COUMARIN 337 IN AQUEOUS SOLUTION: INTERPLAY BETWEEN EXCITATION AND HYDRATION

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Abstract. Excitation of the C337, highly fluorescent dye in an aqueous solution was studied by the TD-DFT. Through the B3PW91/6-311++G(d, p)/IEFPCM theory level, we obtained the C337 vibronic absorption spectrum which exactly reproduces the experimental maximum. Significant differences are shown between the results of calculating the transition energies using the models of vertical and vibronic transitions. Upon excitation, the main shift of the electron density occurs from C10 to C4 neighboring atom. Thus, large-scale ICT not occur. The effect of excitation on the vibrational spectra of C337 was analyzed. A single C337 molecule and its five different hydration complexes with strongly bound water molecules have been analyzed. Various hydrate complexes of the dye have been studied, and the effect of hydration on its excitation vibrational properties has been elucidated. It was taken into account that a water molecule can attach to the nitrogen atom N1 ("A" type) and the C=O carbonyl ("B" type), and cyano C≡N ("C" type) groups of the dye.

Key words: TD-DFT/DFT, coumarin 337 (523), excitation, hydration, vibronic spectrum, aqueous solution.

INTRODUCTION

Coumarin 337 (C337, also occasionally referred to as C523, Fig. 1) is a highly fluorescent dye used in lasers [1-3] and solar cells [3].

C337 is a member of the 7-aminocoumarins family with a nitrogen atom in position 7 which is rigidly fixed (Fig. 1). This structural feature excludes rotational relaxation and non-radiative TICT [1] which caused a high quantum yield of fluorescence Φ. So, in ethanol, $\Phi=0.65$ [1,4]. In water, the fluorescence quantum yield of C337 is even higher and amounts to $\Phi=0.67$ [4].

The chromophore of C337 is formed by julolidyl ABC moiety (electron donor), and a lactone D ring with oxo and cyano groups (electron acceptors, see Fig. 1). Therefore, due to dye excitation, ICT is possible [1]. The spatial structure of C337 was investigated in Ref. [4] by X-ray diffraction. Aliphatic A and B rings are flexible, so they can have different conformations.

In addition to the C337 structural characteristics, its fluorescence [1,4], hyperpolarizability [5], and dipole moments of ground and excited states [6-8] have been investigated in sufficient detail. The non-covalent binding of the dye with other molecules [9-11], including electron transfer in these heterocomplexes [9,10] was also studied. In solutions, C337 exhibits positive solvatochromism [4-8], which corresponds to the electronic transition of the $\pi\rightarrow\pi^*$ type [12]. This is also consistent with the increase in the dipole moment of the dye in the excited state as compared to the ground state experimentally established [6-8].

Theoretical studies of the C337 photoexcitation in solutions were carried out in three early works semi-empirically [4,5,13] and the most recent one by TD-DFT [14]. In Ref. [4], using the CNDO model, dipole moments, π-electron densities on atoms, and bond lengths in the ground (S_0) and first excited (S_1) singlet states were calculated. Also, the authors of Ref. [4] suggested the enhancement of hydrogen bonds between the solvent and the lactone ring of the dye upon excitation. In Ref. [5], the hyperpolarizability of the C337 molecule and the dipole moment of its ground state were obtained using the PM3 method. The authors of Ref. [13] also calculated the dipole moments and the energies of vertical transitions by the AM1 approach. In Ref. [14], the energies of the six vertical electronic transitions were calculated at the B3LYP/TZVP/vacuum theory level.

Thus, the performed review of the literature shows that, despite the abundance of experimental data on the C337 optical properties, their theoretical study remains poor, especially for the aqueous environment. At the same time, the
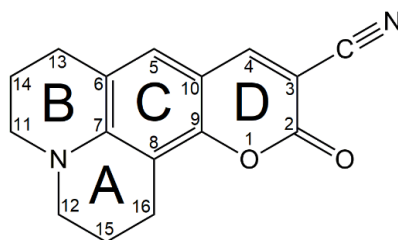

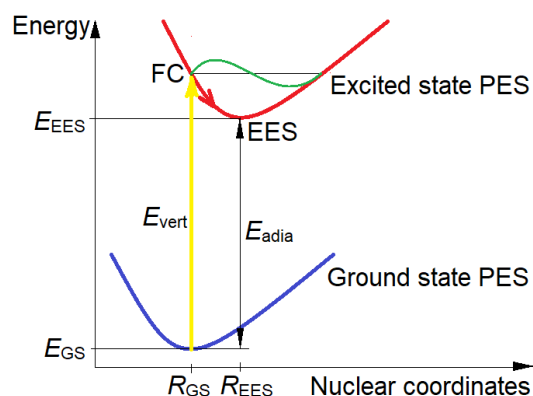**Figure 1.** Chemical structure of C337

Figure 2. Energetic diagram of vibronic transition

unique property of C337 to intensively fluoresce in a water medium, which causes its biomedical applications, requires a detailed theoretical explanation. In addition to the implicit specification of the solvent, theoretical studies of photoexcitation of a dye in a solution also require analyzes of site-specific interactions (hydrogen bonds), as well as vibronic (rather than purely electronic) transitions. These two important aspects were considered separately by other authors for two other famous 7-aminocoumarins with a structurally rigidized 7-amino group in an aqueous medium – C102 (C480) [15-17] and C343 (C519) [18,19]. In the present work, we have applied these two approaches together in the analysis of the C337 excitation in an aqueous solution.

