FTIR Spectroscopy of Flavonols in Argon and Methanol/Argon Matrixes at 10 K. Reexamination of the Carbonyl Stretch Frequency of 3-Hydroxyflavone

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The FTIR spectra of six argon-matrix-isolated flavonols were measured. Carbonyl stretching frequencies for the following compounds were the following: flavone, 1669 cm^{-1}; chromone, 1676 cm^{-1}; 5-hydroxyflavone (5HF), 1660 cm^{-1}; 3-hydroxyflavone (3HF), 1652 cm^{-1}; 5-methoxyflavone (5MF), 1672 cm^{-1}; and 3-methoxyflavone (3MF), 1658 cm^{-1}. The 3HF carbonyl stretching frequency assignment represents a correction to the literature values: (1628.6 cm^{-1} in an argon matrix and 1621 cm^{-1} in the liquid phase).[1,2−5] The hydroxyl stretch modes for 5HF and 3HF were observed at 2935 and 3320 cm^{-1}, respectively, in agreement with the literature values.[2−5] While the hydroxyl stretch modes predict that the 5HF intramolecular-hydrogen bond to the carbonyl is stronger than that of 3HF, the carbonyl stretch frequency of 3HF is red-shifted more than that of 5HF. In analogy to hydroxyl-substituted flavones, methoxyl substitution at the flavone 3 position also results in a greater carbonyl red-shift than at the 5 position. Relative to the methoxyflavones, the effect of hydroxyl substitution on the carbonyl is clearly greater in 5HF than in 3HF. Density functional calculations at the B3LYP/6-31G(d) level are consistent with the experimental findings. Calculated OH···O intramolecular hydrogen bond distances and O−H···O angles were 1.70 Å and 149° for 5HF and 1.94 Å and 122° for 3HF, consistent with greater hydrogen-bonding in 5HF than in 3HF. Changes in the bond distances from 5MF to 5HF are consistent with hydrogen bonding, encouraging a resonance form resembling the excited-state proton-transfer tautomer of 5HF that weakens the carbonyl. Similarly, changes in the bond distances from 3MF to 3HF suggest that hydrogen bonding stabilizes a zwitterionic resonance form that also weakens its carbonyl. This zwitterionic resonance form of 3HF resembles the excited state proposed for its unusual fluorescence and could be responsible for the facile energy transfer to this state.

Introduction

The flavonols, being partially responsible for deep yellow colors of certain flowers, form one of the largest groups of organic natural products in the plant kingdom. Flavonols have also been shown in animal studies to be efficient antioxidants and anticoagulants and recently have been found to exhibit anti-cancer and anti-viral activity.[6−8] Most natural flavonols bear hydroxyl groups, methoxyl groups, and/or linkages to sugar residues (as in “glycones”). More than 85% of these naturally occurring flavonols have a hydroxyl group in the 5 position and a sugar linkage in the 3 position.[9] Matsuura[9] has demonstrated that the 5-hydroxyl moiety is responsible for the remarkable photochemical stability of flavonols and has suggested that this provides an important biological function in protecting plants from photodegradation. For these reasons, there is considerable interest in the photophysics of 3- and 5-substituted flavones as models for complex natural flavonols.

Of particular interest, 5-hydroxyflavone (5HF) and 3-hydroxyflavone (3HF) can tautomerize in their $^1\pi,\pi^*$ excited states to a hydroxy-ketone[10] and a pyrilium hydroxy-zwitterion, respectively.[11] In 1991, 5HF was shown to undergo an excited-state proton transfer (ESPT) from the $^1\pi,\pi^*$ state in hydrocarbon solutions at 298 K leading to a very weak (and previously unobserved) hydroxy-ketone tautomer fluorescence at 665 nm.[10] Though nonluminescent in alcohol solvents at 298 K, 5HF is phosphorescent in alcohol glasses at 77 K.[12] In contrast, 3HF exhibits fluorescence from its $^1\pi,\pi^*$ excited state in alcohol solvents at room temperature and strong ESPT from the pyrilium hydroxy-zwitterion in hydrocarbon solvents.[11,12] Due to the relatively high quantum yield and large Stokes shift observed for its tautomer emission, 3HF and its derivatives show promise as proton-transfer laser dyes.[11] The prominent role of ESPT in the photophysics of hydroxyflavones indicates that the nature of intramolecular hydrogen bonding in their monomers is key to understanding the unusual excited-state properties of these highly important molecules. The correct ground-state structures and infrared vibrational frequencies are essential to this effort.

