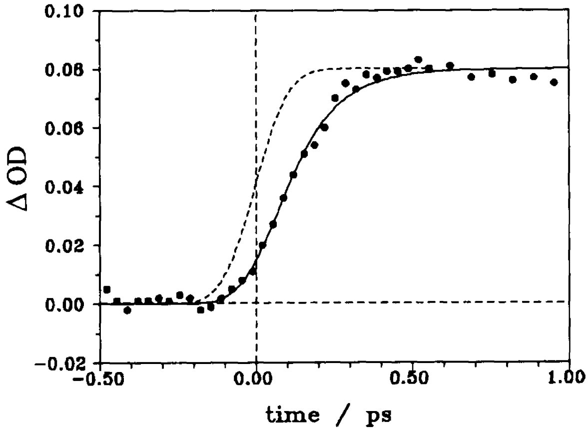

Fig. 3. Rise of transient absorption at 616 nm.

Lineshape- and Deuteration Studies of Jet-Cooled 3-HF

Isolated, jet-cooled 3-HF (cf. Fig. 4a) has an observed vibronic origin band at 28080.3 cm^{-1} (Ernsting and Dick, 1989); a vibrational progression in a 44 cm^{-1} mode can be assigned to phenyl torsion. The vibronic bands have Lorentzian lineshape with FWHM in the range 3.7-4.5 cm^{-1}, corresponding to lifetimes (because of the absence of pure dephasing) around 1.5 ps. The most striking feature of the jet spectroscopy of 3-HF, however, is the existence of a broad background for fluorescence excitation which also appears to depend on cooling conditions. It has been customary to ignore this background and to concentrate on spectral structure.

Fig. 4b shows the fluorescence excitation spectrum of deuterated 3-DF, the composition of which was checked by MS and NMR. Upon deuteration one obtains a more complicated spectrum, as was already mentioned by Ito et al.

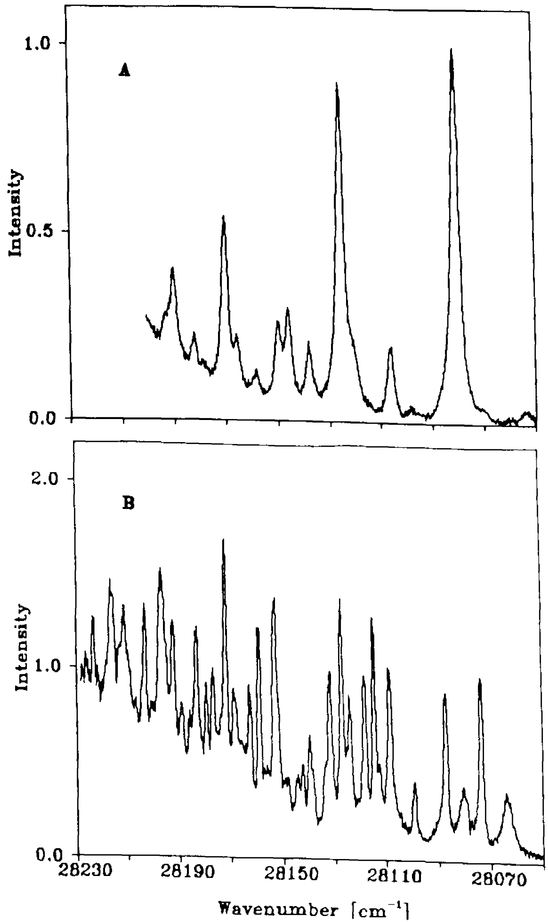

Fig. 4. Fluorescence excitation spectra of jet-cooled 3-HF (a) and 3-DF (b).

(1992). For every original band there appear at least three bands in the 3-DF spectra. Prominent bands have their linewidth reduced to 1.8 cm^{-1}, while other broad bands emerge from the background.

