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Characterization of adsorption and electronic excited states of quercetin on titanium dioxide nanoparticles

Agata Zdyb [a], Stanisław Krawczyk [b],*

[a] Lublin University of Technology, Faculty of Environmental Engineering, Nadbystrzycka 40B, 20-618 Lublin, Poland
[b] Maria Curie-Skłodowska University, Institute of Physics, Pl. M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland

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ABSTRACT

Adsorption of quercetin on colloidal titanium dioxide nanoparticles in ethanol and its excited-state electronic structure were investigated by means of electronic and vibrational spectroscopies. The changes in electronic charge redistribution as reflected by the dipole moment difference, $\Delta\mu$, between the ground and excited electronic states were measured with electroabsorption spectroscopy and analyzed using results of TD DFT computations. Adsorption of quercetin causes a red shift of its absorption spectrum. Raman spectra of quercetin analyzed with reference to analogous data for morin indicate binding of quercetin through the hydroxy groups of the catechol moiety. The difference dipole moment, which is 5.5 D in free quercetin, increases to 11.8 D in opposite direction in adsorbed quercetin, and is associated with charge-transfer to the Ti atom. The computed transition energy, intensity, vector $\Delta\mu$ and molecular orbitals involved in the electronic transition at different molecular configurations indicate a bidentate chelating mode of binding of quercetin.

1. Introduction

Quercetin and morin belong to the group of flavonoid compounds that naturally occur in higher plants. These two flavonoids are well known for their antioxidant behavior and DNA protection through reaction with free radicals. Chelating of metal ions plays an important role in both natural environment and biochemistry of living species since it influences bioavailability and toxicity of some metals. The complexation of flavonoids with metal ions is widely investigated because this process leads to formation of fluorescent complexes used in analytical detection of metal traces and in ligand identification [1–4]. Another potential possibility for application of flavonoid dyes can be their use as photosensitizers in dye-sensitized solar cells and in photocatalysis.

Most of the research on quercetin and morin complexation properties focuses on the stoichiometry of flavonoid–metal complexes, as these compounds present several possible modes of metal binding related to their structural differences [1,3,5,6]. The molecular structure of quercetin shown in Fig. 1 contains the chromone part (rings A and C) and the catecholic ring B. There are three sites for binding of metal ions. They involve the 3-hydroxy-4-keto and 5-hydroxy-4-keto groups in the chromone rings A and C, and the orto-dihydroxy groups in the catechol moiety at C3′ and C4′ positions. The latter possibility of metal binding is absent in morin which is an isomeric form of quercetin with more spaced hydroxyl groups at C2′ and C4′. Our previous study of

morin complexation with TiO_2 surface shows an initial involvement of the 3-hydroxy-4-keto group [7].

The electronic absorption spectroscopy and computations of electronic structure of differently OH-substituted flavonoids have indicated substantial changes in the electronic structure of the lowest electronic excited state evoked by complexed metal ions [5,6,8,9]. Although the charge-transfer contribution to the electronic transitions was postulated and seems to be supported by large spectral red shifts, no quantitative measures have been provided for the metal ion-induced charge redistribution. This paper describes a study on the mode of binding and the spectral changes that appear in electronic absorption, Raman and electroabsorption spectra of quercetin when adsorbed on TiO_2. The experimental data supported by quantum chemical computations provide a quantitatively consistent picture of electronic structure modification in the excited-state of quercetin caused by its binding at TiO_2 surface.

2. Methods

Quercetin and morin were purchased from Sigma-Aldrich and used as received. Colloidal solution of TiO_2 nanoparticles in anhydrous ethanol was prepared by hydrolysis of titanium tetraisopropoxide [10] in the presence of 0.2% acetic acid. Transmission electron microscopy using Titan G2 60-300 (from FEI) confirmed the small size of nanoparticles with the mean diameter of 5 nm. Adsorption of quercetin dye on TiO_2 nanoparticles was achieved by adding the dye solution in ethanol to the TiO_2 colloid and was confirmed by UV–VIS and Raman spectra.

