Solvent effect on the absorption and fluorescence of ergone: Determination of ground and excited state dipole moments

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ABSTRACT

The effect of solvents on the absorption and emission spectra of ergone has been studied in various solvents at 298 K. The bathochromic shift was observed in absorption and fluorescence spectra with the increase of solvents polarity, which implied that transition involved was π → π*. And the normalized transition energy value E(0) showed some scintillation when plotted versus Δε. The ground state and excited state dipole moments were calculated by quantum-mechanical second-order perturbation method as a function of the dielectric constant (ε) and refractive index (n). The result was found to be 1.435 D and 2.520 D in ground state and excited state respectively. And also, the density functional calculations were used to obtain the ground state and excited state dipole moments for it has proven to be suitable for calculating electronic excitation energy. And the result is consistent with the experimental.

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1. Introduction

In the clinical practice of traditional Chinese medicine (TCM), Polyporus umbellatus (Polyporaceae) is often used as anti-cancer and diuretic agent along with other crude drugs over a very long period of time [1]. Our previous experimental results have shown that ergosta-4,6,8(14),22-tetraen-3-one (ergone) is one of the main bioactive components of P. umbellatus [2–7]. Because there exist π-electron system in the molecule, so it may show optical property which is highly sensitive to its surroundings, it is reasonable to use it as a polarity probe and it also can be applied in medicine and chemistry. So, the multiple pharmacological activities of ergone make it worth carrying out a further comprehensive study on the physiopathological properties and was reported first.

It is well known that the molecular structure mainly determines the activity of the compound [8], and the insight about this can be obtained from its’ ground and excited state dipole moment values. And it has found that solvatochromatic due to the change of electronic distribution, which leading to higher dipole moment in excited state [9]. In general, changing the solvent is accompanied by a change in polarity, dielectric constant and change in polarizability of the environment. So, the change of solvent influences the ground state and excited state differently and a systematic analysis of the solvent effect is helpful in understanding the behavior of the excited state. And, solvatochromatic, to some extent, may be useful to detect the polarity of the surrounding medium.

The dipole moment of the ground and excited state is related to the electron distribution. Thus, the change of solvent affects the ground and excited state, respectively. So, it is important to study the dipole moments of ground and exited-state of the molecules for it offers information about the change in the electronic distribution on excitation. Besides, one can speculate that there exists electronic transition as π → π* from Fig. 1. It is known that π → π* bands show a red shift in the solvents with the increase of polarity and its opposite effect gives rise to a hypsochromic shift (blue shift) [10].

Until now, there are quite a few methods to be used, such as electronic polarization of fluorescence, electric-dichroism, microwave conductivity and stark splitting [11–13]. Among the numerous ways of determining excited state and ground state dipole moment, the solvatochromatic method, which depending on a linear correlation between the wave numbers of the absorption and fluorescence maxima and a solvent polarity function that including both dielectric constant (ε) and refractive index (n) of the solvents [14–16]. That is quite popular and simple. In the present paper, the above method was used to study the property of ergone.

2. Experimental

The standard of ergone (Fig. 1) was synthesized, and structure was characterized and compared with the data reported in
1. Methanol was recorded prepared the fluorescence method excited fluorescence polar different /ETBa 3. [19].

Results

In literature be trend out basis taken method without further purification. All the absorption spectra were recorded by UV–vis ratio recording spectrophotometer (Hitachi model U-2501) and the fluorescence spectra data was collected by fluorescence spectrofluorometer (Hitachi F-7000). All of the measurements were performed at room temperature (298 K). Double distilled water was used throughout the work. The solvatochromic method was used to calculate the dipole moment in ground and excited state. All calculations in the present study were performed using the Amsterdam Density Functional package (ADF) 2009.01 program [17]. Geometry optimization in the ground state was carried out using B3LYP density functional calculations [18], with the DZP basis sets (all-electron double zeta plus polarization function) [19].