The spectroscopic characterization of the vibrations in the flavones has proven to be nontrivial. Initial studies by Simpson et al. reported carbonyl stretch frequencies of flavone and 5HF in carbon tetrachloride as 1649 and 1652 cm^{-1}, respectively,[2] and Balekrishna et al. reported in a subsequent study that 5HF and 3HF in carbon tetrachloride absorb at 1652 and 1619 cm^{-1}, respectively, and 3HF absorbs at 1625 cm^{-1} in a room-temperature KBr matrix. In contrast, Hayashi et al.[4] reported the 5HF and 3HF carbonyl stretch frequencies as 1612 and 1605 cm^{-1} and hydroxyl stretch frequencies of 2900 and 3350 cm^{-1}, respectively, also in a room-temperature KBr matrix. The hydroxyl stretch frequencies suggested stronger intramolecular bonding between the hydroxyl and carbonyl groups of 5HF than for 3HF, but the carbonyl frequencies seemed to indicate the opposite. To resolve this issue, Hayashi et al. crystallographically characterized 4′-bromo-5-hydroxyflavone and 4′-bromo-3-hydroxyflavone and found carbonyl bond lengths of 1.245(5) and 1.232(6) Å, respectively (standard deviations in parentheses), indicating stronger hydrogen bonding in the former and implying

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that hydrogen bonding in 5HF is stronger than that in 3HF.[4] This argument is complicated by the fact that 4′-bromo-5-hydroxyflavone crystallized as a monomer and 4′-bromo-3-hydroxyflavone crystallized as an intermolecularly double-hydrogen-bound dimer, making a direct comparison of carbonyl bond lengths dubious. Since analogous dimerization also is likely present in crystals of 3HF, direct comparison of spectra in KBr matrixes also may be suspect. To address this issue, we have spectroscopically examined 3HF and 5HF as well as flavone, 3-methoxyflavone (3MF), 5-methoxyflavone (5MF), and chromone by matrix isolation techniques that allow the spectra of the monomeric species to be obtained with confidence.

Experimental Section

Fourier transform infrared (FTIR) spectra were collected at 1.0 cm^{-1} resolution in the spectral region between 4000 and 400 cm^{-1} using a Nicolet Magna-IR 750 and/or Nicolet 800 spectrometer equipped with an MCT detector, KBr beam splitter, and a globar source. The infrared systems were interfaced to OMNIC or NICOS software, respectively, for data acquisition and processing.

A closed-cycle liquid-helium refrigeration system (Air Products HC-2) was used to cool the substrate window to 10 K. Cesium iodide substrate windows were used for the FTIR experiments. Temperature readings were made with a temperature controller (Air Products) connected to a sensor above the sample holder inside the cryostat. The cold head of the cryostat was aligned so it could be manually rotated between matrix deposition and spectrum acquisition positions.

The vacuum shroud of the closed-cycle refrigeration system and the attached vacuum lines were maintained at a pressure of approximately 10^{-7} Torr using oil diffusion pumps (Kontes) and liquid nitrogen-cooled cold traps connected to mechanical pumps. The pressures were determined by thermocouple gauges (Varian 801) and cold cathode ionization gauges (Varian 860A-2).