METHODS

For all calculations, the Gaussian 16 software [20] was applied. The aqueous media was described implicitly by the IEFPCM approach [21]. Water molecules forming strong H-bonds with the C337 molecule were specified explicitly (see below). Under the Franck-Condon principle [22], the electronic transition occurs at fixed nuclear coordinates R_{GS} of the ground state. In other words, this transition is vertical in the "nuclear coordinates-energy" diagram (Fig. 2).

Corresponding excited Franck-Condon (FC) state is non-equilibrium. This state activates the vibrations of the nuclear core (see Fig. 2, green wave). The solvent reaction for the FC state was modeled by a state-specific description [23]. Then, the dye relaxes into an equilibrium excited state (EES) by adjusting the nuclei following to an electron shell ($R_{GS} \rightarrow R_{EES}$, red arrow in Fig. 2). The aqueous environment relaxes also; the solvent reaction field of EES is given by the equilibrium solvation model [24]. The adiabatic energy term $E_{adia}=E_{EES}-E_{GS}$ is used (see Fig. 2). In this case, the adiabatic Hessian model was used: both PESs were calculated and the force constants are evaluated at the respective equilibrium structures (R_{GS} and R_{EES}, see Fig. 2) by harmonic approximation.

The vibronic absorption spectra of C337 were calculated by the time-independent DFT approach of Baiardi et al. [25] built into Gaussian 16. The 6-311++G (d, p) basis set recommended for excited states [26] was used. Unfortunately, the experimental absorption spectrum of an aqueous solution of C337 is absent in the literature; only its maximum (λ_{max}=452 nm [4]) is known. However, our unpublished studies of other 7-amino-substituted coumarins (C314, C343, and C334) show that for them the best coincidence of the shape of the calculated absorption spectrum with the experimental one is achieved at a value of HWHM=900 cm^{-1}. Therefore, for the broadening of the bands of vibronic transitions in C337, the same value is adopted in this work. To broaden the calculated IR spectra, we used the HWHM=4 cm^{-1} value. The temperature T=298 K was used for simulations. The visualizations of the spectra and surfaces were performed by the Gaussview 6 software package [27].

RESULTS AND DISCUSSION

The investigation starts from the choice of a functional, which repeats most accurately the experimental absorption spectrum of C337 aqueous solution (λ_{max}=452 nm which is equivalent to E_{max}=2.74 eV [4]). It is known that E_{vert}, E_{adia}, and E_{vibron} (maxima of vibronic absorption spectra) depend on the X fraction of the Hartree-Fock exchange: with X rising, these three energies grow also [28,29]. The comparison with the experimental energy E_{max} should not be E_{vert} (as was for the C337 case in Ref. [14]), but E_{vibron} [18,30]. It is known from the theoretical works [4,5,13,14] that the C337 absorption spectrum in the visible range has one band of the singlet (HOMO→LUMO, $S_0 \rightarrow S_1$) transition of $\pi \rightarrow \pi^*$ type. As an initial probe, we used the most popular B3LYP functional (X=20%) [31]. However, it gave the E_{vibron}=2.71 eV value slightly underestimated compared with the experimental E_{max}=2.74 eV energy (Table 1). Therefore, after that, to achieve the best match, two other functionals with the same X value were applied, of which B3PW91 gave fine coincidence with the experiment (see Table 1). B3PW91 is a historically first hybrid density functional, which combines Becke exchange [32] with Perdew and Wang correlation [33]. Both components involve local densities and density gradients. The Becke part includes a single parameter that fits the exchange functional to accurate computed atomic data.
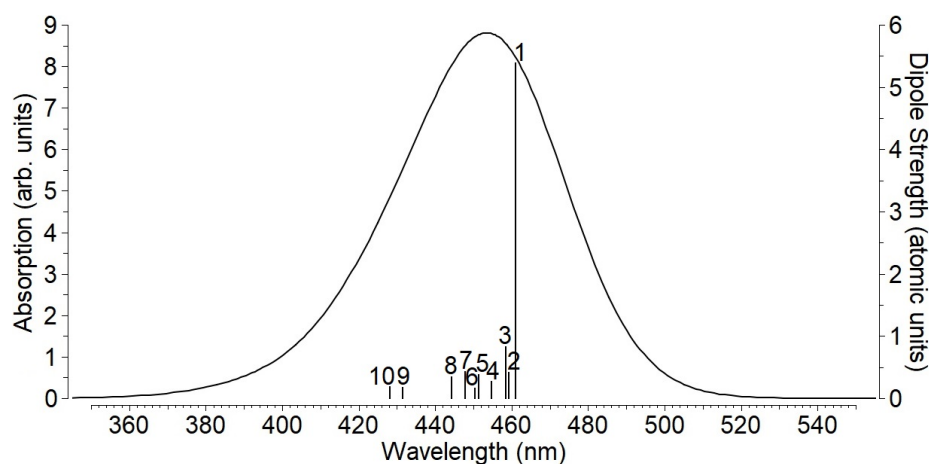
Figure 3. The vibronic absorption spectrum of C337 in an aqueous solution. Vertical sticks with corresponding numbers present vibronic transitions