3. Results and discussion

In order to analyze a polarizable dipole moment, many nonpolar, polar aprotic solvents were used to make the absorption and fluorescence spectra at room temperature. Absorption maximum was obtained around 332.4 nm in the case of nonpolar solvents, while in polar aprotic solvents it was about 348.2 nm in methanol. The general trend in the fluorescence spectra was a bathochromic shift with the increase in polarity, the emission maximum being 471.8 nm in methanol and 430.2 nm in cyclohexane. The pronounced results can be achieved from Fig. 2. Besides, quantum-mechanical second-order perturbation method was applied and the Onsager model was taken into consideration, the related equation as follows [17,20–22]:

$$ v_a - v_f = m_1 f(e, n) + \text{const} \quad (1) $$

$$ v_a + v_f = m_2 [f(e, n) + 2g(n)] + \text{const} \quad (2) $$

where $v_a$ and $v_f$ are the wavenumbers of the absorption and emission maxima respectively, $g(n)$ is the solvent polarity parameter and $f(e, n)$ are defined as follows:

$$ f(e, n) = \frac{2n^2 + 1}{n^2 + 2} \left[ \frac{e - 1}{e + 1} - \frac{n^2 - 1}{n^2 + 2} \right] $$

and

$$ g(n) = \frac{1}{2} \left[ \frac{n^4 - 1}{n^4 + 2} \right] $$

here $e$ is the dielectric constant and $n$ is the refractive index with

$$ m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} $$

and

$$ m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} $$

here $h$ denotes the Planck’s constant and $c$ is the velocity of light in vacuum. The parameters $m_1$ and $m_2$ can be calculated from the Eqs. (1) and (2), they are the slopes of the straight lines (Fig. 3A and B), and the values of $\mu_g$ and $\mu_e$ can be obtained from Eqs. (5) and (6) as [16]

$$ \mu_g = \frac{m_2 - m_1}{2} \left[ \frac{hca^3}{2m_1} \right]^{1/2} $$

$$ \mu_e = \frac{m_2 + m_1}{2} \left[ \frac{hca^3}{2m_1} \right]^{1/2} $$

and

$$ \mu_e = \frac{m_1 + m_2}{m_1 - m_2} \mu_g (m_2 > m_1) $$

The value of the solute cavity radius $a$ was calculated from the molecular volume by Suppan’s equation [23]

$$ a = \left( \frac{3M}{4\pi N} \right)^{1/3} $$

Here $N$ is the Avogadro’s number, $M$ is the solute’s weight and $\delta$ is the solid-state density of solute molecule. Then the dipole moment can be calculated by above parameters. Besides, according to Ravi et al. [24] the excited state dipole moment also can be obtained by following equation:

$$ v_a - v_f = 11, 307.6 \left( \frac{\Delta \mu}{\Delta \mu_B} \right)^2 \left( \frac{a^2}{a_0^2} \right)^3 E_N^N + \text{const} $$

**Fig. 2.** Absorption (B) and fluorescence spectra (A) of ergone in different solvents with increasing polarity.
Since the values of $\Delta \mu_d$ and $d_p$ are known (9 D and 6.2 Å) [25], $E_N^N$ is defined using water and tetramethylsilane (TMS) as extreme reference solvents with an equation [26]

$$E_N^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} = \frac{E_T(\text{solvent}) - 30.7}{32.4}$$

