

Supporting Information for

Combined IR/IR and IR/UV spectroscopy on the proton transfer coordinate of isolated 3-hydroxychromone in the electronic ground and excited state

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a) ESPT scheme for the 3-HC monomer

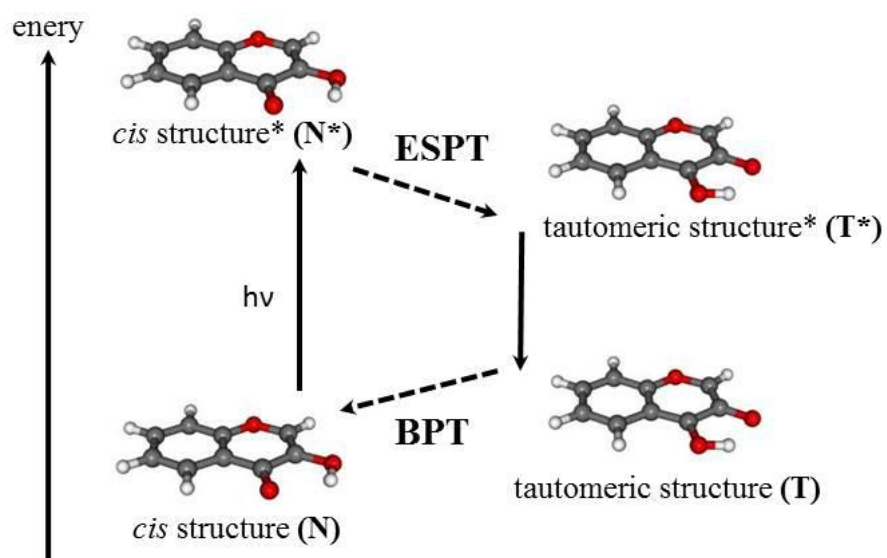


Figure S1 Typical scheme of a proton transfer after electronic excitation.
(ESPT = Excited state proton transfer, BPT = Back proton transfer)

b) Monohydrate in the S₀ state

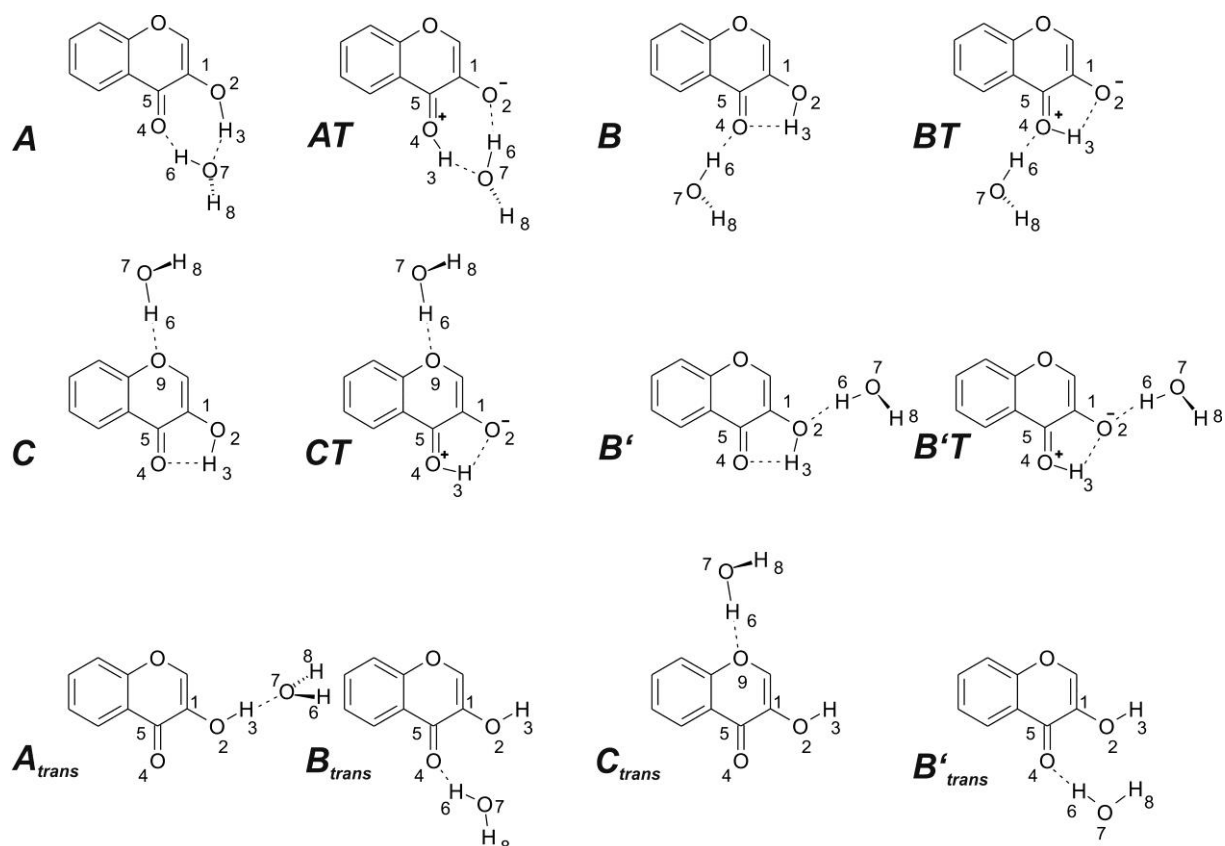


Figure S2 Possible structures of 3-hydroxycromone with one water molecule.