* Corresponding author.
E-mail addresses: a.zdyb@pollub.pl (A. Zdyb), skraw@hektor.umcs.lublin.pl (S. Krawczyk).
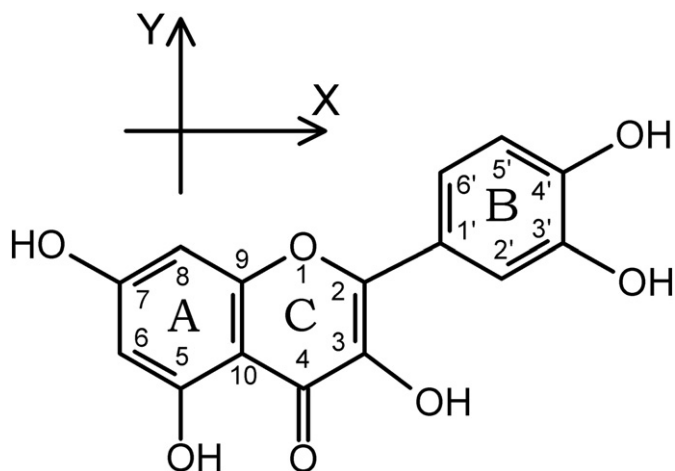
Fig. 1. Quercetin structure and atom numbering scheme.

The samples for the electroabsorption measurements were colloidal solutions frozen between two conducting glass plates and kept at 80 K. The Stark spectra were recorded using the setup and methods described in details previously [11]. Briefly, a sinusoidal voltage of 800–1500 V was applied to the electrically conducting sample windows and the second harmonic component in the transmitted light intensity was detected and recorded together with the total light intensity. The sample absorbance and its electric field-induced changes, ΔA, were calculated from the recorded signals and were further processed by fitting the electroabsorption spectrum according to theory [12,13] which describes ΔA as a linear combination of the absorption spectrum itself and its first and second derivatives with respect to the wavenumber:

$$\Delta A(\nu) = a_0 A(\nu) + a_1 \cdot \nu \frac{dA(\nu)}{d\nu} + a_2 \cdot \nu \frac{d^2 A(\nu)}{d\nu^2}. \tag{1}$$

The first term in Eq. (1) was neglected since its contribution to the fits turned out to be insignificant. The change of the permanent dipole moment vector, $\Delta\mathbf{\mu}$, and the change in molecular polarizability tensor in the form of its trace, $Tr(\Delta\mathbf{\alpha})$, that occur on electronic excitation, were derived from the fit coefficients a_1 and a_2 which depend on these quantities in the following way:

$$a_1(\chi) = \frac{f^2 F^2}{15hc} \left[\frac{5}{2} Tr(\Delta\mathbf{\alpha}) + \left(\frac{3}{2}\mathbf{m} \cdot \Delta\mathbf{\alpha} \cdot \mathbf{m} - \frac{1}{2} Tr(\Delta\mathbf{\alpha}) \right) \cdot (3\cos^2\chi - 1) \right] \tag{2}$$

$$a_2 = \frac{f^2 (\Delta\mu)^2}{10\sqrt{2}h^2 c^2} F^2 \left[(3\cos^2\delta - 1)\cos^2\chi + 2 - \cos^2\delta \right]. \tag{3}$$

The angle χ between the electric vector of light and the applied electric field within the sample was set experimentally by rotating the sample in linearly polarized light beam. The angle δ between $\Delta\mathbf{\mu}$ and the transition dipole moment was obtained from the linear dependence of a_2 in Eq. (3) on $\cos^2\chi$. The value of $Tr(\Delta\mathbf{\alpha})$ was obtained from $a_1(\chi)$ determined at the magic angle χ (54.7°). The local field factor ($f \approx 1.1$–1.3) is included in electrooptical parameters quoted here, whose values thus represent $f \cdot \Delta\mu$ and $f^2 \cdot Tr(\Delta\mathbf{\alpha})$.

