Transition Energy, Spectral Fine Structure, and Absorption Coefficient of Norbixin (9’-cis-6,6’-diapocarotene-6,6’dioic acid) in Different Polar Solvents

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Abstract. Transition energy, spectral fine structure, and absorption coefficient of norbixin in different polar solvents has been investigated. Eight polar solvents were used for dissolving norbixin separately, including methanol, ethanol, propylene carbonate, acetone, dichloromethane, ethyl acetate, chloroform, and dimethyl carbonate. Spectra of norbixin in the resulting solutions were determined by UV-visible spectrophotometry at atmosphere condition. The effect of solvents on transition energy was analyzed according to Onsager cavity model and Hansen theory. The approximate absorption coefficient was determined with the Beer-Lambert law. The result show that the UV-visible absorption spectra of norbixin depend on the solvent. The greater the refraction index of the solvent and the norbixin-solvent dispersion interaction cause the transition energy of norbixin was smaller. The change in spectral fine structure has some relevance or correlation with the solvatochromic effect on π → π* transitions, the intermolecular interactions, and the S₂ state of norbixin. The absorbance of norbixin in various solvents, increased linearly with concentration.

Keyword: absorption, norbixin, spectrophotometry, transition energy.

1. Introduction

Annatto (CAS Number: 1393-63-1) is designated as E160b and has some common synonyms like C.I. natural orange 4, C.I. 75120, achiote, annotta, arnatto, Arnatto, arnotta, bija, rocou, roucou, roucouter, roucouter, orlean, orleanstraugh, terre orellana, beni-no-ki, urucu, urucum, or kesumba [1]. Annatto dyes are widely used in food and are finding increasing interest also for their application in the pharmaceutical and cosmetics industry. Bixin (methyl hydrogen 9’-cis-6,6’-diapocarotene-6,6’-dioate, C₂₅H₃₀O₄, Figure 1a) is the main non-polar pigment extracted from annatto seeds and accounts for 80% of the carotenoids in the outer coat of the seeds; norbixin (9’-cis-6,6’-diapocarotene-6,6’dioic acid, C₂₄H₂₈O₄, Figure 1b) being the water-soluble form of the bixin [2]. Oil-soluble bixin is generally used in fatty food applications, whereas norbixin, because of its ability to bind strongly with protein, is especially suited for the colouring of high protein content foods [3].

Figure 1a. Cis-bixin structure

Figure 1b. Cis-norbixin structure
The following three commercial processes have been applied to extract carotenoid pigment from dehydrated annatto seeds: indirect extraction with solvents, direct extraction using aqueous alkali solutions and direct extraction using oil. The oil extraction produces a dye that is primarily in the form of bixin. Aqueous alkali extraction saponifies the methyl carboxyester group of the bixin, producing norbixin as the principal natural dye [4,5]. Besides the traditional methods with variation of solvents at room temperature, some extraction techniques using soxhlet, microwaves, ultrasounds, supercritical carbon dioxide fluid and accelerated solvent extraction methods have also been investigated [6-11].

Furthermore, the analytical models for the determination of bixin and norbixin yield most frequently used are UV–visible spectroscopy and high performance liquid chromatography (HPLC). Various solvents have also been used as the mobile phases in HPLC analysis for the quantification of bixin and norbixin. This quantification is typically achieved by measuring the absorbance of stock solutions, and using the values obtained to calculate the concentration of bixin or norbixin. The values obtained with this approach are dependent on the absorption coefficient of bixin or norbixin in the solvents used [12-16].

We previously investigated the effects of aprotic solvents on the spectroscopic characteristics of bixin [17]. We reported that the UV–visible absorption spectra of bixin were found to be solvent dependent. The transition energy of bixin in solution was dependent principally on the refractive index of the solvents and the bixin–solvent dispersion interaction. The absorbance of bixin in various solvents, with the exception of hexane, increased linearly with concentration.

The information about λ max shifts is important to understand the modification of the transition energies of dyes in various solvents, whereas the absorption coefficient could be used as a diagnostic tool, particularly for estimations of total dyes concentration in a mixture or an extract. The value and changes in the spectral fine structure may potentially as an indicator of the intermolecular interactions of dyes with solvents, which have become important in further applications. These changes provide important information about the various physical and organic reaction of dyes, which have become important in various fields of pure and applied chemistry, such as solvent extraction and the purification of dyes, the design and synthesis of new sensitizers based on dyes for medicinal purposes (e.g. photodynamic therapy) and sensitizing dyes for solar cells [6,18].