The C337 spectrum calculated at the B3PW91/ (6–311++G (d, p)/IEFPCM theory level, is shown in Fig. 3. On it, vibronic transitions show themselves superfluous in that they give the short-wave slope, on which they are located, a greater flatness in comparison with the long-wave one. Water, being a highly polar solvent, smoothes vibronic bands.

However, in the experimental absorption spectrum of C337 in cyclohexane, they can be observed as individual peaks [11].

Thus, further analysis will be performed at the B3PW91/(6–311++G(d,p)/IEFPCM theory level. The coordinates of the C337 atoms in the GS and EES are presented in Table S2. The model of C337 vertical transitions in Ref. [14] gave underestimated (λ_{max}=373 nm at the B3LYP/TZVP/vacuum theory level) wavelength value calculated.

The calculations with an implicit specification of the water environment will be references to trace the influence of hydration on dye excitation. Five patterns of C337 H-bonds with waters were used in the present work following Ref. [15-17,34,35] for C102. Namely, bindings with the nitrogen atom of chromophore ("A" type), the carbonyl oxygen atom ("B" type), and the nitrogen atom of cyano group ("C" type) were considered. The "B" and "C" bonding types are possible with single or double waters. In the case of binding to each of these groups of two water molecules, we will designate them, respectively, "B1", "B2", "C1", and "C2" (Fig. 4).

The briefly structural description of C337 hydration complexes is the following. The endocyclic O1 atom of the lactone D ring is a hydrogen-bond acceptor but obstacles from the neighboring aliphatic hydrogens of the C16 atom (see atom numbering in Fig. 1) do not allow waters to bind with this oxygen. The H11 and H12 hydrogens block the water access to the N1 atom from the chromophore plane. However, the water bounds with an N1 atom situating over it ("A"-type H-bond). The water molecule bounded with the C337 carbonyl group (H-bond of "B" type) is located in the chromophore plane on the side of the C=O line. These features agree with Ref. [15] for C102. The water bound to the cyano group of the dye ("C" type) is in line with the C≡N bond (see Fig. 4). In the "B+C" complex, waters are situated in the chromophore plane. For the "2B+2C" complex, the angles between H-bonds connecting waters and dye carbonyl and cyano groups are 95° and 87°, respectively. In this case, all four water molecules, due to mutual steric obstacles, lie outside the plane of the dye chromophore, and a hydrogen bond is formed between two of them ("B2" and "C1", see Fig. 4).

The "A"-type H-bonds are cleaved when optimizing the excited state. This is explained by the electron density redistribution (see below) and agrees with Ref. [15] for C102. Therefore, their parameters for "A", "A+B", and "A+2B" hydrate complexes were calculated for the GS and FC only. However, "B"- and "C"-types H-bonds are strengthened due to excitation, which corresponds to their shortening (Table 2). This regularity is consistent with the assumption of other authors [4] about C337 hydration (see Introduction) as well as with Refs. [15-17] for C102. For the "2B" hydrated complex of C102 studied by the Monte Carlo simulation [35], one H-bond between the water molecule and the carbonyl group was much more stable than the other. Following our results, the strengths of "B1" and "B2", "C1" and "C2" bonds are close to each other (see Table 2). It is consistent with Ref. [16] for C102. The introduction of additional water molecules weakens the original hydration H-bonds (B1 vs. B, and C1 vs. C). Remember that B2 and C1 water molecules are also linked by H-bond (see Fig. 4). The hydrogen bond of the water molecule with the carbonyl group (B, B1, and B2) turns out to be somewhat stronger than with the cyano group (C, C1, and C2). The "A"-type H-bond is significantly weaker than the "B" and "C" types. It is also interesting to note that the addition of a bound "A"-type water molecule slightly weakens the H-bonds of "B" and "C" types ("A+B+C" vs. "B+C", and "A+2B+2C" vs. "2B+2C", see Table 2).