The host matrix was prepared using ultrahigh purity grade 5 argon (So-Cal Airgas 99.999% purity). The compounds used were flavone (Aldrich, 99% purity), 3HF (Aldrich, 99% purity), 5HF (Apin Chemicals Ltd., 99% purity), chromone (Aldrich, 99% purity), 3MF (Aldrich, 99% purity), and 5MF (Sigma, 99% purity). All compounds were used without recrystallization. A vapor mixture was prepared by subliming the compound into a heated stream of the argon gas (or argon/methanol mixture) which was then directed onto the substrate window. The rate of deposition of the gas mixture was approximately 1−2 mmol/h for approximately 30 min. The flavonol concentrations were not known; however, the molecules were assumed to be in the monomer state since the argon flow rate was maximized and the flavonol sublimation temperature was minimized (approximately 125−180 °C) to obtain the sharpest infrared absorption bands possible. Higher flavonol concentrations resulted in aggregation effects. As an additional experiment, the argon was diluted with methanol (anhydrous, Aldrich 99.8% purity) to ratios of 50:1 to 800:1 and then mixed with the heated flavone.

The molecular structures of flavone, 3HF, 5HF, 3MF, 5MF, and chromone were optimized by the energy-gradient technique by the B3LYP/6-31G(d) method. The harmonic frequencies of each optimized structure were calculated by using the analytic second-derivative matrix along the nuclear coordinates. The IR intensities of each vibration were evaluated for all minimum structures at the B3LYP level. The scale factor, 0.964, was determined by the average ratio between the experimental and the B3LYP-calculated frequencies of the carbonyl vibrations. The initial structures for the flavone/methanol and 3HF/water hydrogen-bond complexes were approximated through an MMFF conformation search followed by geometry optimization of representative conformers by the AM1 method. The lowest energy conformers for both complexes were optimized and their harmonic frequencies were calculated by the B3LYP/6-31G(d) method as described above for the other flavones. The program used was Gaussian 98M.[13]

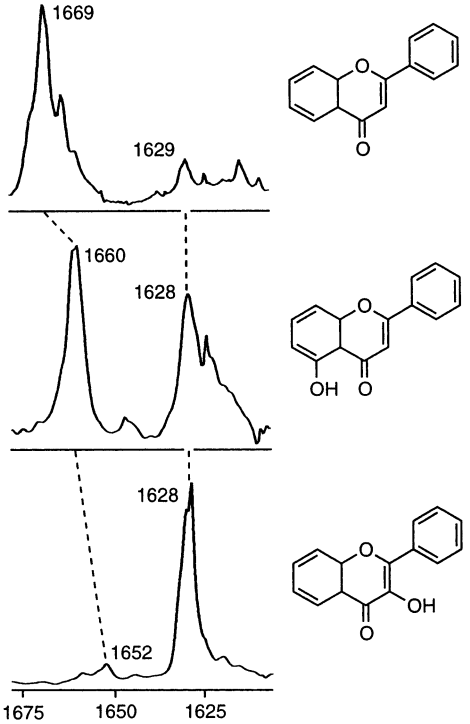


Figure 1. FTIR spectra of argon matrix-isolated flavone, 5-hydroxyflavone (5HF), and 3-hydroxyflavone (3HF) at 10 K, depicting the carbonyl stretch region.

Results and Discussion

1. Carbonyl Stretch Frequency Data. Figure 1 depicts FTIR spectra of flavone, 5HF, and 3HF in an argon matrix at 10 K. These spectra are stacked to illustrate the similarities and differences between 2000 and 1400 cm^{-1}. When the peak heights of the three spectra are normalized at the 1628 cm^{-1} C=C stretch band, relative peak heights of 51:14:1 are observed for the prominent carbonyl bands of flavone at 1669 cm^{-1} and 5HF at 1660 cm^{-1} and the analogous though unusually weak band of 3HF at 1652 cm^{-1}, respectively. In addition to the enormous differences in absorbance, these three bands exhibit a dramatic range in frequency from 1669 to 1660 to 1652 cm^{-1}. In contrast, the bands for the three compounds in the 1628 cm^{-1} C=C stretch region exhibit similar absorbances and constant frequencies relative to their corresponding spectra. Similar observations were reported in an unpublished resonance Raman spectral study[14] of the same compounds in 10^{-4} M 3-methylpentane solutions at room temperature. When compared to the approximately constant frequency and absorbance of the 1628 cm^{-1} band in the three spectra, the bands at 1669 cm^{-1} (flavone), 1660 cm^{-1} (5HF), and 1652 cm^{-1} (3HF) are likely carbonyl stretches exhibiting dramatic range of frequency and absorptivity.