Table S1 Geometry parameters obtained for *A*, *B*, *C*, *B'*, *AT*, *BT*, *CT*, *B'T* and *A_{trans}*, *B_{trans}*, *C_{trans}*, *B'_{trans}* type structures (*cf.* Figure S2) of the 3-HC(H₂O)₁ cluster in the S₀ state calculated at the DFT (B3LYP/TZVP) level of theory. The bond lengths are given in Å and the bond angles in degree.

| | <i>A</i> | <i>B</i> | <i>C</i> | <i>B'</i> |
|------------------------------|--|--|---|---|
| | <i>E_{rel}</i> (cm ⁻¹) 0 | <i>E_{rel}</i> (cm ⁻¹) 839 | <i>E_{rel}</i> (cm ⁻¹) 2070 | <i>E_{rel}</i> (cm ⁻¹) 1312 |
| <i>r</i> _{C1-O2} | 1.342 | <i>r</i> _{C1-O2} 1.351 | <i>r</i> _{C1-O2} 1.350 | <i>r</i> _{C1-O2} 1.361 |
| <i>r</i> _{O2-H3} | 0.953 | <i>r</i> _{O2-H3} 0.975 | <i>r</i> _{O2-H3} 0.976 | <i>r</i> _{O2-H3} 0.977 |
| <i>r</i> _{H3-O7} | 1.913 | <i>r</i> _{H3-O4} 2.085 | <i>r</i> _{H3-O4} 2.096 | <i>r</i> _{O2-H6} 2.013 |
| <i>r</i> _{H6-O7} | 0.948 | <i>r</i> _{O4-C5} 1.241 | <i>r</i> _{H6-O7} 0.966 | <i>r</i> _{H3-O4} 2.068 |
| <i>r</i> _{O4-H6} | 2.022 | <i>r</i> _{O4-H6} 1.899 | <i>r</i> _{H6-O9} 2.130 | <i>r</i> _{O4-C5} 1.234 |
| <i>r</i> _{O4-C5} | 1.211 | <i>r</i> _{H6-O7} 0.973 | <i>r</i> _{O4-C5} 1.231 | <i>r</i> _{H6-O7} 0.968 |
| <i>Φ</i> _{C1-O2-H3} | 112.6 | <i>Φ</i> _{C1-O2-H3} 105.2 | <i>Φ</i> _{C1-O2-H3} 105.1 | <i>Φ</i> _{C1-O2-H3} 104.8 |
| <i>Φ</i> _{O2-H3-O7} | 169.0 | <i>Φ</i> _{O2-H3-O4} 116.2 | <i>Φ</i> _{O2-H3-O4} 116.3 | <i>Φ</i> _{O2-H3-O4} 117.1 |
| <i>Φ</i> _{H3-O7-H6} | 79.6 | <i>Φ</i> _{H3-O4-H6} 144.0 | <i>Φ</i> _{H3-O4-C5} 82.6 | <i>Φ</i> _{C1-O2-H6} 113.0 |
| <i>Φ</i> _{O7-H6-O4} | 137.5 | <i>Φ</i> _{O7-H6-O4} 167.1 | <i>Φ</i> _{O7-H6-O9} 156.4 | <i>Φ</i> _{O2-H6-O7} 149.0 |
| <i>Φ</i> _{H6-O4-C5} | 138.6 | | | <i>Φ</i> _{H3-O2-H6} 142.2 |

| <i>AT</i> | | <i>BT</i> | | <i>CT</i> | | <i>B'T</i> | |
|-----------------------------------|-------|-----------------------------------|-------|-----------------------------------|-------|-----------------------------------|-------|
| $E_{\text{rel}} (\text{cm}^{-1})$ | 4382 | $E_{\text{rel}} (\text{cm}^{-1})$ | 6938 | $E_{\text{rel}} (\text{cm}^{-1})$ | 7552 | $E_{\text{rel}} (\text{cm}^{-1})$ | 5484 |
| $r_{\text{C1-O2}}$ | 1.273 | $r_{\text{C1-O2}}$ | 1.270 | $r_{\text{C1-O2}}$ | 1.265 | $r_{\text{C1-O2}}$ | 1.277 |
| $r_{\text{O2-H6}}$ | 1.608 | $r_{\text{O2-H3}}$ | 1.701 | $r_{\text{O2-H3}}$ | 1.801 | $r_{\text{O2-H3}}$ | 1.867 |
| $r_{\text{H6-O7}}$ | 1.006 | $r_{\text{H3-O4}}$ | 1.025 | $r_{\text{H3-O4}}$ | 1.009 | $r_{\text{O2-H6}}$ | 1.818 |
| $r_{\text{H3-O7}}$ | 1.557 | $r_{\text{O4-C5}}$ | 1.317 | $r_{\text{H6-O7}}$ | 0.965 | $r_{\text{H3-O4}}$ | 0.999 |
| $r_{\text{H3-O4}}$ | 1.022 | $r_{\text{H6-O4}}$ | 2.041 | $r_{\text{H6-O9}}$ | 2.243 | $r_{\text{O4-C5}}$ | 1.316 |
| $r_{\text{O4-C5}}$ | 1.308 | $r_{\text{H6-O7}}$ | 0.967 | $r_{\text{O4-C5}}$ | 1.310 | $r_{\text{H6-O7}}$ | 0.981 |
| $\Phi_{\text{C1-O2-H6}}$ | 122.4 | $\Phi_{\text{C1-O2-H3}}$ | 85.2 | $\Phi_{\text{C1-O2-H3}}$ | 84.3 | $\Phi_{\text{C1-O2-H3}}$ | 83.7 |
| $\Phi_{\text{O2-H6-O7}}$ | 156.0 | $\Phi_{\text{O2-H3-O4}}$ | 128.7 | $\Phi_{\text{O2-H3-O4}}$ | 125.5 | $\Phi_{\text{O2-H3-O4}}$ | 123.1 |
| $\Phi_{\text{H6-O7-H3}}$ | 84.4 | $\Phi_{\text{H3-O4-H6}}$ | 128.7 | $\Phi_{\text{H3-O4-C5}}$ | 101.0 | $\Phi_{\text{C1-O2-H6}}$ | 108.2 |
| $\Phi_{\text{O7-H3-O4}}$ | 174.6 | $\Phi_{\text{O7-H6-O4}}$ | 157.1 | $\Phi_{\text{O7-H6-O9}}$ | 144.1 | $\Phi_{\text{O2-H6-O7}}$ | 159.7 |
| $\Phi_{\text{H3-O4-C5}}$ | 115.2 | | | | | $\Phi_{\text{H3-O2-H6}}$ | 168.0 |