One may ask whether the spectral complication upon H/D exchange arises from inhomogeneity in the electronic ground state, or from complications in the excited state. We performed saturation experiments which allow an assignment of the various narrow bands in Fig. 4b to at least three different spectra, each of which is a replica of the spectrum for original 3-HF but shifted by different amounts. We conclude that deuteration leads to inhomogeneous broadening: the ground state vibrational level structure rearranges at thermal energies. The affected normal modes in the electronic ground state must contain strong contributions from positional changes in the hydroxyl hydrogen atom. We surmise that out-of-plane modes of a skeletal nature may be involved, with double-minimum potentials the existence of which may not matter for 3-HF but which become influential for 3-DF.

Semiempirical Calculations

With MNDO/AM1 + CI calculations, the phenyl torsion (angle π) and the torsion of the hydroxyl group (angle ϕ) were simultaneously investigated. Fig. 5 summarises the results for phenyl torsion for the S_0 and S_1 states. In the ground state in its internally H-bonded form, the phenyl group is predicted to be twisted by 28.3° from planarity, while the excited state should be planar. These findings are consistent with crystal structure data (Etter et al., 1986). As a consequence, one expects a Franck-Condon progression for the torsional mode which is red-degraded over a large spectral range. Instead we find a blue-degraded short progression in the torsional mode (Fig. 4a).

There remains the possibility that the observed line spectrum belongs to some metastable conformer in the ground state while the background (which is dominant in terms of integrated band strength) belongs to 3-HF in its normal form. Therefore we have twisted the hydroxyl group further away from planarity towards the transform (with respect to the carbonyl group) while relaxing the phenyl torsional angle π. A relative minimum was found at $\phi = 159.7°$, $\pi = -44°$, with an electronic potential energy 1091 cm^{-1} above the normal form. At the conditions of the jet expansion, about 10% of the sample should exist in this trans-configuration.

In conclusion, the following hypothesis is presented:

The spectral background for isolated 3-HF is assigned to the normal form. Its ESIPT reaction has a characteristic time constant of 160-240 fs. The lack of spectral structure is caused by the corresponding linewidth of 27 cm^{-1} in combination with spectral congestion.

The line spectrum for isolated 3-HF is tentatively assigned to a trans-like conformer. The vibronic lifetime of 1.4 ps reflects trans/cis isomerisation of the

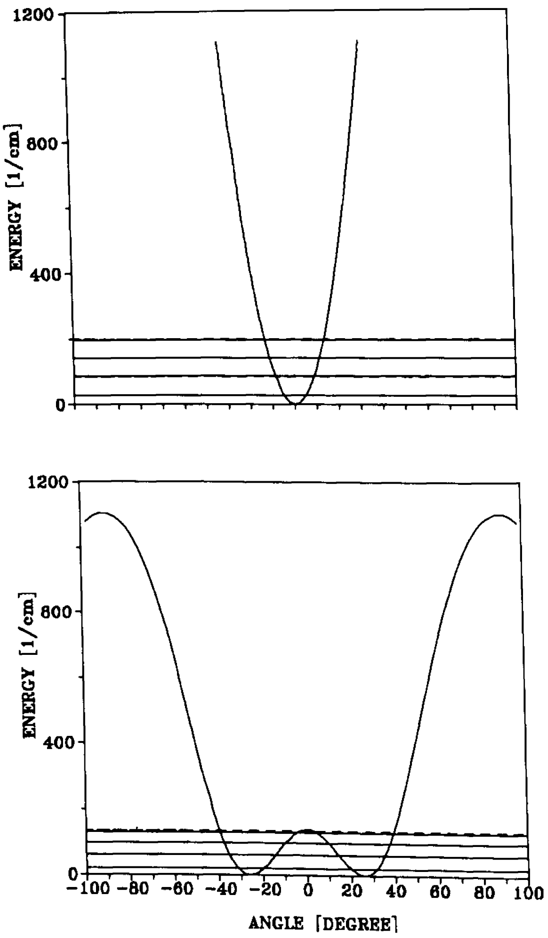

Fig. 5. Torsional potentials and eigen energies for 3-HF in its normal form.

hydroxyl group in the excited state rather than proton transfer. In addition, the PES should be complex with double minima along a normal coordinate which involves the motion of the hydroxyl proton.

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