FTIR spectra of flavone in an argon matrix with added methanol exhibit a new band at 1650 cm^{-1} (Figure 2) that correlates with increasing concentration of methanol (methanol/argon ratios vary from 1:100 to 1:400). Similar effects are observed for 5HF and 3HF with new bands appearing at 1646 and 1644 cm^{-1}, respectively. The 1628 cm^{-1} bands of flavone,

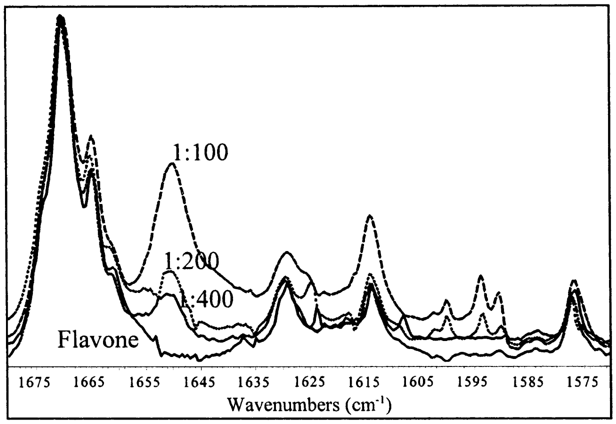


Figure 2. FTIR spectra of flavone in MeOH/argon mixed matrixes at 10 K. Concentrations of MeOH/Ar were varied from 1:100 to 1:400.

TABLE 1: Frequencies of the HO Stretches in Hydroxyflavones

	frequency (cm^{-1})	
	exp	calcd[a]
5-hydroxyflavone (5HF)	2935	3099
3-hydroxyflavone (3HF)	3320	3325

[a] Calculated at the B3LYP/6-31G(d) level and scaled by 0.963.

5HF, and 3HF remain unchanged by added methanol. Since methanol has no absorption bands in the 1500 to 1700 cm^{-1} region, these new bands represent methanol−flavone interactions likely entailing hydrogen bonding between the methanol hydroxyl and the flavone carbonyls.[15] The frequencies of the new bands for flavone, 5HF, and 3HF indeed follow the same order as the carbonyl stretches. This behavior supports the reassignment of the 3HF carbonyl stretching frequency which represents a correction to previously reported values.[1,2−5]

2. Hydroxyl Stretch Frequency Data. The H−O/H−C stretch region of the spectra of flavone, 5HF, and 3HF are not shown since the assignments are straightforward. Each compound exhibits a band near 3075 cm^{-1}, representing H−C stretches. The remaining bands in the 5HF and 3HF spectra at 2935 and 3320 cm^{-1}, respectively (Table 1), likely represent their H−O stretches. Hayashi et al. [4] similarly assign 2900 and 3350 cm^{-1} as the H−O stretch bands for 5HF and 3HF, respectively, and two earlier studies similarly assign bands at 2950−2600 and 3400 cm^{-1} as H−O stretches for 5HF and 3HF, respectively.[5] The lower H−O stretch frequency for 5HF versus 3HF is indicative of stronger intramolecular hydrogen bonding within 5HF between its hydroxyl substituent and carbonyl.