Raman spectra were recorded with FT Raman spectrometer Nicolet NXR (Thermo Scientific) using 1064 nm excitation wavelength in backscattering geometry. The samples were prepared by adding the dye in stoichiometric amount to the TiO_2 colloid in ethanol and by evaporating the solvent.

The electronic structure calculations were performed with the DFT method and the TD DFT for excited states, implemented in the Gaussian 09 program [14]. Trial computations using the BLYP functional with standard basis function sets (6-31G and 6-31G*) were found to underestimate the excitation energies and overestimate the spectral shift and dipole moments. To obtain these three quantities acceptably close to experimental data, the use of B3LYP functional and 6-31G(d,p) basis turned out to be appropriate, in line with findings reported in other studies on similar systems [8,15]. This level of DFT theory was thus used, together with the PCM solvent model and chloroform or ethanol as the solvent (without relevant differences) to reproduce the spectral and electrooptical features of free and adsorbed quercetin. The dipole moment difference between the ground and the excited state was calculated with the finite field method, assuming the electric field intensities of ± 0.0005 a.u. down the cartesian coordinate axes.

3. Results and discussion

3.1. Free quercetin

The low temperature absorption spectrum of free quercetin shown in Fig. 2A exhibits clear vibronic structure not seen in the normal temperature spectrum which is also shown there. Part B of Fig. 2 shows the electroabsorption spectrum (points) and the best fit being a linear combination of absorption derivatives (Eq. (1)). We found the zeroth-derivative component to be very small and dependent on the fitted range, with no significance for the estimates of electrooptical
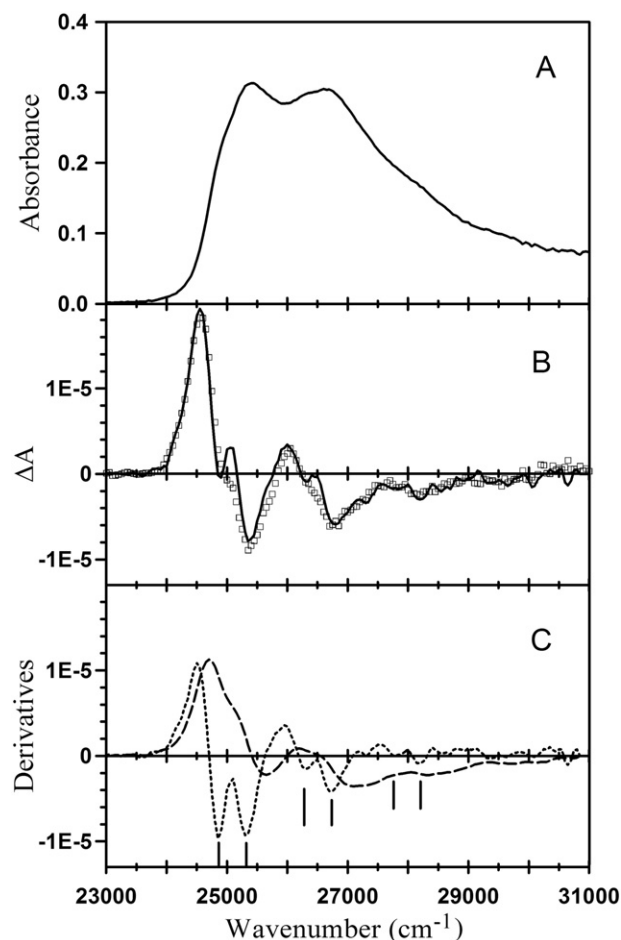

Fig. 2. Absorption and electroabsorption spectra of quercetin (2 mM in EtOH at T = 80 K). A — Absorption spectra at normal temperature (dotted) and at 80 K (continuous line); B — electroabsorption spectrum (points) at 80 K recorded with electric field intensity $1.25 \cdot 10^5$ V/cm (r.m.s.), and the fit (solid line); C — the first derivative component (dashed line) and the second derivative component (dotted line) of the fit shown in part B.