Table 1. Calculated energies for C337 excitation in aqueous solution

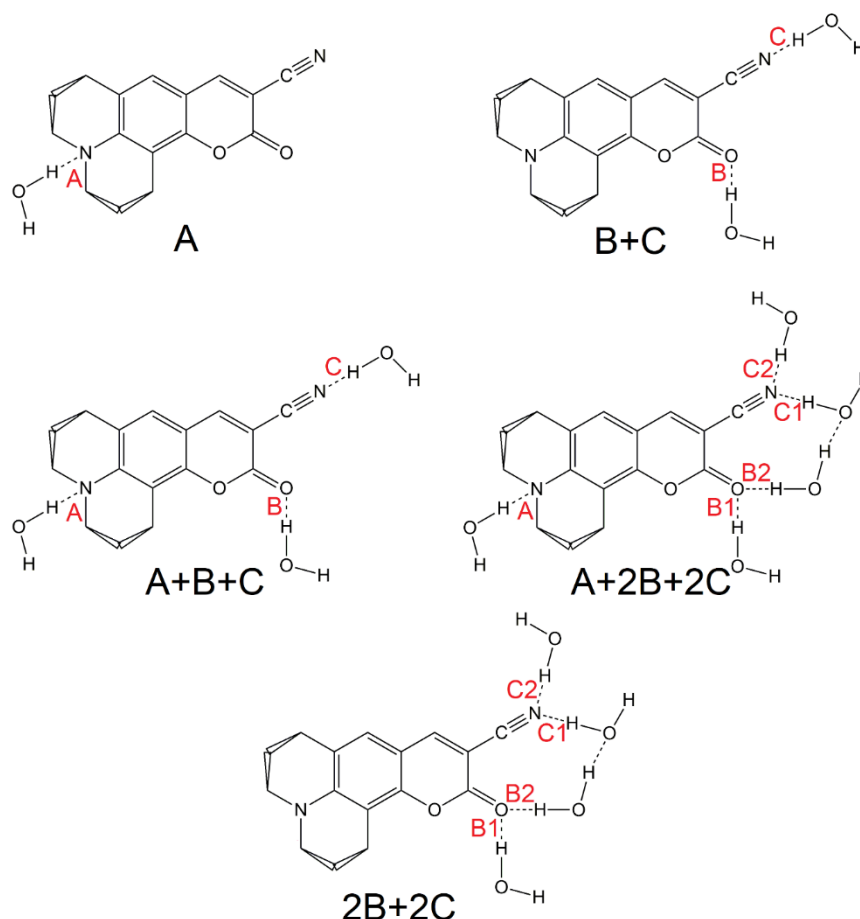| Hybrid functional	λ_{vert} (nm)	E_{vert} (eV)	λ_{adia} (nm)	E_{adia} (eV)	λ_{vibron} (nm)	E_{vibron} (eV)
B3LYP	406	3.05	446	2.78	457	2.71
B3P86	402	3.08	441	2.81	450	2.76
B3PW91	403	3.08	443	2.80	453	2.74

Figure 4. C337 hydrated complexes

Let us describe the influence of hydration on frontier Mos shown in Figs. 5 and 6. As seen in Fig. 6, the LUMOs are identical for a single C337 molecule and its hydration complexes. Wherein, LUMOs do not cover hydration water molecules. At the same time, HOMOs capture waters bound to the dye by the "A"-type. However, waters bound to the C337 by "B" and "C" types are not covered by HOMOs (see Fig. 5). The water molecule binding by "A" type leads to a short-wavelength shift, and by "B" and "C" types – long-wavelength one (Table 3). This agrees with cleavage of "A"-type H-bond which is energetically unfavorable, and, respectively, energetically favorable strengthening of "B"- and "C"-type H-bonds due to excitation. A hypsochromic shift for the "A+B+C" complex in comparison with a single dye molecule occurs which agrees with Refs. [30,31] for C102.

Table 2. Lengths (distances between acceptor and donor atoms in Å) of H-bonds in hydrated C337 complexes