3. Substitutional Effects. Figure 3 shows the double bond stretching frequency region for chromone, 5MF, and 3MF in argon at 10 K, and Table 2 lists the carbonyl stretch frequencies for flavone, 5HF, 3HF, 5MF, 3MF, and chromone. Each spectrum exhibits the C=C stretch band at approximately 1624 cm^{-1}. The carbonyl frequencies for chromone, 3MF, and 5MF are assigned as 1676, 1672, and 1658 cm^{-1}, respectively. Comparison of the chromone and flavone spectra shows that phenyl substitution on chromone results in a −7 cm^{-1} shift in the carbonyl stretch frequency. Comparison of the carbonyl stretch frequencies of 3MF, 5MF, and flavone shows that methoxyl substitution at the 5 and 3 positions results in shifts of +3 cm^{-1} and −11 cm^{-1}, respectively. To the extent that hydroxyl and methoxyl substitution can be considered analogous, the significantly larger shift in the carbonyl stretch from 5MF to 5HF (−12 cm^{-1}) compared to that from 3MF to 3HF (−6 cm^{-1}) is consistent with the stronger intramolecular hydrogen bonding in 5MF indicated by the corresponding HO stretch frequencies.

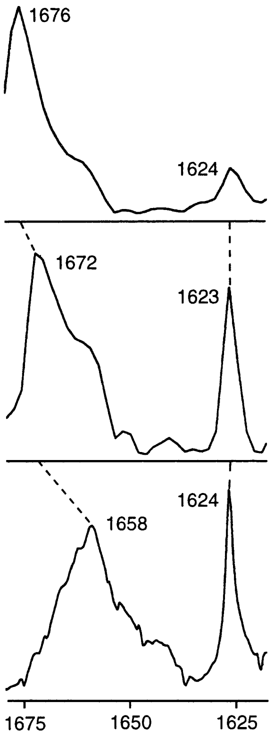


Figure 3. FTIR spectra of argon matrix-isolated chromone, 5-methoxyflavone (5MF), and 3-methoxyflavone (3MF) at 10 K, depicting the carbonyl stretch region.

TABLE 2: Frequencies of the Carbonyl CO Stretches in Flavonols

	frequency (cm^{-1})	
	exp	calcd[a]
flavone	1669	1679
flavone/methanol	1650	1643
5-hydroxyflavone (5HF)	1660	1653
3-hydroxyflavone (3HF)	1652	1644
5-methoxyflavone (5MF)	1672	1668
3-methoxyflavone (3MF)	1658	1659
chromone	1676	1689

[a] Calculated at the B3LYP/6-31G(d) level and scaled by 0.963.

4. Theoretical Results. The calculated carbonyl stretch frequencies of flavone, 5HF, 3HF, 5MF, 3MF, and chromone and hydroxyl stretch frequencies of 5HF and 3HF at the B3LYP/6-31G(d) level are shown in Tables 1 and 2 together with experimental values. Differences in the calculated frequencies mirror those in the observed values and lend further support for the C=O stretch reassignment for 3HF.

The corresponding normal vibration modes for 5HF and 3HF suggest a possible explanation for the large differences in the absorbances observed among the C=O stretches. In both cases, the C=O stretch is coupled to the in-plane H−O−C scissor motion such that the H−O−C angle expands as the C=O and C−OH distances contract and vice versa. In the case of 3HF, the expansion of the C−O dipoles appears closely balanced by the swing of the H−O bond away from the nearly stationary midpoint between the oxygens. This collective movement has the appearance of a "breathing" quadrupole with little net dipolar change. This results in a weak oscillator strength and an unusually small calculated IR intensity for the C=O stretching mode (only 0.83 of that of the C=C stretch). In the case of 5HF, the relative amplitude of the H−O scissoring is significantly greater than the motion of the C−O stretches amounting to a significant net dipolar change, a stronger oscillator strength, and a stronger calculated IR intensity for the C=O stretch of 5HF (1.20 of that of the C=C stretch). The calculated IR intensities for 3HF and 5HF are both dramatically weaker than that of flavone (with its C═O stretch being 5.0 times more intense that of the C═C stretch.) These values are consistent with the observed peak heights for 3HF (0.11), 5HF (1.32), and flavone (4.35).