Bixin and norbixin are responsible for the reddish-orange color of the annatto seeds and their extract due to their conjugated double bond system. Bixin and norbixin possess nine linear conjugated double bonds thereby making them to exhibit photo-protective effect [19]. However, though very similar, their chemical properties present differences activity in their applications. For this reason, here, we decided to investigate the effects of different polar solvents on the UV–visible absorption spectrum of norbixin.

2. Experimental Section
2.1 Materials
Annatto seeds obtained from West Kalimantan-Indonesia, potassium hydroxide, and hydrochloric acid. Solvents consisting of methanol, ethanol, propylene carbonate, acetone, cyclohexane, dichloromethane, ethyl acetate, chloroform, and dimethyl carbonate. All the solvents used were HPLC grade and were supplied by Sigma–Aldrich, Germany.

2.2 Instrumentation
UV-visible spectrophotometry (Shimadzu UV-1800) and Fourier Transform Infra Red (FTIR-Shimadzu).

2.3 Procedure
The first step was the preparation of norbixin from dry annatto seeds. Seeds were treated with the acetone and cyclohexane (2:3 v/v) under magnetic stirring for 6 hours at room temperature followed by solvent
removal, crystallization and drying. It contains several colored components, major is cis-bixin and a
minor colouring principle is trans-bixin [11]. In the next step of the process, aqueous alkali (5% w/v
potassium hydroxide) was added to the resultant powder which was then stirred for 6 hours at room
temperature, was filtered and acidified with concentrated hydrochloric acid a few drops slowly from
sides until pH 2 to precipitate norbixin. The precipitate was filtered, washed, dried, and milled to give a
granular powder. The resulting powder of norbixin was analyzed by UV-visible spectrophotometry and
FT-IR.

A double-beam UV–visible spectrophotometer was used to investigate the effects of different polar
solvents on the UV–visible absorption spectrum of norbixin. The absorption spectra was recorded over
a wavelengths 300–600 nm, at normal pressure and room temperature. Quartz cuvettes with a 1 cm path
length were used for measurements in solution. The estimated experimental error was 1 nm on the band
maximum.

A 10 mg/L stock solution of norbixin was prepared by dissolving a few crystals in solvent. Four dilutions
were then prepared, to give concentrations of 8, 6, 4, and 2 mg/L, respectively. All the experiments were
performed in a room with the lights turned off and the blinds lowered. The solvent effect on the transition
energy of bixin was analyzed with the Onsager cavity model and Hansen parameters, and an
approximate absorption coefficient was obtained with the Beer–Lambert law [17].

3. Results and Discussion

3.1 Norbixin analysis

Since norbixin and bixin possess nine linear conjugated double bonds and they differ only on one side
of the end group, their peak signatures of UV-Vis spectra are remarkably similar. The absorption
maxima of norbixin in acetone are expected at 429.0, 456.6, and 487.4 nm. However, The FTIR spectra
(Figure 2) show the difference between norbixin and bixin spectrum. For the norbixin, the H-C-H
bending vibration due to methyl and methylene groups at 2957 cm⁻¹, 2917 cm⁻¹, and 2850 cm⁻¹ are
absent. The ester group vibration at 1731 cm⁻¹, 1453 cm⁻¹, 1376 cm⁻¹, and 1182 cm⁻¹ are also not
observed. In stead, stronger carboxylic acid vibrations are observed in agreement with the structure of
norbixin. There are specific bands at 3421 cm⁻¹ for the -O-H stretching vibration of carboxylic acid, at
1718 cm⁻¹ for the C=O steching of carboxylic group, and at 1620 cm⁻¹ for the O-H bending vibration.
A band at 965 cm⁻¹ showed that the norbixin extracted in this study was trans-norbixin.

![Figure 2. FTIR Spectra of Norbixin and Bixin](image)

3.2 Solvent effect on the transition energy

As a common carotenoid, norbixin shows a three peak absorption curve in the visible spectral region in
polar solutions. There are three typical peaks that associate with the initial and final electronic states.
Figure 3 shows that a comparison of the UV–visible spectra of norbixin revealed a pronounced dependence on the solvent, a feature typical of the electronic absorption spectra of polyene compounds. Figure 3 show a strong absorption band corresponding to the transition energy from $S_0 \left(1^1A_g \right) \rightarrow S_2 \left(1^1B_u \right)$ that show two types of electronic transitions $\pi \rightarrow \pi^*$ and typical for carotenoid pigments [20]. The three structure peaks of carotenoids correspond to the three lowest vibration bands of the electronic transition $S_0 \rightarrow S_2$, which are called 0–0, 0–1 and 0–2 [21].