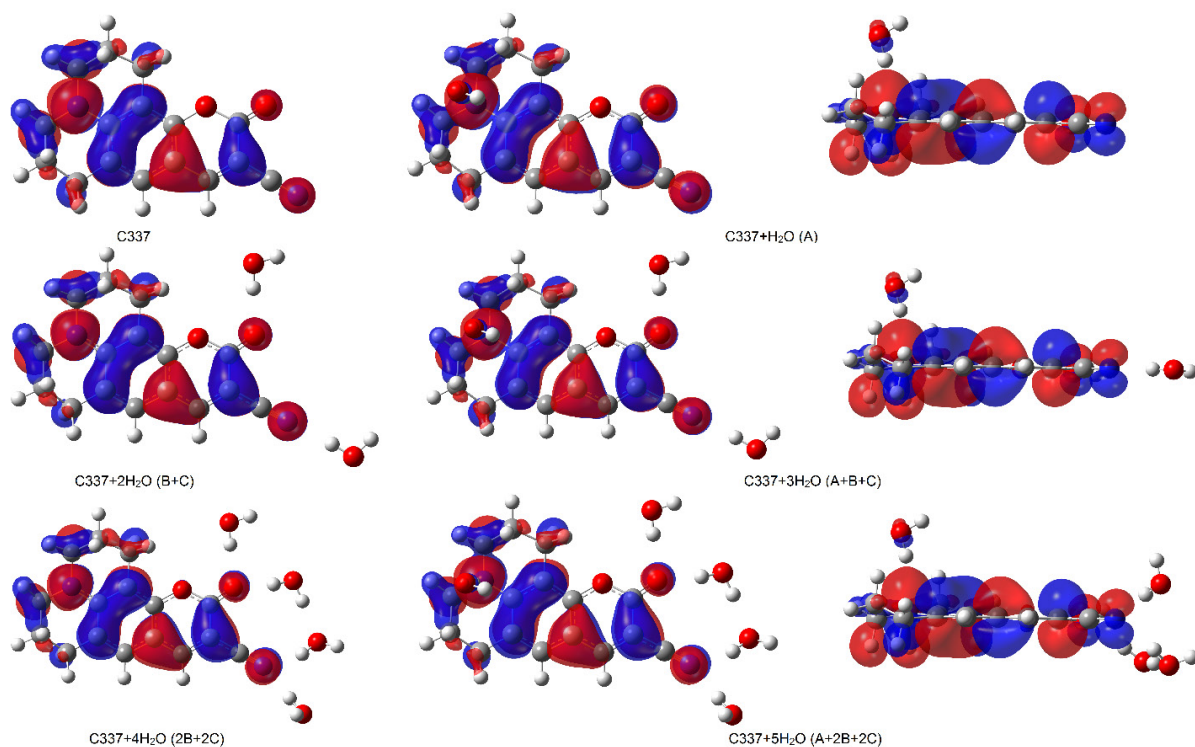| System	H-bond	Ground state	Excited equilibrium state
A		3.150	-
B+C	B	2.836	2.816
	C	2.942	2.935
A+B+C	A	3.186	
	B	2.845	-
	C	2.951	
A+2B+2C	A	3.263	
	B1	2.871	
	B2	2.959	-
	C1	2.988	
	C2	3.002	
2B+2C	B1	2.863	2.844
	B2	2.950	2.928
	C1	2.978	2.971
	C2	2.992	2.981

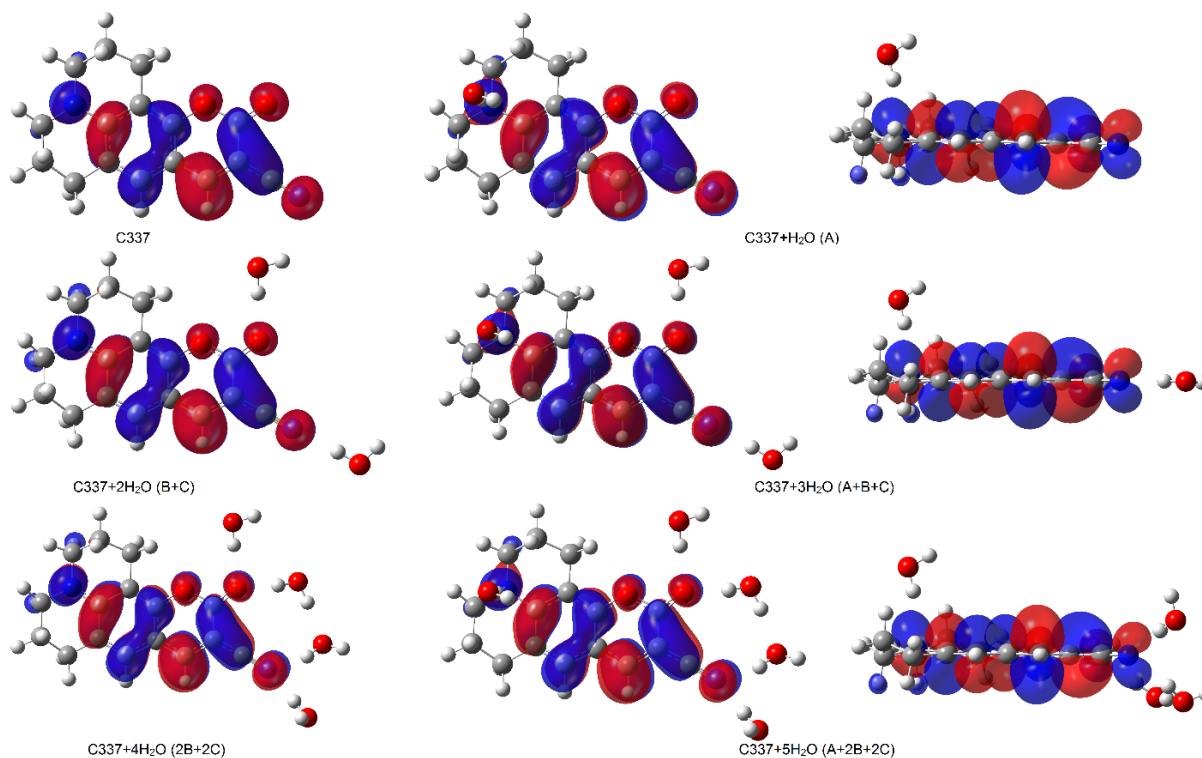**Figure 5.** HOMOs of a C337 and its hydrated complexes