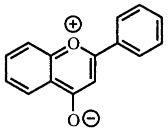
Hydroxyl stretch frequencies calculated for 5HF and 3HF (3099 and 3325 cm^{-1}, respectively) mirror the observed differences as reported in Table 1. Shorter hydroxyl hydrogen−carbonyl oxygen OH···O distances and larger O−H···O angles calculated for 5HF (1.70 Å and 149°) versus 3HF (1.94 Å and 122°) are indeed indicative of stronger hydrogen bonding in 5HF. Though strong hydrogen bonding is evident in both 3HF and 5HF, these interactions appear to have small effects on the calculated carbonyl bond lengths (1.23, 1.25, and 1.24 Å for flavone, 5HF, and 3HF, respectively). This suggests that though hydrogen bonding is evident, this interaction has only a small influence on the structure of the carbonyl itself.

The calculated C═O stretch frequencies for the hydroxyl and methoxyl substituted flavonols reflect trends in the observed data. Methoxyl substitution in the 5 and 3 positions of flavone resulted in red-shifts of 11 and 20 cm^{-1}, respectively, in the calculated carbonyl vibration frequencies with respect to the parent flavone (Table 2), as could be expected for an electron donating group. Since the calculated carbonyl C═O bond distances exhibit no significant changes from flavone (Table 3) and the calculated methoxyl C−O distances are indistinguishable, the observed spectral effects of methoxyl substitution seem to represent simple substitution effects. Hydroxyl substitution in the 5 and 3 positions resulted in larger calculated red-shifts of 26 and 35 cm^{-1}, respectively, in the calculated carbonyl vibrational frequencies versus flavone (Table 2), but the red-shift from 5MF to 3MF (9 cm^{-1}) is about the same as that from 5HF to 3HF (9 cm^{-1}), approximately in agreement with experiment.

The large shift for 5HF from 5MF is consistent with strong intramolecular hydrogen bonding evident in the short H···O distance and large O−H···O angle between the carbonyl and the hydroxyl groups. 5HF also appears to exhibit a significant structural contribution from the proton-shifted tautomer as seen by the calculated bond distances of 5HF compared to 5MF (Table 3) that further weakens the 5HF carbonyl: the hydroxyl/methoxyl C−O distance contracted (0.025 Å), the carbonyl C═O distance expanded (0.018 Å), and the adjacent C−C bond contracted (0.026 Å).

The structure of flavone with methanol hydrogen bound to its carbonyl was also calculated at the B3LYP/6-31G(d) level and found to exhibit a large red-shift (36 cm^{-1}) with respect to free flavone (Table 2), consistent with the observed behavior. In the flavone−methanol complex, the O−H···O interaction is in the flavone ring plane, indicating hydrogen bonding to a sp^2 lone pair on the carbonyl oxygen. The analogy of this system to the intramolecular hydrogen bonding in 5HF suggests that the latter can indeed account for much of the red-shift in the carbonyl stretch of 5HF.