![UV–Vis Spectra of Norbixin in Different Solvents](image)

**Figure 3.** UV-Vis Spectra of Norbixin in Different Solvents

There are 7 additional conjugated double bonds in norbixin structure, with 4 alkyl substituents, and also substitution at position $\gamma$ and another at position $\delta$. According to the Woodward Fieser rule to calculate the absorption maximum of norbixin, the maximum absorption of norbixin should observed at a wavelength of 461 nm, without considering the solvents used. In solvent such as water, there will be a 8 nm wavelength shift, so the absorption maximum would change from 461 to 453 nm [22]. In this study, the absorption maximum of norbixin in different polar solvents are observed in wavelength range 472 to 454 nm.

In methanol and ethanol, it can be observed that there is a broadening on the absorption spectra of norbixin. This can be associated with the $S_2$ state ($1^1B_u$) couple with electrons in non-bonding orbitals from oxygen atoms in the carbonyl group that leads to band broadening. This non-bonding orbitals stabilized by the hydrogen bonds between solvent molecules and oxygen atoms in carbonyl groups and result in a shift of the $n\pi^*$ states to higher energy and broadening the absorption spectra [23]. Broadening of the spectra can also be associated with the dipole interactions between the solute-solvent molecules. The interaction between the transition dipole of solute and the permanent dipole of the solvent will facilitate the fluctuations of ground-state conformations along low-frequency molecular vibrational coordinates, therefore broadening the absorption spectrum [24].

Based on Table 1 it can be observed a bathochromic shift on the absorption spectra of the norbixin pigment as the solvent polarity increases. This can be associated with the excited state at the $S_0\rightarrow S_2$ transition is more polar compared to the ground state, the interaction of dipole-dipole with polar solvents
will decrease the energy at the excited state compared to the ground state. If polar solvents reduce energy in a ground state rather than an excited state, a hypsochromic shift will be observed [25].

Table 1. Physical constants of the solvents and parameters of the absorption spectra

| Solvent               | Onsager cavity model | Hansen parameters | Dipole Moment | 0-0 bands position |
|-----------------------|----------------------|-------------------|---------------|-------------------|
|                       | $R(n^2)$  | $R(\epsilon)$  | $\delta_D$  | $\delta_P$  | $\delta_H$  | $D$  | $\lambda$ (nm)  | $\upsilon$ (10$^3$ cm$^{-1}$) |
| Methanol              | 0.203     | 0.913            | 15.1         | 12.3         | 22.3         | 1.70 | 454              | 22.17          |
| Ethanol               | 0.221     | 0.887            | 15.8         | 8.8          | 19.4         | 1.69 | 455              | 21.98          |
| Propylene carbonate   | 0.252     | 0.954            | 20.0         | 18.0         | 4.10         | 4.90 | 464              | 21.55          |
| Dimethyl sulfoxide    | 0.284     | 0.938            | 18.4         | 16.4         | 10.2         | 3.96 | 472              | 21.14          |
| Acetone               | 0.220     | 0.872            | 15.5         | 10.4         | 7.00         | 2.88 | 457              | 21.88          |
| Dichloromethane       | 0.255     | 0.728            | 17.0         | 7.30         | 7.10         | 1.60 | 467              | 21.41          |
| Ethyl acetate         | 0.227     | 0.626            | 15.8         | 5.30         | 7.20         | 1.78 | 456              | 21.93          |
| Chloroform            | 0.267     | 0.565            | 17.8         | 3.10         | 5.70         | 1.04 | 471              | 21.28          |
| Dimethyl carbonate    | 0.226     | 0.412            | 15.5         | 3.90         | 9.70         | 0.91 | 456              | 21.93          |

a Value obtained from Ref. [24].
b Value obtained from the HSPiP application notes program.

The solubility of norbixin in different polar solvents and the interactions between solute molecules and solvents in this study are explained with Hansen Parameter theory. There are three types of interactions in organic compounds that can be analyzed based on this theory: (1) dispersion interactions ($\delta_D$), (2) permanent dipole-dipole interactions ($\delta_P$) and (3) hydrogen bonding interactions ($\delta_H$). The relation of $S_0\rightarrow S_2$ bixin transition energy and bixin-metal complex to the solvent physical constants: the refractive index function ($R(n^2)$) and the dielectric constant ($R(\epsilon)$) function are analyzed with the Onsager Cavity model theory [26-28].

