Supporting Information

7-Hydroxyflavone Revisited: Spectral, Acid-base Properties and interplay of the Protolytic Forms in the Ground and Excited States.

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H_0 scale correction for the mixture methanol-water-sulphuric acid

Figure 1S. Correlation between H_0 scales in methanol-water-sulphuric acid and water-sulphuric acid.

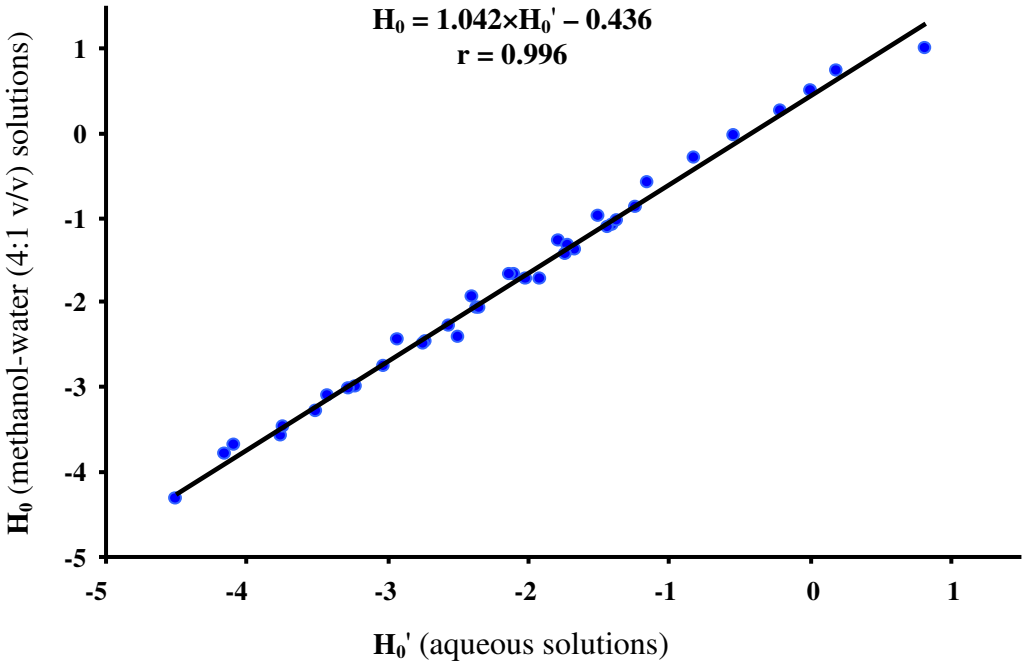
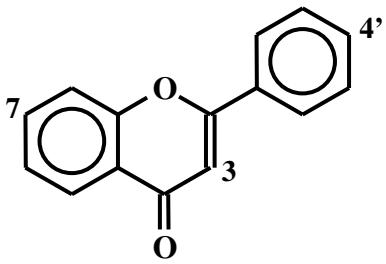


Table 1S. Dissociation constants of flavones used as H_0 indicators.



Flavone	7-methoxy	4'-hydroxy	3,4'-dimethoxy	3-hydroxy-4'-methoxy	3-hydroxy
pK_a	-0.72 ± 0.04; -0.75 [17]	-0.93 ± 0.03	-2.10 ± 0.03	-2.37 ± 0.04	-2.88 [6]

Regression analysis of solvatochromic and solvatofluorochromic effects

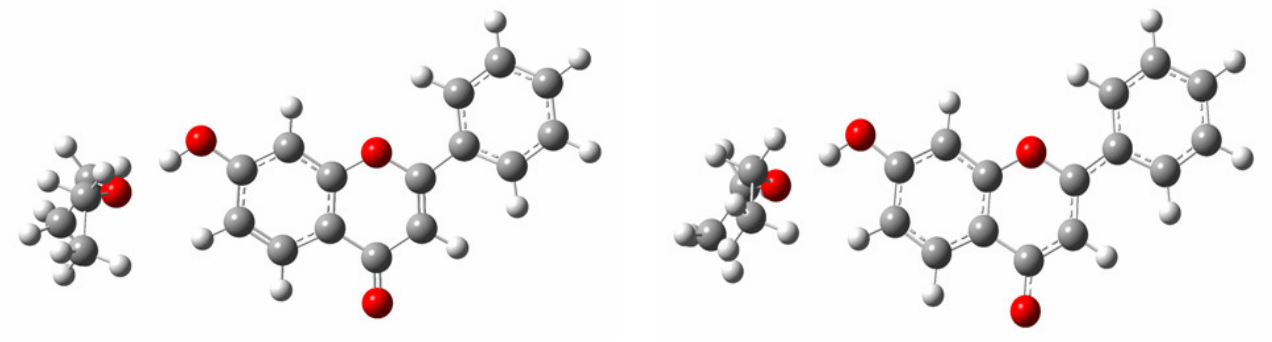
Table 2S. Statistical parameters of regression analysis equations.