| <i>A_{trans}</i> | | <i>B_{trans}</i> | | <i>C_{trans}</i> | | <i>B'_{trans}</i> | |
|-----------------------------------|-------|-----------------------------------|-------|-----------------------------------|-------|-----------------------------------|-------|
| $E_{\text{rel}} (\text{cm}^{-1})$ | 3107 | $E_{\text{rel}} (\text{cm}^{-1})$ | 3807 | $E_{\text{rel}} (\text{cm}^{-1})$ | 5003 | $E_{\text{rel}} (\text{cm}^{-1})$ | 3829 |
| $r_{\text{C1-O2}}$ | 1.351 | $r_{\text{C1-O2}}$ | 1.356 | $r_{\text{C1-O2}}$ | 1.358 | $r_{\text{C1-O2}}$ | 1.362 |
| $r_{\text{O2-H3}}$ | 0.976 | $r_{\text{O2-H3}}$ | 0.964 | $r_{\text{O2-H3}}$ | 0.965 | $r_{\text{O2-H3}}$ | 0.965 |
| $r_{\text{O4-C5}}$ | 1.221 | $r_{\text{O4-C5}}$ | 1.226 | $r_{\text{O4-C5}}$ | 1.219 | $r_{\text{O4-C5}}$ | 1.225 |
| $r_{\text{H3-O7}}$ | 1.840 | $r_{\text{O4-H6}}$ | 2.059 | $r_{\text{H6-O7}}$ | 0.966 | $r_{\text{O4-H6}}$ | 1.979 |
| $r_{\text{H6-O7}}$ | 0.964 | $r_{\text{H6-O7}}$ | 0.970 | $r_{\text{H6-O9}}$ | 2.070 | $r_{\text{H6-O7}}$ | 0.970 |
| $\Phi_{\text{C1-O2-H3}}$ | 110.9 | $\Phi_{\text{C1-O2-H3}}$ | 111.7 | $\Phi_{\text{C1-O2-H3}}$ | 110.6 | $\Phi_{\text{C1-O2-H3}}$ | 110.5 |
| $\Phi_{\text{O2-H3-O7}}$ | 178.2 | $\Phi_{\text{C5-O4-H6}}$ | 125.3 | $\Phi_{\text{O9-H6-O7}}$ | 170.9 | $\Phi_{\text{C5-O4-H6}}$ | 134.4 |
| $\Phi_{\text{H3-O7-H6}}$ | 116.2 | $\Phi_{\text{O4-H6-O7}}$ | 159.5 | | | $\Phi_{\text{O4-H6-O7}}$ | 170.7 |

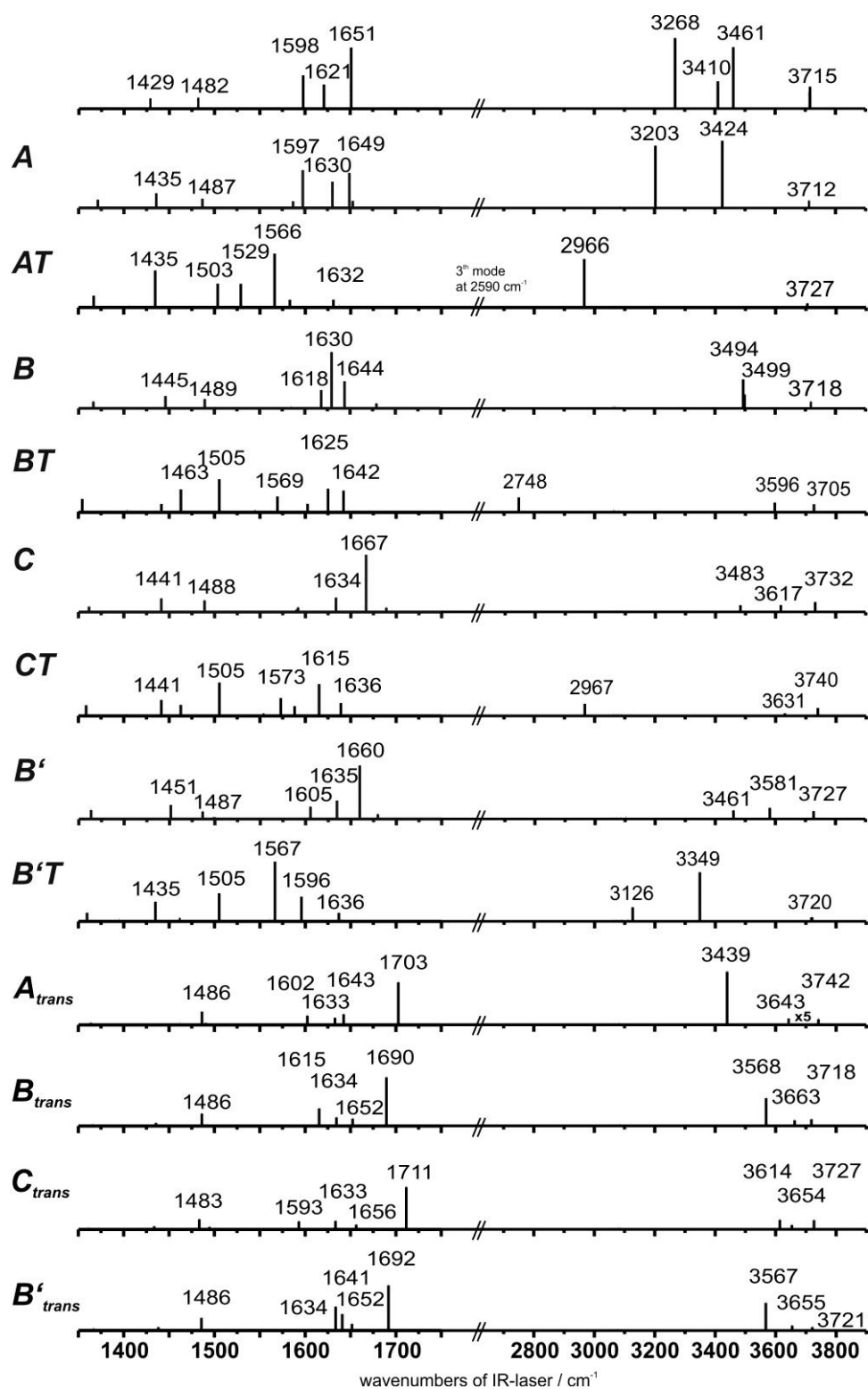


Figure S3 The upper trace schematically depicts the experimental S_0 state spectrum *via* the ion signal of 3-hydroxychromone, which is compared to the calculated stick spectra of different monohydrate isomers (DFT/B3LYP/TZVP, scaling factor OH stretching region: 0.9613; scaling factor CO stretching/OH bending region: 0.99. For a better illustration the calculated intensities in the OH stretching region were doubled.)

c) Monohydrate in the S_1 state

Table S2 Geometry parameters obtained for A , B , C , B' , AT , BT , CT , $B'T$ and A_{trans} , C_{trans} type structures of the 3-HC(H₂O)₁ cluster in the S_1 state calculated at the TD-DFT (B3LYP/TZVP) level of theory. The bond lengths are given in Å and the bond angles in degree.