Figure 6. LUMOs of a C337 and its hydrated complexes

Table 3. Calculated energies and wavelengths for excitations of single C337 dye and its hydrated complexes (B3PW91/(6–311++G(d,p)/IEFPCM theory level)

System	λ_{vert} (nm)	E_{vert} (eV)	λ_{adia} (nm)	E_{adia} (eV)	λ_{vibron} (nm)	E_{vibron} (eV)
C337	403	3.08	443	2.80	453	2.74
A (C337+H_2O)	395	3.14	-	-	-	-
B+C (C337+2H_2O)	405	3.06	446	2.78	457	2.71
2B+2C (C337+4H_2O)	408	3.04	449	2.76	459	2.70
A+B+C (C337+3H_2O)	400	3.10	-	-	-	-
A+2B+2C (C337+5H_2O)	404	3.07	-	-	-	-

The hydration does not influence the shape of the C337 absorption spectrum. Also noteworthy is the smaller number of vibronic transitions for the "2B+2C" complex compared to "B+C" (7 vs. 10). In addition, vibrations #2 and #3 involved in them are associated with the water molecules.

Analysis of calculated IR spectra of C337 and its hydration complexes allows the following conclusions to be drawn. In the ground state of a single C337 molecule, the most intense are the shear vibrations of the chromophore rings in its plane (#60, #77, #79, and #80). Upon excitation, they essentially weaken, as well as the carbonyl group's vibrations become the strongest. Due to excitation, the intensity of vibrations of the latter remains almost unchanged, and the intensity of compression-extension of the cyano group increases significantly. This pattern is also observed for the "B+C"-type complex. Water molecules bound to C337 introduce to the IR spectra their vibrations but they have almost no effect on the intensity of vibrations of the carbonyl and cyano groups with which they are bounded, reducing their frequency by $\Delta\nu\approx-50$ cm^{-1}. It is interesting to note that excitation has the same effect on these vibrations mentioned above: the vibrations of the water hydrogens involved in the H-bonds with the C337 carbonyl and cyano groups are much stronger compared to uninvolved ones. The "B2" and "C2" water molecules add in the IR spectra weaker corresponding vibrations compared with "B1" and "C1". Note that the "B2" and "C2" H-bonds themselves are weaker than "B1" and "C1" (see Table 2). The connection of two water molecules to the carbonyl group increases the intensity of their vibrations in the excited state as compared to the ground state. At the same time, the intensity of vibrations of the cyano group increases with the addition of the second water molecule bound to it. In this case, excitation has little effect on the intensity of vibrations of hydrogens of water molecules. The vibration of the "A"-type water hydrogen is essentially less intensive than by the "B" and "C" types. This regularity is shown also in Figs. S7 and S8, in which the hydrogen vibration of water molecule bound to the endocyclic nitrogen atom of the dye has significantly less intensity than in water hydrating its carbonyl or cyano groups. Note that in Ref. [10], when measuring the IR spectrum of the ground state of C337 in acetonitrile, the absorption band of the carbonyl group is in the range of 1690-1740 cm^{-1}, and that of the cyano group is 2220-2250 cm^{-1}, which is in good agreement with our calculated IR spectra.

The electron density distribution was described by Mertz-Kollman charges [36] of non-hydrogen atoms. Let's analyze the atomic charges of a single dye molecule. Fig. S12 shows that in the ground state C2, C9, and C31 are positively charged, while O1, O2, N3, and C3 atoms have negative charges. These atoms belong to the lactone D ring and carbonyl and cyano groups attached to it. During GS→FC excitation, the electron density shifts mainly from the C10 atom to the C4 nearest neighbor. Also, a weak shift from N1 to C5, C11, and C12 took place (Fig. 7). Therefore, the large-scale ICT [1], following our calculations, does not occur. Atomic charges change due to FC→EES relaxation in comparison with GS→FC excitation are slight ($q_{EES}-q_{FC}<0.08$ e).