Based on the Hansen theory parameters and Onsager cavity model (Figure 4) it can be observed that the electronic transition $S_0\rightarrow S_2$ of norbixin that responsible for the main absorption band is strongly dependence by the polarizability of the solvent, $R(n^2) = (n^2-1)/(n^2+2)$, where $n$ is refractive index of solvents. The transition energy of norbixin was lowest in dimethyl sulfoxide and the highest in methanol (Table 1). The transition energy being lower as the refractive index of the solvent increase. Dimethyl sulfoxide has the highest refractive index, while methanol has the lowest refractive index, as the refractive index value of the solvent increases from methanol to dimethyl sulfoxide, the $S_0\rightarrow S_2$ transition energy of norbixin will shift to a greater wavelength (batochromic shift). The refractive index of the solvent will affect the maximum absorption shift in the carotenoid pigments [29]. This can occur due to the dispersion interaction between the large dipole moment of the carotenoid and the solvent molecule [30].

Refractive index of the solvent will also strongly dependent on the dispersion interaction ($\delta_D$). In this study, norbixin also shows a linear relationship between the $S_0\rightarrow S_2$ transition energy and the dispersion interaction ($\delta_D$). Dispersion interaction in norbixin can occur due to the presence of polyene chain chromophores in their structure that may involved in this intermolecular forces. Based on Fig. 4 the
$S_0 \rightarrow S_2$ transition energy of norbixin decrease as the dispersion interaction ($\delta_D$) increases. The dispersion interaction of a molecule also governed by the density of the solvent. The dispersion interaction increases as the density of the solvent increase from methanol to chloroform (see Figure 4). This can be associated with the increasing amount of solvent molecules surrounding the solute (norbixin molecule) and therefore, the redshift of the absorption are observed [32].

![Figure 4](image)

**Figure 4.** Transition energies of norbixin against the physical constant of solvents: methanol (1), ethanol (2), propylene carbonate (3), dimethyl sulfoxide (4), acetone (5), dichloromethane (6), ethyl acetate (7), chloroform (8), and dimethyl carbonate.

### 3.3 Solvent effect on absorption coefficients of norbixin

As observed in Table 2 the variation of norbixin absorption coefficient is depending on polarity of solvent, nature of solvent and the solvent-solute interactions. The absorbance value and absorption spectra of compound will be affected by the environment of solvent molecules that surrounding the solute molecules. The highest absorption coefficient of norbixin are found in chloroform and acetone. In chloroform and acetone, the large batochromic shift (471 nm in chloroform) and (457 nm in acetone) was observed and increased absorbance, these probably due to best solubility and lack of aggregation of the norbixin pigment. As increasing the solubility of the solvent, the absorbance will also increase. According to Lambert-Beer’s law, there is a linear relationship between the molar absorption coefficient and the absorbance, the higher the absorbance, the higher the molar absorptivity. The increasing of absorption coefficient can also be caused by high polarity index of solvents [32]. The same result was
observed in studies by Scotter [33] who reported that norbixin has more affinity in polar organic solvents. The dicarboxylic acid in norbixin structure make its more polar than other apocarotenoid pigment such as bixin (oil-soluble pigment).

**Table 2.** Parameters for evaluating the validity of the standards and value of absorption coefficient of norbixin in different solvents

| Solvent             | Slope  | Intercept | Correlation Coefficient |
|---------------------|--------|-----------|-------------------------|
| Methanol            | 45.20  | -0.0013   | 0.9999                  |
| Ethanol             | 24.45  | 0.0837    | 0.9935                  |
| Propylene carbonate | 37.20  | -0.0003   | 0.9998                  |
| Dimethyl sulfoxide  | 60.31  | -0.0049   | 0.9994                  |
| Acetone             | 105.1  | -0.0015   | 0.9992                  |
| Dichloromethane     | 48.24  | -0.0004   | 0.9991                  |
| Ethyl acetate       | 33.23  | -0.0008   | 0.9996                  |
| Chloroform          | 137.6  | 0.0037    | 0.9999                  |
| Dimethyl carbonate  | 33.80  | 0.0020    | 0.9998                  |