| A | | B | | C | | B' | |
|------------------------------------|-------|------------------------------------|-------|------------------------------------|-------|------------------------------------|-------|
| E_{rel} (cm ⁻¹) 3880 | | E_{rel} (cm ⁻¹) 5158 | | E_{rel} (cm ⁻¹) 6248 | | E_{rel} (cm ⁻¹) 5804 | |
| r_{C1-O2} | 1.356 | r_{C1-O2} | 1.323 | r_{C1-O2} | 1.368 | r_{C1-O2} | 1.380 |
| r_{O2-H3} | 0.981 | r_{O2-H3} | 0.999 | r_{O2-H3} | 0.964 | r_{O2-H3} | 0.965 |
| r_{H3-O7} | 1.794 | r_{H3-O4} | 1.880 | r_{H3-O4} | 2.429 | r_{O2-H6} | 2.019 |
| r_{H6-O7} | 0.973 | r_{O4-C5} | 1.261 | r_{H6-O7} | 0.966 | r_{H3-O4} | 2.477 |
| r_{O4-H6} | 1.908 | r_{O4-H6} | 1.891 | r_{H6-O9} | 2.071 | r_{O4-C5} | 1.329 |
| r_{O4-C5} | 1.339 | r_{H6-O7} | 0.974 | r_{O4-C5} | 1.329 | r_{H6-O7} | 0.968 |
| $\Phi_{C1-O2-H3}$ | 111.4 | $\Phi_{C1-O2-H3}$ | 102.6 | $\Phi_{C1-O2-H3}$ | 110.3 | $\Phi_{C1-O2-H3}$ | 110.1 |
| $\Phi_{O2-H3-O7}$ | 171.5 | $\Phi_{O2-H3-O4}$ | 123.0 | $\Phi_{O2-H3-O4}$ | 102.9 | $\Phi_{O2-H3-O4}$ | 98.9 |
| $\Phi_{H3-O7-H6}$ | 99.4 | $\Phi_{H3-O4-H6}$ | 145.4 | $\Phi_{H3-O4-C5}$ | 78.0 | $\Phi_{C1-O2-H6}$ | 114.5 |
| $\Phi_{O7-H6-O4}$ | 127.7 | $\Phi_{O7-H6-O4}$ | 169.9 | $\Phi_{O7-H6-O9}$ | 168.5 | $\Phi_{O2-H6-O7}$ | 155.7 |
| $\Phi_{H6-O4-C5}$ | 121.9 | | | | | $\Phi_{H3-O2-H6}$ | 126.2 |

| AT | | BT | | CT | | $B'T$ | |
|---------------------------------|-------|------------------------------------|-------|------------------------------------|-------|------------------------------------|-------|
| E_{rel} (cm ⁻¹) 0 | | E_{rel} (cm ⁻¹) 1959 | | E_{rel} (cm ⁻¹) 2250 | | E_{rel} (cm ⁻¹) 1361 | |
| r_{C1-O2} | 1.339 | r_{C1-O2} | 1.335 | r_{C1-O2} | 1.344 | r_{C1-O2} | 1.337 |
| r_{O2-H6} | 1.881 | r_{O2-H3} | 2.091 | r_{O2-H3} | 2.209 | r_{O2-H3} | 2.153 |
| r_{H6-O7} | 0.974 | r_{H3-O4} | 0.976 | r_{H3-O4} | 0.969 | r_{O2-H6} | 1.956 |
| r_{H3-O7} | 1.708 | r_{O4-C5} | 1.351 | r_{H6-O7} | 0.966 | r_{H3-O4} | 0.974 |
| r_{H3-O4} | 0.992 | r_{O4-H6} | 2.033 | r_{H6-O9} | 2.052 | r_{O4-C5} | 1.341 |
| r_{O4-C5} | 1.334 | r_{H6-O7} | 0.967 | r_{O4-C5} | 1.329 | r_{H6-O7} | 0.971 |
| $\Phi_{C1-O2-H6}$ | 126.7 | $\Phi_{C1-O2-H3}$ | 82.1 | $\Phi_{C1-O2-H3}$ | 81.2 | $\Phi_{C1-O2-H3}$ | 81.6 |
| $\Phi_{O2-H6-O7}$ | 142.1 | $\Phi_{O2-H3-O4}$ | 116.4 | $\Phi_{O2-H3-O4}$ | 111.3 | $\Phi_{O2-H3-O4}$ | 114.2 |
| $\Phi_{H6-O7-H3}$ | 89.6 | $\Phi_{H3-O4-H6}$ | 118.9 | $\Phi_{H3-O4-C5}$ | 108.5 | $\Phi_{C1-O2-H6}$ | 111.3 |
| $\Phi_{O7-H3-O4}$ | 177.1 | $\Phi_{O7-H6-O4}$ | 166.1 | $\Phi_{O7-H6-O9}$ | 157.5 | $\Phi_{O2-H6-O7}$ | 157.2 |
| $\Phi_{H3-O4-C5}$ | 114.2 | | | | | $\Phi_{H3-O2-H6}$ | 166.8 |

| A_{trans} | | C_{trans} | |
|------------------------------------|-------|------------------------------------|-------|
| E_{rel} (cm ⁻¹) 4652 | | E_{rel} (cm ⁻¹) 6512 | |
| r_{C1-O2} | 1.358 | r_{C1-O2} | 1.366 |
| r_{O2-H3} | 0.977 | r_{O2-H3} | 0.964 |
| r_{O4-C5} | 1.323 | r_{O4-C5} | 1.321 |
| r_{H3-O7} | 1.821 | r_{H6-O9} | 2.042 |
| r_{H6-O7} | 0.964 | r_{H6-O7} | 0.966 |
| $\Phi_{C1-O2-H3}$ | 110.7 | $\Phi_{C1-O2-H3}$ | 110.3 |
| $\Phi_{O2-H3-O7}$ | 178.7 | $\Phi_{O2-H3-O7}$ | 175.1 |
| $\Phi_{H3-O7-H6}$ | 117.4 | | |