The addition of explicit water molecules bound to C337 by "B+C" or "2B+2C" types, respectively, lead to noticeable changes in the dye atomic charges (ring D, carbonyl, and cyano groups) of the ground state compared to a single C337 molecule. Respectively, the photoinduced electron density redistributions for a single C337 molecule and its hydrate "B+C" and "2B+2C" complexes differ insignificantly from each other. Also, there is no noticeable photoinduced polarization of water oxygens and hydrogens involved in "B"-type H-bonds with the dye (Fig. 8). From Fig. 8 it can also be seen that the photoinduced redistribution of the electron density is local.

On the contrary, the binding of "A"-type water molecule significantly affects the charge of the endocyclic nitrogen atom and its C6 and C7 neighbors in the ground and excited FC states. Nevertheless, a slight decrease in the positive charge of the N1 atom upon excitation is sufficient to break the "A"-type H-bond of the water molecule with it (see above). The photoinduced changes in the atomic charges for other dye atoms in the "C337+H$_2$O (A)" system are almost the same as for a single dye molecule. The "A" water molecule is highly polarized upon GS→FC excitation (see Fig. 8). The "A+B+C" and "A+2B+2C" complexes combine parameters of "A", "B+C", and "2B+2C" systems described above.

The analysis of electron density distribution performed helps to explain the C337 dipole moments (Table 4). The dipole moment increases essentially upon excitation: $\mu_{GS}>\mu_{FC}\approx\mu_{EES}$. This feature is qualitatively consistent with the experimental result $\mu_{EES}=2.3\times\mu_{GS}$ of other authors [4], and with the C337 positive solvatochromism [4-8]. Ref. [5] gives the experimental $\mu_{GS}=10.2$ D and theoretical (PM3) $\mu_{GS}=9.20$ D values. Theoretical (AM1) calculations from Ref. [13] give $\mu_{GS}=9.68$ D and $\mu_{EES}=15.1$ D. Ref. [6] reports the experimental $\mu_{GS}=1.95$ D and $\mu_{EES}=5.97$ D values with the angle between them being $\varphi\approx2°$. In Ref. [7], $\mu_{GS}=1.8$ D and $\mu_{EES}=4.9$ D experimental values were obtained. According to our calculations, $\mu_{FC}\approx\mu_{EES}\approx1.5\times\mu_{GS}$. As can be seen, these values differ significantly from each other and are much less than
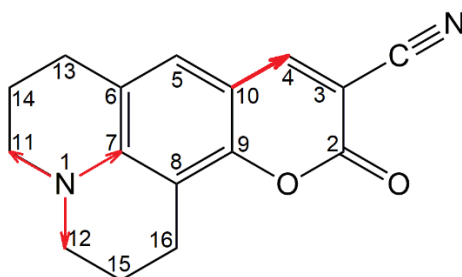

Figure 7. Electron density displacements upon GS→FC transition

C337+H₂O (A)