N	Equation	*n*	*R*	*S*
1a	ν_{abs} = -1791.2×π* + 34045	7	0.906	350.85
1b	ν_{abs} = -5208.0×Y + 35050	7	0.880	393.10
2a	ν_{abs} = -3030.0×π* + 2456.6×β + 34259	14	0.806	672.92
2b	ν_{abs} = -6088.1×Y + 3.83×B + 35145	14	0.747	643.04
3a	ν_{fl} = -1023.4×π* – 1159.5×β + 26085	14	0.810	236.87
3b	ν_{fl} = -3788.6×Y + 26330	14	0.760	250.83
4	$\Delta\nu_{St}$ = -2950×β + 10500	14	0.750	495.40
5a	$\nu_{fl}(A_p^*)$ = -1231.3×π* + 19090	9	0.883	156.87
5b	$\nu_{fl}(A_p^*)$ = -16159×Y + 25845	9	0.947	107.33
6a	$\Delta\nu_{St}(A_p^*)$ = 2107.7×π* + 13047	9	0.943	178.69
6b	$\Delta\nu_{St}(A_p^*)$ = 13035×Y +6.58×B + 6565	9	0.949	182.20
7a	$\nu_{fl}(A^*)$ = -1696.7×π* + 19560	9	0.954	128.07
7b	$\nu_{fl}(A^*)$ = -13660×Y – 3.80×B + 25850	9	0.937	161.27
8a	$\Delta\nu_{St}(A^*)$ = 1473.4×π* + 7635	7	0.917	56.91
8b	$\Delta\nu_{St}(A^*)$ = 5795×Y + 5680	7	0.718	99.53
9a	$\Delta\nu_{St}(A^*)$ = 1461×π* + 7955	7	0.901	299.06
9b	$\Delta\nu_{St}(A^*)$ = 4683×Y + 7025	7	0.900	300.33
10a	$\Delta\nu_{St}(A^*)$ = 378×π* + 9860	7	0.700	85.90
10b	$\Delta\nu_{St}(A^*)$ = 1050×Y + 9670	7	0.914	48.64
11	$\Delta\nu_{St}(A^*)$ = 2237×π* + 7315	7	0.890	101.90

N – number of the equation in the text of manuscript, ***n*** – quantity of solvents, ***R*** – correlation coefficient, ***S*** – standard error of estimate

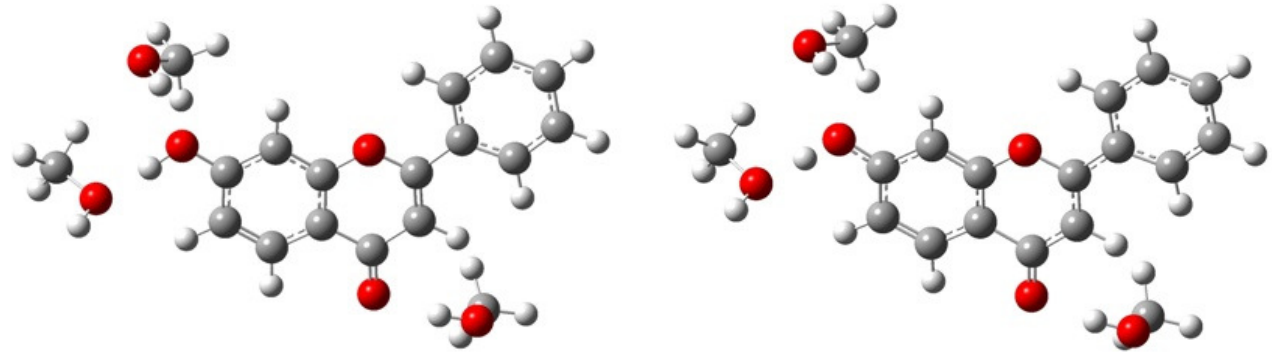
Structure of 7HF complexes in the ground and excited states

7HF – diethyl ether complex



S_0 state S_1 state

7HF – methanol complex

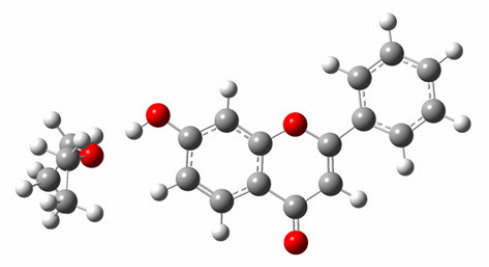


S_0 state S_1 state

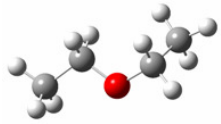
Figure 2S.

Calculation of Gibbs energy of hydrogen bond formation ($\Delta G_{f,298}$).