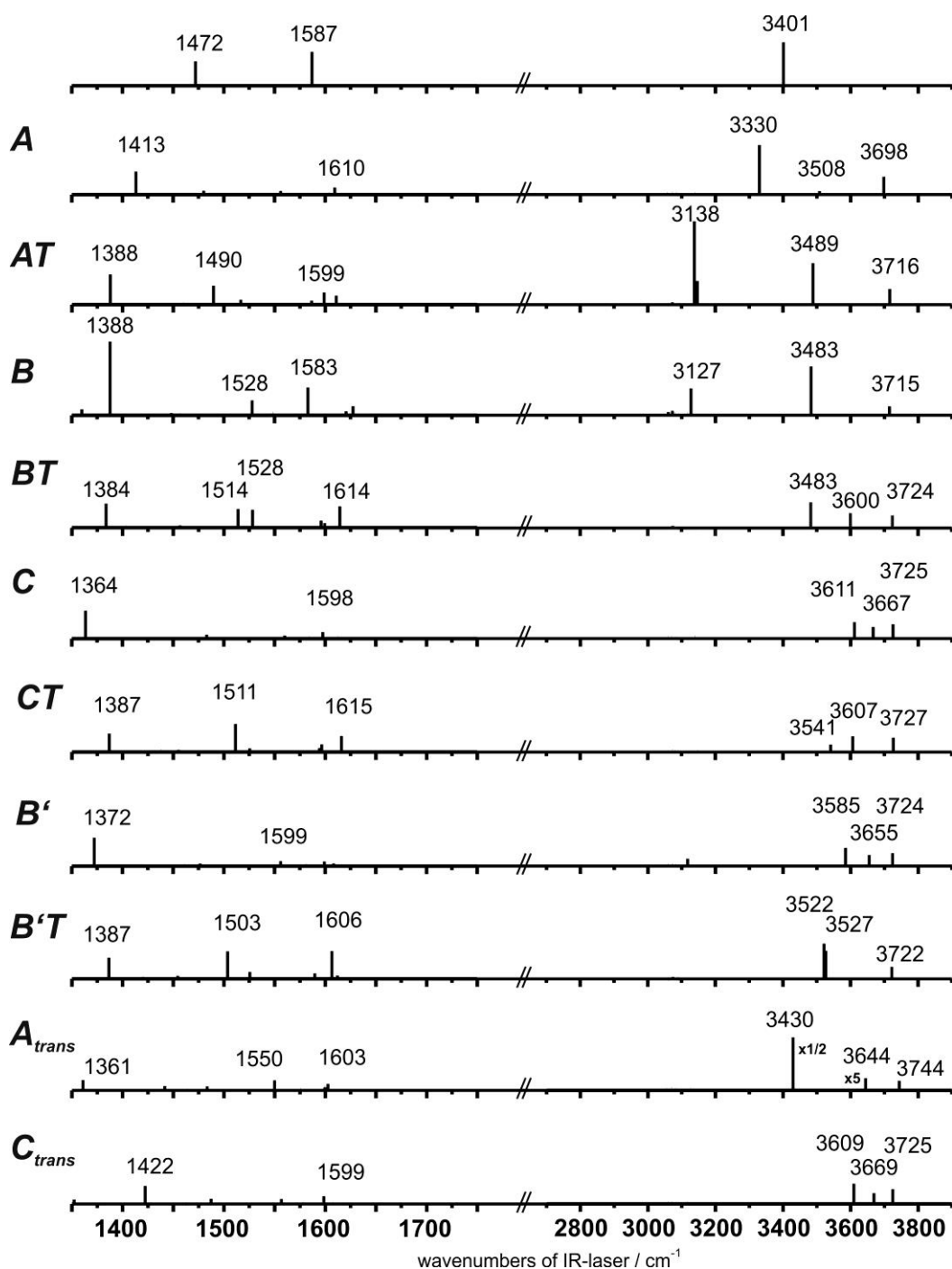


Figure S4 The upper trace schematically depicts the experimental S_1 state spectrum *via* the ion signal of 3-hydroxychromone, which is compared to the calculated stick spectra of different monohydrate isomers (TD-DFT/B3LYP/TZVP, scaling factor OH stretching region: 0.9613; scaling factor CO stretching/OH bending region: 0.99.)

d) Dihydrate in the S_0 state

Additionally structures for clusters with two water molecules (*cf.* Figure S5) and the corresponding most important geometry parameters have been calculated. In case of the most stable dihydrate structure *I* both water molecules are inserted between the CO and OH functionality acting as a bridge. In structure *D*, being 1390 cm^{-1} (17 kJ/mol) less stable than *I*, only one water molecule is in a bridging function, the second one is attached to the first one as hydrogen-bonding donor. In structure *E* (1005 cm^{-1} (12 kJ/mol) less stable) the first water molecule is inserted and at the same time acts a hydrogen-bonding donor for the second one. The second water molecule can also be bonded to the oxygen atom of the chromone unit resulting in an even less stable structure (*F*: 2028 cm^{-1} (24 kJ/mol)). For the *I* and *D* structure the tautomeric forms *IT* and *DT* were also calculated which are significantly less stable in the electronic ground state (*IT*: 4315 cm^{-1} (52 kJ/mol), *DT*: 5519 cm^{-1} (66 kJ/mol)).