The comparable shift in the calculated carbonyl stretch frequency for 3HF from 3MF in light of its weaker intramolecular hydrogen bonding compared to 5HF suggests that the hydroxyl group in the 3 position has an important electronic impact on the flavone ring. Significant changes in the calculated bond distances and bond orders (Table 3) from 3MF to 3HF suggest that the hydroxyl group enhances the contribution of a specific zwitterionic resonance structure I-3HF from among the three zwitterionic forms of flavone I, II, and III. Intramolecular hydrogen bonding between the carbonyl and hydroxyl groups could stabilize the accumulation of negative charge on the carbonyl oxygen making these structures more important in 3HF and 5HF than 3MF and 5MF. The bond orders and distances to the ring oxygen exhibit modest changes from 5MF to 5HF, suggesting the 5-hydroxyl group has little influence on the relative contributions of these zwitterionic forms (Table 3). In contrast, the bond orders and distances to the ring oxygen from 3MF to 3HF change significantly, suggesting an enhanced contribution of zwitterionic form I-3HF and attenuated contributions from II-3HF and III-3HF. This is further evidenced by the changes in the bond orders and lengths of the rest of the ring and the expansion and weakening of the carbonyl. In addition to these structural peculiarities, 3HF exhibits a coplanarity between the phenyl ring and the remainder of the flavone system (with a dihedral angle of 0.05°) unlike flavone itself, 3MF, 5MF, and 5HF that exhibit dihedral angles of 19.1, 23.7, 17.4, and 18.7°, respectively, between these rings. The increase of bond order and corresponding contraction of the hydroxyl C−O (0.068 and −0.013 Å, respectively) and phenyl-flavone C−C (0.028 and −0.007 Å, respectively) bonds from 3MF to 3HF suggest that significant π-donation from the hydroxyl group into the phenyl ring encourages the phenyl coplanarity. Since the zwitterionic form I-3HF best supports this π-donation, the ortho-placement of the hydroxyl and phenyl groups likely encourages this form over forms II-3HF and III-3HF.



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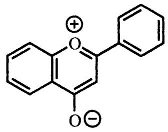

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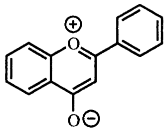


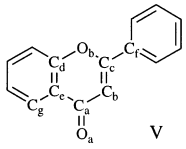
III

The predisposition of 3HF toward zwitterionic form I-3HF is likely responsible for its prominent fluorescence from a structurally similar proton-transfer zwitterionic excited state (IV) in solution and dry frozen matrixes (Scheme 1). The loss of

TABLE 3: Calculated Bond Lengths of Substituted Flavonols[a]

bond[b]	distance (Å) [bond order][c] flavone	3MF	3HF	5MF	5HF
O_a-C_a	1.231 [1.673]	1.233 [1.649]	1.242 [1.589]	1.232 [1.662]	1.250 [1.558]
O_b-C_c	1.365 [1.001]	1.370 [0.990]	1.377 [0.975]	1.362 [1.000]	1.360 [1.015]
O_b-C_d	1.373 [0.974]	1.364 [0.987]	1.359 [1.006]	1.373 [0.975]	1.374 [0.972]
C_a-C_b	1.458 [1.113]	1.470 [1.082]	1.462 [1.091]	1.459 [1.115]	1.448 [1.138]
C_b-C_c	1.358 [1.633]	1.372 [1.559]	1.369 [1.511]	1.355 [1.635]	1.360 [1.613]
C_c-C_f	1.475 [1.068]	1.476 [1.074]	1.468 [1.096]	1.475 [1.067]	1.474 [1.070]
C_d-C_e	1.400 [1.338]	1.399 [1.332]	1.403 [1.315]	1.410 [1.335]	1.405 [1.310]
C_e-C_a	1.482 [1.036]	1.474 [1.053]	1.455 [1.085]	1.486 [1.046]	1.460 [1.097]
C_e-C_g	1.404 [1.339]	1.406 [1.326]	1.408 [1.311]	1.424 [1.288]	1.422 [1.251]
$C_b-O(H,Me)$		1.366 [0.981]	1.353 [1.049]		
$C_g-O(H,Me)$				1.365 [0.996]	1.340 [1.117]

[a] Calculated at the B3LYP/6-31G(d) level. [b] See structure V. [c] Calculated as Wilberg bond indices in the NAO basis.