Parameters for evaluating the validity of the standards in Table 2 shows the linearity of the analytical curves or correlation coefficient that greater than 0.99. Recent studies by Silva et al. [22] stated that in order to determine the absorption coefficient, the uncertainty estimation should be calculated. The linearity of the analytical curves must be equal to 1 or greater than 0.99 and percentage contribution of uncertainty for absorption coefficient (%U) should be less than 5% as an indication of accuracy in the result. The slope values in table 2 can be an estimate of the absorption coefficient of norbixin in different types of solvents. Of the solvents that used to determine the absorption coefficient of norbixin, methanol and acetone are solvents that have a comparative absorption coefficient value with the reported values in previous publications. Recent studies by Silva et al. [22] reported that in methanol the absorption coefficient values were 2896 at 452 nm and 2553 at 457 nm in acetone. The differences in values obtained in this study may be caused by the different sources of pigment and presence of degradation or residual product produced in extraction process. These values can be used as a reference and as a comparison of absorption coefficient values for norbixin in different polar solvents.

**3.4 Solvent effect on spectral fine structure of norbixin**

Besides the polarizability and the dispersion interaction ($\delta_D$) dependent $S_0\rightarrow S_2$ transition energy, we also noticed a large difference in the %III/II ratio or the spectral fine structure of the absorption spectra of norbixin with different polar solvents. The spectral fine structure is defined as the ratio of the height of the longest wavelength absorption peak (designated III) and that of the middle absorption peak (designated II), taking the minimum between the two peaks multiplied by 100 as a baseline [34]. Since the spectral fine structure is dependent on the number of conjugated double bonds and the chromophore in carotenoid pigments [29], the ratio of %III/II can be a diagnostic tool in the analysis of carotenoid absorption spectra.
As observed in Figure 5, solvent polarity also influences the spectral fine structure of norbixin. Typically, the spectral fine structure of carotenoid pigments is greater in solvents with low polarity than lower in solvents with high polarity [35]. In this study, we found that greater value of the spectral fine structure of norbixin (%III/II band ratio) is observed in acetone, dimethyl carbonate, and chloroform which has lower polarity than methanol and ethanol, which in this solvents a lower value of the spectral fine structure are observed. This is a good agreement with previous data in this study that shows good solubility of norbixin in acetone and chloroform based on the value of \(S_0 \rightarrow S_2\) transition energy and absorption coefficient.

Furthermore, the decreasing of %III/II band ratio in the presence of polar solvents i.e. methanol and ethanol compared with other solvents can be due to the broadening of the vibronic bands in these solvents (Figure 5). The change or decrease in spectral fine structure has some relevance or correlation with the solvatochromic effect on \(\pi \rightarrow \pi^*\) transitions, the intermolecular interactions, and the \(S_2\) state of carotenoid [36]. For this case in methanol and ethanol, the changes in spectral fine structures ratio may be attributed to hydrogen bonds and dipole interactions of these solvents with the norbixin. This interaction is apparently different from other solvents. We conclude that the value and changes in the spectral fine structure may potentially as an indicator of the intermolecular interactions of norbixin with solvents, which have become important in norbixin further applications.