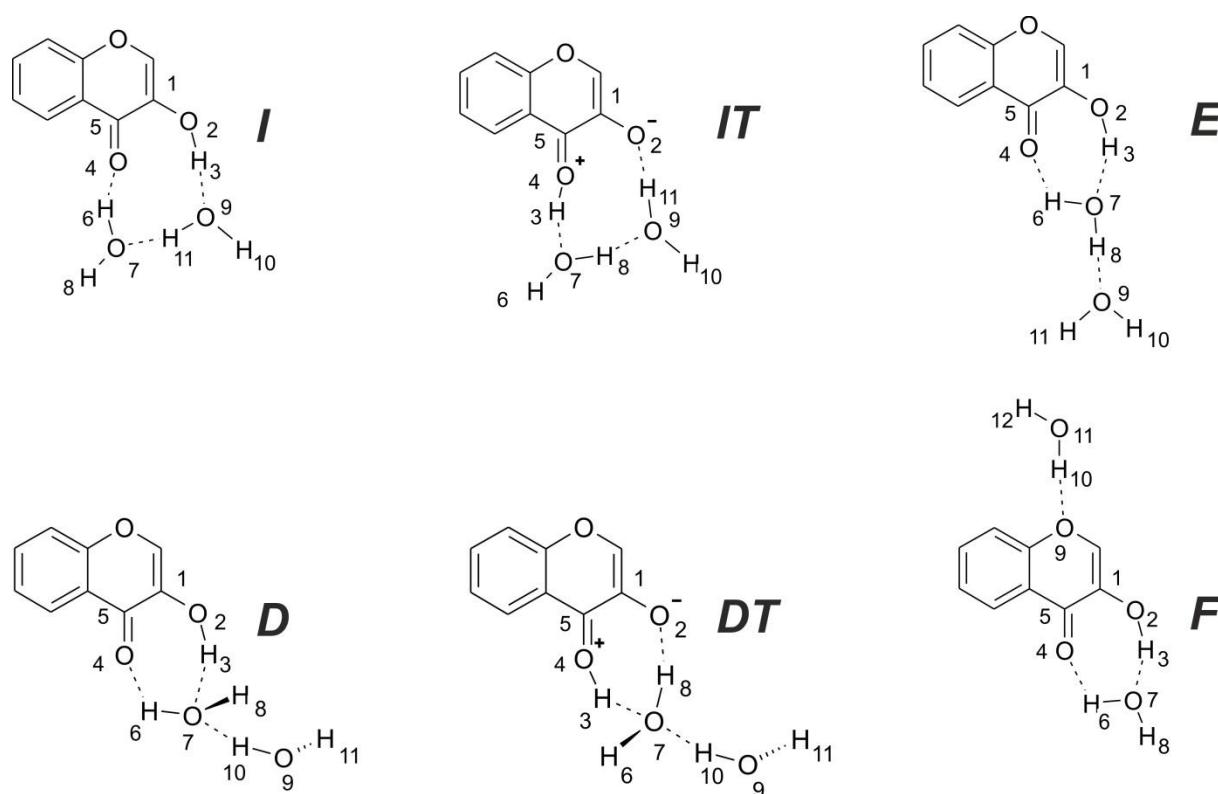


Figure S5 Possible structures of 3-hydroxychromone with two water molecules.

Table S3 Geometry parameters obtained for *I*, *IT*, *E*, *D*, *DT* and *F* type structures of the 3-HC(H₂O)₂ cluster in the S₀ state calculated at the DFT (B3LYP/TZVP) level of theory. The bond lengths are given in Å and the bond angles in degree.

| <i>I</i> | | <i>IT</i> | | <i>E</i> | |
|--|-------|---|-------|---|-------|
| E _{rel} (cm ⁻¹) 0 | | E _{rel} (cm ⁻¹) 4315 | | E _{rel} (cm ⁻¹) 1005 | |
| r _{C1-O2} | 1.339 | r _{C1-O2} | 1.267 | r _{C1-O2} | 1.343 |
| r _{O2-H3} | 0.993 | r _{O2-H11} | 1.685 | r _{O2-H3} | 0.998 |
| r _{H3-O9} | 1.736 | r _{H11-O9} | 0.988 | r _{H3-O7} | 1.675 |
| r _{O9-H11} | 0.982 | r _{O9-H8} | 1.711 | r _{O7-H6} | 0.973 |
| r _{H11-O7} | 1.779 | r _{H8-O7} | 0.990 | r _{H6-O4} | 1.924 |
| r _{O7-H6} | 0.975 | r _{O7-H3} | 1.608 | r _{O4-C5} | 1.236 |
| r _{H6-O4} | 1.818 | r _{H3-O4} | 1.019 | r _{H8-O9} | 1.887 |
| r _{O4-C5} | 1.236 | r _{O4-C5} | 1.303 | Φ _{C1-O2-H3} | 113.8 |
| Φ _{C1-O2-H3} | 114.9 | Φ _{C1-O2-H11} | 147.5 | Φ _{O2-H3-O7} | 179.4 |
| Φ _{O2-H3-O9} | 158.8 | Φ _{O2-H11-O9} | 161.0 | Φ _{H3-O4-H6} | 88.5 |
| Φ _{H3-O9-H11} | 112.2 | Φ _{H11-O9-H8} | 90.3 | Φ _{O7-H6-O4} | 141.7 |
| Φ _{O9-H11-O7} | 163.9 | Φ _{O9-H8-O7} | 164.8 | Φ _{H6-O4-C5} | 127.8 |
| Φ _{H11-O7-H6} | 90.4 | Φ _{H8-O7-H3} | 107.3 | Φ _{H3-O7-H8} | 117.8 |

| <i>D</i> | | <i>DT</i> | | <i>F</i> | |
|---|-------|---|-------|---|-------|
| E _{rel} (cm ⁻¹) 1390 | | E _{rel} (cm ⁻¹) 5519 | | E _{rel} (cm ⁻¹) 2028 | |
| r _{C1-O2} | 1.351 | r _{C1-O2} | 1.277 | r _{C1-O2} | 1.344 |
| r _{O2-H3} | 0.982 | r _{O2-H8} | 1.537 | r _{O2-H3} | 0.989 |
| r _{H3-O7} | 1.806 | r _{H8-O7} | 1.021 | r _{H3-O7} | 1.736 |
| r _{O7-H6} | 0.981 | r _{O7-H3} | 1.616 | r _{O7-H6} | 0.978 |
| r _{H6-O4} | 1.791 | r _{H3-O4} | 1.010 | r _{H6-O4} | 1.835 |
| r _{O4-C5} | 1.239 | r _{O4-C5} | 1.311 | r _{O4-C5} | 1.237 |
| r _{O7-H10} | 2.033 | r _{O7-H10} | 1.925 | r _{H10-O9} | 2.139 |
| Φ _{C1-O2-H3} | 112.3 | Φ _{C1-O2-H8} | 122.4 | Φ _{C1-O2-H3} | 113.5 |
| Φ _{O2-H3-O7} | 167.8 | Φ _{O2-H8-O7} | 160.5 | Φ _{O2-H3-O7} | 179.6 |
| Φ _{H3-O7-H6} | 82.0 | Φ _{H8-O7-H3} | 81.7 | Φ _{H3-O7-H6} | 85.0 |
| Φ _{O7-H6-O4} | 149.7 | Φ _{O7-H3-O4} | 173.5 | Φ _{O7-H6-O4} | 147.3 |
| Φ _{H3-O7-H10} | 82.0 | Φ _{H8-O7-H10} | 120.4 | Φ _{H6-O4-C5} | 128.5 |
| Φ _{O7-H10-O9} | 157.0 | Φ _{O7-H10-O9} | 178.4 | Φ _{O11-H10-O9} | 155.4 |