V

TABLE 4: Calculated Bond Lengths of Hydrogen Bond Complexes[a]

bond[b]	distance (Å) [bond orders]	
	flavone:MeOH	3HF:H_2O
O_a-C_a	1.242 [1.598]	1.247 [1.543]
O_b-C_c	1.364 [1.004]	1.372 [0.985]
O_b-C_d	1.370 [0.980]	1.355 [1.006]
C_a-C_b	1.450 [1.142]	1.464 [1.110]
C_b-C_c	1.360 [1.610]	1.381 [1.488]
C_c-C_f	1.474 [1.074]	1.472 [1.095]
C_d-C_e	1.401 [1.332]	1.400 [1.318]
C_e-C_a	1.474 [1.055]	1.461 [1.088]
C_e-C_g	1.405 [1.332]	1.409 [1.308]
$C_b-O(H,Me)$		1.347 [1.062]

[a] Calculated at the B3LYP/6-31G(d) level. [b] See structure V.

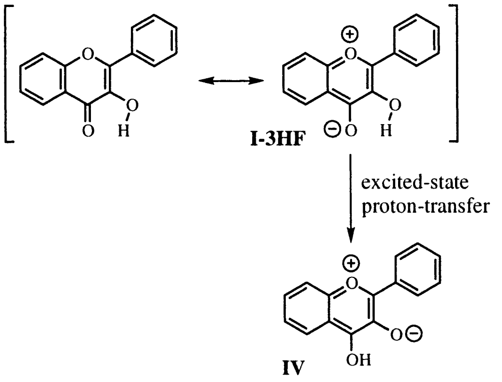
this fluorescence[11] in glassy solvents at 77 K containing trace amounts of water impurities is consistent with intermolecular hydrogen bonding with water disrupting the intramolecular hydrogen bonding and the consequent electronic arrangement within 3HF. Indeed, the structure of a 3HF−water complex calculated at the B3LYP/6-31G(d) level exhibited a dihedral angle of 11.9° between the phenyl ring and the remainder of the flavone system, suggesting disruption of the π-interaction of the phenyl ring with the remainder of the flavone system. This optimized structure shows the water hydrogen binding to both the carbonyl and hydroxyl groups of 3HF and the $C{=}O\cdots H{-}O\cdots H{-}O$ interactions all in the plane of the main flavone ring system. The calculated bond lengths and orders (Table 4) show significant differences from those of 3HF, further suggesting a significant impact of hydrogen bonding to water. Within a frozen matrix, water cannot dissociate and the structure of 3HF including the ring coplanarity cannot be reestablished; as a result, ESPT cannot occur and instead the characteristic fluorescence of 3HF would be expected. Kasha, et al.[11] postulated that the coplanar phenyl ring plays a role in the charge migration to the excited-state proton-transferred pyrilium structure.

5. Significance of Results on the Photophysics of 5HF and 3HF. The results presented in this paper suggest that the intramolecular hydrogen bonding interactions to the carbonyl oxygen lone pairs have a significant influence on the structures of 5HF and 3HF and their electronic states. Of particular interest is the possible elevation of the energy of the $^1n,\pi^*$ state above the $^1\pi,\pi^*$ state, resulting in fluorescence or excited-state proton transfer from the lower $^1\pi,\pi^*$ state (Scheme 1), depending on the solvent. Such effects would be consistent with the excited-state proton-transfer spectra in 5HF and 3HF in hydrocarbon solvents at room temperature and 3HF in alcohol solvents. The excited states of 5HF, 3HF, flavone, and their hydrogen-bonded complexes with water are being examined computationally.

Conclusion

Overall, this experimental and theoretical study has clarified several important aspects of the spectroscopy of 3HF and 5HF. First, this work corrected the assignment of the carbonyl stretch of 3HF and confirmed stronger intramolecular hydrogen bonding in 5HF versus 3HF. This survey has also revealed two surprising spectroscopic features of 3HF—the intramolecular hydrogen bonding between the hydroxyl group and the carbonyl results in a remarkably weak oscillator strength and the significant contribution of a zwitterionic resonance form to the structure of 3HF that weakens the carbonyl. In 5HF, the proton-transfer tautomer also appears to significantly contribute to its structure. This work offers important insight into the photophysics of flavonols.

SCHEME 1: Resonance Forms of 3-Hydroxyflavone (3HF) in the Ground State and the Proton-Transfer Tautomer in the Excited State



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