so the change in dipole moment is determined by

$$\Delta \mu = \left\{ \frac{81m}{(6.2/a)^3 \times 11.3076} \right\}^{1/3}$$

Table 1

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\epsilon$</th>
<th>$n$</th>
<th>$F_1$</th>
<th>$F_2$</th>
<th>$E_N^N$</th>
<th>$\nu_a - \nu_f$ (cm$^{-1}$)</th>
<th>$(\nu_a + \nu_f)/2$ (cm$^{-1}$)</th>
<th>$\nu_a$ (cm$^{-1}$)</th>
<th>$\nu_f$ (cm$^{-1}$)</th>
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<tbody>
<tr>
<td>Methanol</td>
<td>33.70</td>
<td>1.329</td>
<td>0.85995</td>
<td>0.6468027</td>
<td>0.762</td>
<td>7523.7051</td>
<td>24,957.27</td>
<td>28,719.13</td>
<td>21,195.42</td>
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<td>Ethanol</td>
<td>24.30</td>
<td>1.361</td>
<td>0.81205</td>
<td>0.651077</td>
<td>0.654</td>
<td>7338.6688</td>
<td>25,060.39</td>
<td>28,668.72</td>
<td>21,331.72</td>
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<tr>
<td>Propanol</td>
<td>20.60</td>
<td>1.385</td>
<td>0.76715</td>
<td>0.642039</td>
<td>0.617</td>
<td>7278.4905</td>
<td>24,997.64</td>
<td>28,616.88</td>
<td>21,358.39</td>
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<tr>
<td>Butanol</td>
<td>17.40</td>
<td>1.399</td>
<td>0.7491</td>
<td>0.653005</td>
<td>0.586</td>
<td>7183.6548</td>
<td>24,995.94</td>
<td>28,587.76</td>
<td>21,401.14</td>
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<tr>
<td>Pentanol</td>
<td>14.80</td>
<td>1.410</td>
<td>0.71579</td>
<td>0.629704</td>
<td>0.568</td>
<td>7181.6683</td>
<td>25,013.28</td>
<td>28,604.12</td>
<td>21,422.45</td>
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<td>Hexanol</td>
<td>13.00</td>
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<td>0.69108</td>
<td>0.62916</td>
<td>0.559</td>
<td>7190.0426</td>
<td>25,091.15</td>
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<tr>
<td>Heptanol</td>
<td>11.30</td>
<td>1.424</td>
<td>0.50252</td>
<td>0.53833</td>
<td>0.549</td>
<td>7160.202</td>
<td>25,122.54</td>
<td>28,702.64</td>
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<tr>
<td>Octanol</td>
<td>9.80</td>
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<td>0.23476</td>
<td>0.40841</td>
<td>0.537</td>
<td>7062.1189</td>
<td>25,138.67</td>
<td>28,669.72</td>
<td>21,607.61</td>
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<tr>
<td>Acetonitrile</td>
<td>36.64</td>
<td>1.344</td>
<td>0.86621</td>
<td>0.71818</td>
<td>0.460</td>
<td>7876.2027</td>
<td>25,753.11</td>
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<tr>
<td>Acetone</td>
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<td>1.359</td>
<td>0.79214</td>
<td>0.654534</td>
<td>0.355</td>
<td>7653.888</td>
<td>25,970.43</td>
<td>29,797.38</td>
<td>22,143.49</td>
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<tr>
<td>Benzene</td>
<td>2.28</td>
<td>1.501</td>
<td>0.00358</td>
<td>0.30007</td>
<td>0.111</td>
<td>6959.0009</td>
<td>26,300.13</td>
<td>29,779.63</td>
<td>22,820.63</td>
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<td>Cyclohexane</td>
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<td>0.000643</td>
<td>0.334155</td>
<td>0.006</td>
<td>6839.2335</td>
<td>26,664.62</td>
<td>30,084.24</td>
<td>23,245.00</td>
</tr>
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</table>
the value of dipole moment in the excited state is higher than the ground state. And the possible reason may be the charge transfer character of the excited state as has been reported in some articles [25,32–34].

4. Conclusion

The absorption fluorescence spectra of ergone exhibits solvatotchromic shift in the solvents studied, which consistent with the assignment of the transition to $\pi \rightarrow \pi^*$. And the solvatotchromic shifts of absorption and fluorescence spectra were used to calculate the ground and excited state pole moments of 1.435 D and 2.520 D respectively. And the TDDFT was also used to validate our results. It was found that conclusion is consistent with experimental.

Acknowledgements

This work was supported by the National Scientific Foundation of China (81001622) and As a Major New Drug to Create a Major National Science and Technology Special” from Ministry of Science and Technology of the People’s Republic of China (No. 2011ZX09401-308-34).

References