4. Conclusions
Transition energy, spectral fine structure and absorption coefficient of norbixin are found to be solvent dependent. The \(S_0 \rightarrow S_2\) transition energy norbixin was lowest in dimethyl sulfoxide and the highest in methanol. Norbixin shows good solubility in organic polar solvents. Higher absorption coefficient of norbixin are found in chloroform and acetone. Based on the Onsager cavity model and Hansen parameter theory, the \(S_0 \rightarrow S_2\) transition energy of norbixin showed a linear relationship with the refractive index function \((R(n^2))\) and the dispersion interaction \((\delta_D)\). The greater value of the spectral fine structure of norbixin is observed in acetone, dimethyl carbonate, and chloroform which has lower polarity than methanol and ethanol, which in this solvents a lower value of the spectral fine structure are observed. The information about solvent effect on norbixin optical properties that present in this study can be used to determined and identify the best solvents that will be used in norbixin further application, such as solvent for extraction and purification, in the energy field as photosensitizers in solar cells.
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References
[1] Tennant D R, O’Callaghan M 2005 Third Int. Congr. Pigments Food Third Int. Congr. Pigments Food 38 911–917
[2] Siva R., Doss F P, Kundu K, Satyanarayana V S V, Kumar V 2010 Ind. Crops Prod. 32 48–53
[3] Satyanarayana A, Prabhakara R P, Balaswamy K, Velu V, Rao D G 2006 J. Food Serv. 17 1–5
[4] JFECFA 2002 Compendium of food additive specifications: addendum 10. Food & Agriculture Org.
[5] Vedavathy S 2003 Nat. Prod. Radiance 2 72–75.
[6] Nobre B P, Mendes R L, Queiroz E M, Pessoa F L P, Coelho J P, Palavra A F 2006 Braz. J. Chem. Eng. 23 251–258
[7] Cardarelli C R, Benassi M de T, Mercadante A Z 2008 LWT - Food Sci. Technol. 41 1689–1693
[8] Vasu S, Palaniyappan V, Kothandam H P, Badami S 2010 Pharm. Lett. 2 479–485.
[9] Van Chuyen H, Hoi N T N, Eun J B 2012 Int. J. Food Sci. Technol. 47 1333–1338
[10] Yolmeh M, Habibi N M B, Farhoosh Renge I, Sild E 2009 J. Chem. Phys. 155 319–324
[11] Rahmalia W, Fabre J F, Mouloungui Z 2015 Proc. Chem. 14 455–464
[12] Scotter M J, Wilson L A, Appleton G P, Castle L 1998 J. Agric. Food Chem. 46 1031–1038
[13] Scotter M J, Wilson L A, Appleton G P, Castle L 2000 J. Agric. Food Chem. 48 484–488
[14] Rodriguez-Amaya D B 2002 A Guide to Carotenoid Analysis in Food, ILSI Press, Washington.
[15] Noppe H, Abuin M S, Verheyden K, Van Loco J, Companyo B R., De Brabander H F 2009 Food Addit. Contam. Part A: Chem. Anal. Control Expo Risk Assess. 26 17–24
[16] Campbell R E, Boogers I A, Drake M A 2014 J. Dairy Sci. 97 1313-1318.
[17] Rahmalia W, Fabre J F, Usman T, Mouloungui Z 2014 Spectrochim. Acta. A. Mol. Biomol. Spectrosc. 131, 455–460
[18] Preston H D, Rickard M D 1980 Food Chem. 5, 4756
[19] Mathews-Roth M M, Wilson T, Fujimori E, Krinsky N I 1974 Photochem. Photobiol. 19, 217–222
[20] Christensen R L 1999 in Frank H A, Young A J, Britton G, Cogdell R J (eds) The Photochemistry of Carotenoids. Advances in Photosynthesis and Respiration, Vol 8. Springer International Publishing.
[21] Llansola-Portoles M J, Pascal A A, Robert B 2017 J. Royal Soc. Interface, 14 135
[22] Silva M G da, Garcia A L, Brito E S, Carvalho P R N 2018 Rev. Inst. Adolfo Lutz 77 1–8.
[23] Frank H A, Bautista J A, Josue J, Pendon Z, Hiller R G, Sharples F P, Gosztola D, Wasielewski M R 2000 J. Phys. Chem. B 104 4569–4577
[24] Liu W L, Wang D M, Zheng Z R, Li A H, Su W H 2010 Chin. Phys. B 19
[25] Yadav 2005 Organic Spectroscopy. Kluwer Academic Publishers.
[26] Hansen C M 2007 Hansen Solubility Parameters - A User’s Handbook (éd. Second Edition), CRC Press, Inc.,: Boca Raton FL
[27] Hansen C M 1988 Solubility Parameter Prediction of the Barrier Properties of Chemical Protective Clothing, ASTM STP 989. S.Z. Mansdorf, R. Sager, and A.P. Nielsen, Eds. Philadelphia,
[28] Onsager L 1936 J. Am. Chem. Soc. 58 1486–1493.
[29] Popova A V 2017 Comptes Rendus de L’Academie Bulgare Des Sciences 70 53–60.
[30] Renge I, Sild E 2011 J. Photochem. Photobiol. A: Chem. 218 156–161
[31] Liu W L, Zheng Z R, Dai Z F, Liu Z G, Zhu R B, Wu W Z, Li A H, Yang Y Q, Su W H 2008 J. Chem. Phys. 128 12
[32] Al Mohaiimed R M, Ansari A A, Aldwayyan A 2018 J. Spectrosc. 2018
[33] Scotter M 2009 Food Additives and Contaminants - Part A Chemistry, Analysis, Control, Exposure and Risk Assessment 26 1–21
[34] Britton G 1995 in Britton G, Liaaen-Jensen S, Pfander H (eds), *Carotenoids: Spectroscopy*, vol 1B. Birkhäuser Verlag : Basel, pp 13-63

[35] Britton G, Liaaen-Jensen S, Pfander H 2004, *Carotenoids: Handbook*, Springer Basel AG : Switzerland

[36] Macpherson A N, Gillbro T 1998 *J. Phys. Chem. A* 102, 5049–5058.