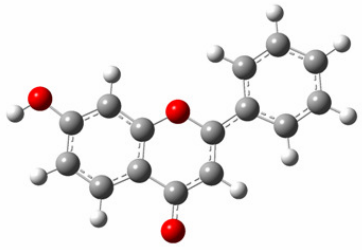
7HF – diethyl ether complex
(geometry of complex and model molecules is optimized in the ground and excied states)



complex 7HF – ether



ether

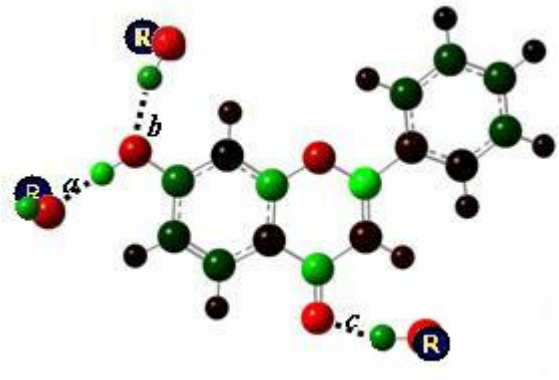


7HF

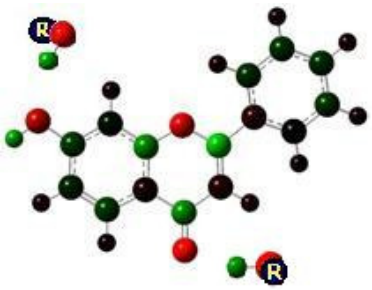
$\Delta G_{f,298}$ of hydrogen bond in S_0 state	=	**$\Delta G_{f,298}$** of complex in S_0 state	–	**$\Delta G_{f,298}$** of ether in S_0 state	–	**$\Delta G_{f,298}$** of 7HF in S_0 state
$\Delta G_{f,298}$ of hydrogen bond in S_1 state	=	**$\Delta G_{f,298}$** of complex in S_1 state	–	**$\Delta G_{f,298}$** of ether in S_0 state	–	**$\Delta G_{f,298}$** of 7HF in S_1 state

Figure 3aS.

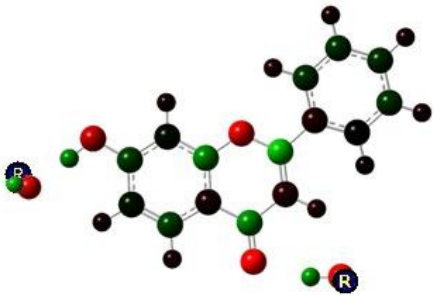
7HF – methanol complex
(geometry of the complex and model molecules is optimized in the ground and excited states)



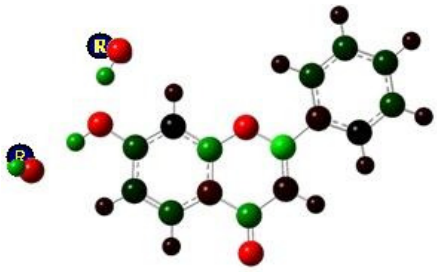
complex 7HF with three methanol molecules (R = CH_3)



complex without hydrogen bond ***a***



complex without hydrogen bond ***b***



complex without hydrogen bond ***c***

model structures

Figure 3bS.

		Calculations of $\Delta G_{f,298}$ of hydrogen bond ***a***				
$\Delta G_{f,298}$ of hydrogen bond ***a*** in S_0 state	=	$\Delta G_{f,298}$ of complex with 3 methanol molecules in S_0 state	–	$\Delta G_{f,298}$ complex without hydrogen bond ***a*** in S_0 state	–	$\Delta G_{f,298}$ of methanol in S_0 state
$\Delta G_{f,298}$ of hydrogen bond ***a*** in S_1 state	=	$\Delta G_{f,298}$ of complex with 3 methanol molecules in S_1 state	–	$\Delta G_{f,298}$ complex without hydrogen bond ***a*** in S_1 state	–	$\Delta G_{f,298}$ of methanol in S_0 state

calculations of $\Delta G_{f,298}$ of hydrogen bond ***b***

$\Delta G_{f,298}$ of hydrogen bond ***b*** in S_0 state	=	$\Delta G_{f,298}$ of complex with 3 methanol molecules in S_0 state	−	$\Delta G_{f,298}$ complex without hydrogen bond ***b*** in S_0 state	−	$\Delta G_{f,298}$ of methanol in S_0 state
$\Delta G_{f,298}$ of hydrogen bond ***b*** in S_1 state	=	$\Delta G_{f,298}$ of complex with 3 methanol molecules in S_1 state	−	$\Delta G_{f,298}$ complex without hydrogen bond ***b*** in S_1 state	−	$\Delta G_{f,298}$ of methanol in S_0 state

calculations of $\Delta G_{f,298}$ of hydrogen bond ***c***

$\Delta G_{f,298}$ of hydrogen bond ***c*** in S_0 state	=	$\Delta G_{f,298}$ of complex with 3 methanol molecules in S_0 state	−	$\Delta G_{f,298}$ complex without hydrogen bond ***c*** in S_0 state	−	$\Delta G_{f,298}$ of methanol in S_0 state
$\Delta G_{f,298}$ of hydrogen bond ***c*** in S_1 state	=	$\Delta G_{f,298}$ of complex with 3 methanol molecules in S_1 state	−	$\Delta G_{f,298}$ complex without hydrogen bond ***c*** in S_1 state	−	$\Delta G_{f,298}$ of methanol in S_0 state