C337+2H₂O (B+C)   C337+4H₂O (2B+2C)
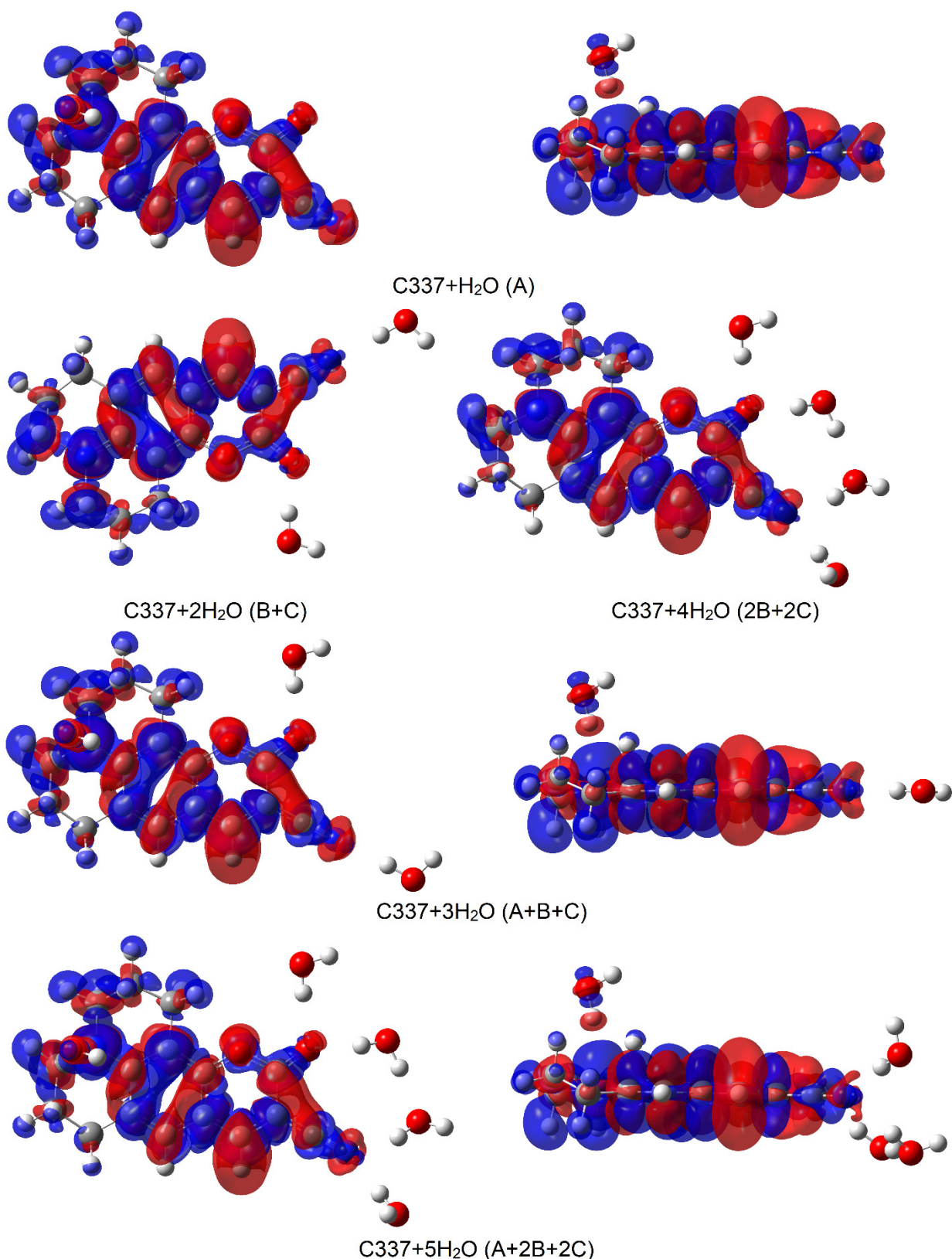
C337+3H₂O (A+B+C)

C337+5H₂O (A+2B+2C)

Figure 8. Electron density differences between Franck-Condon and ground states for hydrated complexes of C337

those obtained in this work (see Table 4). The μ is directed along with the BCD line in the GS, and in FC and EES ($\mu_{FC} \approx \mu_{EES}$) – at a $\varphi \approx 11°$ angle to it (see scheme inside Table 4). These μ changes are explained by the electron density displacement from the C10 atom to the C4 atom (see above). The transition dipole moment M is oriented along the C337 x-axis (see Table 4). Unfortunately, the M values for the C337 excitation from other authors lack.

Table 4. Calculated moments (D) of C337 in an aqueous media. Cartesian coordinate axes coincide with the main inertia axes of the molecule

Dipole moment	GS	FC	EES	Transition moment	
μ_x	-16.3	-24.7	-23.7	M_x	-8.75
μ_y	3.24	1.98	2.12	M_y	-0.346
μ_z	-0.540	-0.694	-0.548	M_z	-0.247
μ	16.6	24.8	23.8	M	8.76

CONCLUSIONS

Vibronic transitions and hydration were considered for theoretical investigation of the coumarin 337 excitation in aqueous media. The B3PW91/6-311++G(d,p)/IEFPCM theory level gives the vibronic absorption spectrum, which good consistent with the experiment. A single C337 molecule and its hydration complexes were considered. Waters attach to the endocyclic nitrogen atom ("A" type), the carbonyl ("B" type), and cyano ("C" type) groups. The hydrogen bond of the "B" type is somewhat stronger than the "C" type. The "A"-type H-bond in the dye ground state is essentially weaker than the "B"- and "C"-types ones. The addition of the water molecules ("2B and 2C" complexes) weakens the initial intermolecular H-bonds ("B" and "C" complexes). HOMOs cover waters bound by the "A" type. However, waters bound by the "B" and "C" types are not captured by HOMOs. Water molecules bounded with dye do not influence the shape of the C337 absorption spectrum. The binding of an "A"-type water molecule provides a blue shift, while "B"- and "C" types water – a redshift. Main electron density shift upon excitation took place from C10 to C4 neighboring atom. Therefore, ICT from one side of the molecule to the other does not take place. There are no noticeable photoinduced polarization of water oxygens and hydrogens involved in "B"- and "C"-types H-bonds with the dye. The "A" water molecule is highly polarized upon excitation. The absolute value of the dipole moment upon excitation increases approximately 1.5 times. At the same time, its direction along the line passing through the centers of the B, C, and D rings changes insignificantly.

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