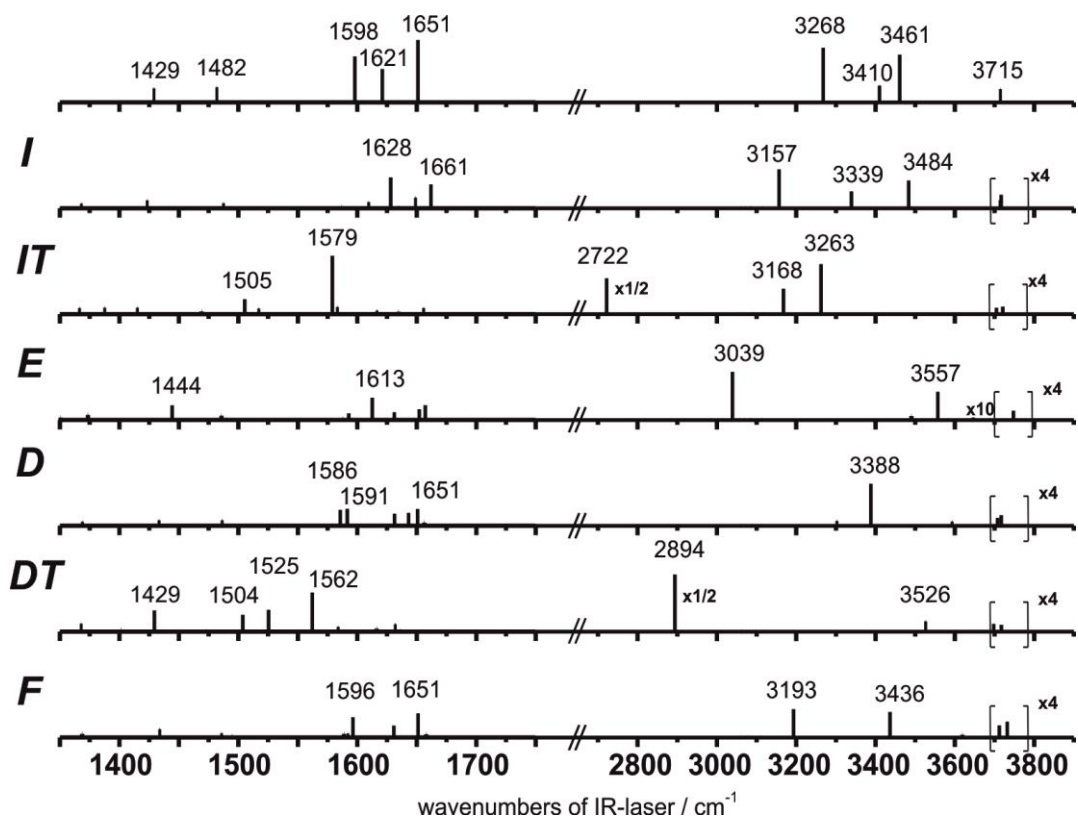


Figure S6 The upper trace schematically depicts the experimental S_0 state spectrum *via* the ion signal of 3-hydroxychromone, which is compared to the calculated stick spectra of different dihydrate isomers (DFT/B3LYP/TZVP, scaling factor OH stretching region: 0.9613; scaling factor CO stretching/OH bending region: 0.99. For a better illustration the calculated intensities in the OH stretching region were tripled.)

e) 3-Hydroxychromone under neon expansion

The UV excitation or ionization laser can affect a fragmentation of water clusters down onto the monomer mass trace (or to a mass trace with a lower number of water molecules). As a consequence a certain percentage *e.g.* of the monomer ion signal is not due to the excitation and ionization of the “true” monomer species but originates from fragmenting hydrates. If now IR/R2PI spectra are measured and the IR laser resonantly excites a vibration of a water cluster it depopulates the vibrational ground state of the S_0 state. Therefore less clusters are available for the UV excitation and ionization photon which means that less clusters fragment down onto the monomer mass trace. This leads to a depletion of the monomer mass signal and thus hydrate bands in the IR/R2PI spectrum of the monomer occur.

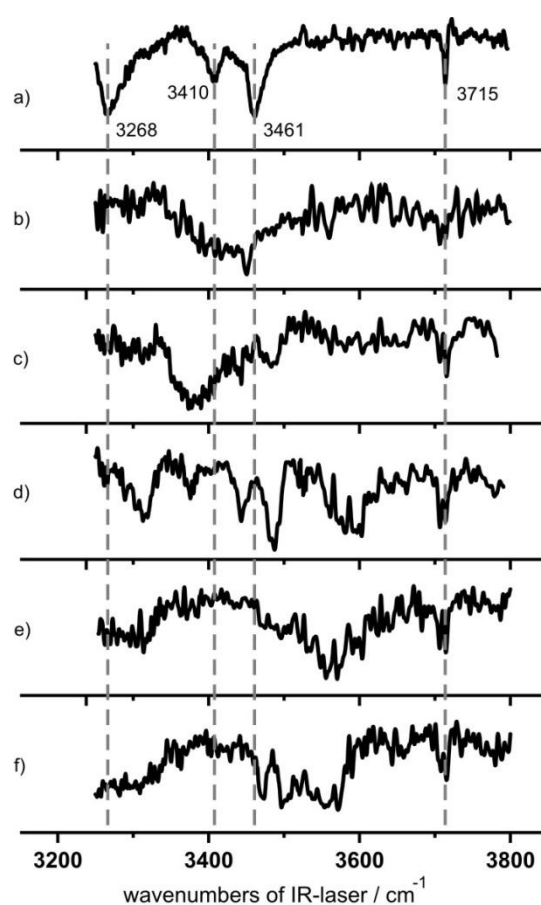


Figure S7 IR/R2PI spectra (with neon as expansion gas) in the range from 3250 to 3800 cm^{-1} on the mass traces of a) 3-hydroxychromone b) 3-HC(H₂O)₁, c) 3-HC(H₂O)₂, d) 3-HC(H₂O)₃, e) 3-HC(H₂O)₄, f) 3-HC(H₂O)₅.

By expanding 3-HC with neon, ion signals of clusters with water could be observed. The corresponding IR/R2PI (S_0 state) spectra obtained in the region from 3250 to 3800 *via* the mass channels of the monomer as well as *via* the mono- up to penta-hydrated clusters are shown in Fig. S7. The IR/R2PI spectra of the monomer mass were identical under helium and neon conditions. However, none of the IR bands in the spectra of the water clusters (in neon) could be correlated with the bands found in the

IR/R2PI spectrum via the monomer mass. This is a clear hint that larger water clusters are formed in the neon expansion, which fragment down onto the mass trace of smaller clusters like the monohydrate but do fragment to the monomer species during dissociation. Two conclusions can be drawn from this: First, the monohydrate mass channel observed in the neon expansion does not represent “true” monohydrate but a fragment of a higher water cluster; second, the additional band in the monomer IR/R2PI spectrum can only originate from the small water clusters like the (non-observable) monohydrate.

f) Synthesis of 3-hydroxychromone

The synthesis consists of two steps. The first step comprises the production of the 2,3-epoxychromone, the second one the synthesis of 3-hydroxychromone. Small changes to the original work from Spadafora *et al.* [1] have been introduced:

A solution of sodium hydroxide (407 mg, 7,5 mmol) and hydrogen peroxide (1,4 ml, 10 mmol, 30 % solution) is slowly added to a solution of chromone (740 mg, 5 mmol) in methylene chloride (7,5 ml). The mixture is stirred for 3 h at 0 °C, quenched with water and extracted with methylene chloride (3 x 30 ml). The organic layers are dried over Na₂SO₄ and evaporate under reduced pressure to give a crude amorphous solid (583 mg, 71 %).

Concentrated HCl (20 ml) is added to 2,3-epoxychromone (501 mg, 3,1 mmol) and the mixture is heated under reflux at 70 °C for 1 h. After cooling to room temperature, water (20 ml) is added and the mixture is extracted with methylene chlorid (3 x 30 ml). The organic layers are washed with saturated aqueous NaHCO₃ solution, dried over MgSO₄ and evaporated under reduced pressure to give a brown solid. This solid is recrystallized with methanol to give a yellow-brown needle of solid. M(C₉H₆O₃)= 162,1 g/mol. Yield: 410 mg (2,5 mmol, 81 %). Mp: 176,5 °C.

[1] M. Spadafora, V. Y. Postupalenko, V. V. Shvadchak, A. S. Klymchenko, Y. Mély, A. Burger and R. Benhida, *Tetrahedron*, 2009, **65**, 7809.

g) Description of the vibrational bands obtained for the types *A*, *B*, *A_{trans}* and *B'T* of 3-HC with one water

Table S4 Description of the strongest vibrational bands obtained for the *A*, *B*, *A_{trans}* and *B'T* type of 3-hydroxychromone with one water molecule in the *S*₀ state (*cf.* Figure S2) (DFT/B3LYP/TZVP).

| <i>A</i> wavenumber / cm ⁻¹ | Character |
|---|---|
| 1435 | O-H bend (3-HC), CH bend, C=C bend |
| 1487 | CH bend, ring deformation |
| 1597 | O-H bend (H ₂ O) |
| 1630 | C-O stretch, C=C stretch, O-H bend (H ₂ O), ring deformation, C-H bend |
| 1649 | C-O stretch, C=C stretch, O-H bend, ring deformation, C-H bend |
| 3203 | O-H stretch (3-HC) |
| 3424 | Bonded O-H stretch (H ₂ O) |
| 3712 | Free O-H stretch (H ₂ O) |
| <i>B</i> wavenumber / cm ⁻¹ | Character |
| 1445 | O-H bend (3-HC), C-H bend, C=C bend |
| 1489 | C-H bend, ring deformation, C-O bend |
| 1618 | O-H bend (H ₂ O) |
| 1630 | C-O stretch, O-H bend (H ₂ O), ring deformation, C-H bend |
| 1644 | C-O stretch, O-H bend (H ₂ O), ring deformation, C-H bend |
| 3494 | O-H stretch (3-HC), O-H stretch (H ₂ O) |
| 3499 | O-H stretch (H ₂ O), O-H stretch (3-HC) |
| 3718 | Free O-H stretch (H ₂ O) |
| <i>A_{trans}</i> wavenumber / cm ⁻¹ | Character |
| 1486 | O-H bend (3-HC), C-H bend, ring deformation |
| 1602 | O-H bend (H ₂ O), C-O bend |
| 1633 | ring deformation, C-H bend |
| 1643 | C-O stretch, O-H bend (3-HC), ring deformation, C-H bend, C=C stretch |
| 1703 | C-O stretch, ring deformation, C-H bend, O-H bend (3-HC) |
| 3439 | O-H stretch (3-HC) |
| 3643 | Sym. O-H stretch (H ₂ O) |
| 3742 | Asym. O-H stretch (H ₂ O) |
| <i>B'T</i> wavenumber / cm ⁻¹ | Character |
| 1435 | O-H bend (3-HC), C-H bend, Ring deformation |
| 1505 | C-H bend, ring deformation, O-H bend |
| 1567 | C-O stretch, ring deformation, C-H bend, C=C stretch |
| 1596 | O-H bend (3-HC), C-O stretch, ring deformation, C-H bend, C=C stretch |
| 1636 | O-H bend (H ₂ O), ring deformation, C-H bend |
| 3126 | O-H stretch (3-HC) |
| 3349 | Bonded O-H stretch (H ₂ O) |
| 3720 | Free O-H stretch (H ₂ O) |

h) Resonance structures of the tautomeric structure of 3-HC

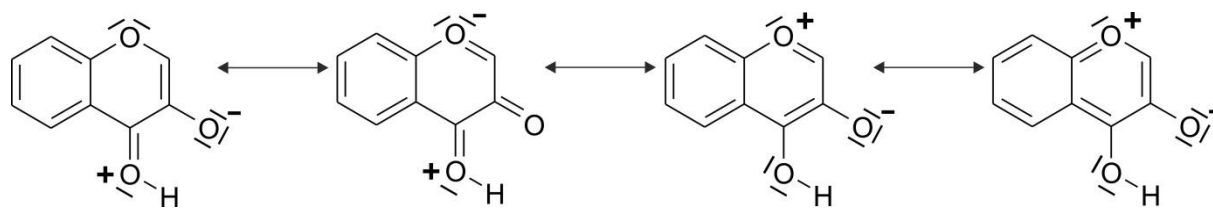


Figure S8 Possible resonance structures of the tautomeric structure of 3-hydroxychromone.