

Measurement of dipole moment of ethyl acetate

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I. INTRODUCTION

Molecules are not a solid object with fixed electrons on nuclei. Thus it is evident that when a extra electric field is exerted upon a molecule, the electrons will have a different series of wavefunctions according to the Schrödinger's equation.

The dipole moment μ can be defined as

$$\mu = \int \rho(\mathbf{r}) \mathbf{r} d^3\mathbf{r} \quad (1)$$

where $\rho(\mathbf{r})$ can be directly given by the norm of the wavefunctions. However, computational resources restrict the programs to obtain an explicit set of wavefunctions that can describe the system precisely. Density functional theory, or simply DFT, is mainly based on energy correction of the multiple electron system, cannot guarantee a satisfying result of the wave functions, which hinders obtaining a correct dipole moment derived from the method mentioned above. But hope is not lost. Considering the electric field as a perturbation, the energy of the system can be expanded in power series of electric field E , namely

$$H' = H'_0 + \frac{\partial H'}{\partial E} E + \frac{1}{2} \frac{\partial^2 H'}{\partial E^2} E^2 + o(E^2) \quad (2)$$

where H'_0 is the eigenvalue of the energy of the unperturbed system. The electric potential energy in a constant electric field is

$$U = - \int \rho(\mathbf{r}) d\tau (\mathbf{E} \cdot \mathbf{r}) = -\mu \cdot \mathbf{E} \quad (3)$$

When the electric field is in the same direction as the dipole moment, it can be found that

$$\frac{\partial H'}{\partial E} = -\mu \quad (4)$$

For a isotropic system polarized by a constant electric field, the induced dipole moment is approximately proportional to the electric field, namely

$$\mu_{\text{ind}} = \alpha \mathbf{E} \quad (5)$$

where α is defined as polarizability. For a anisotropic system, the polarizability should be defined as a two-dimensional tensor,

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \quad (6)$$

or simply

$$p_i = \alpha_i^j E_j \quad (7)$$

in Einstein's notation. With regard to (3), it is observed

$$U' = -\alpha \mathbf{E}^2 \quad (8)$$

thus

$$\alpha = -\frac{1}{2} \frac{\partial^2 H'}{\partial E^2} \quad (9)$$

In thermodynamics, the direction of the polar molecules is governed by the outer electric field. The direction follows the Boltzmann distribution, namely

$$P(\theta, \phi) d\theta d\phi = e^{-\alpha} e^{\beta \mu E \cos \theta} d\theta d\phi \quad (10)$$

where P represents the distribution probability function, α and β the constants. α can be regarded as a normalization coefficient, while β is equivalent to $1/kT$ in Boltzmann distribution. θ is the angle of μ deviated from the direction of electric field, and ϕ is the angle on the cross-section surface. Thus the observatory dipole moment is equal to the mean value of dipole moment over the distribution,

$$\langle \mu \rangle = \frac{\iint \mu \cos \theta e^{\beta \mu E \cos \theta} d\theta d\phi}{\iint e^{\beta \mu E \cos \theta} d\theta d\phi} = \frac{\int \mu \cos \theta e^{\beta \mu E \cos \theta} d\theta}{\int e^{\beta \mu E \cos \theta} d\theta} \quad (11)$$

with the consideration that the dipole moment is directed parallel to the electric field due to symmetry. This is an extraordinary integral. To give analytical result, the variable is replaced by

$$\begin{cases} z = e^{i\theta} \\ \cos \theta = \frac{z+z^{-1}}{2} \\ d\theta = ie^{-i\theta} dz = \frac{idz}{z} \end{cases} \quad (12)$$

thus

$$\begin{aligned} e^{\beta \mu E \cos \theta} &= e^{\beta \mu E (z+z^{-1})/2} \\ &= \sum_{n=0}^{\infty} \frac{(\beta \mu E)^n (z+z^{-1})^n}{2^n n!} \end{aligned} \quad (13)$$

The integrals are rewritten as

$$\langle \mu \rangle = \frac{\mu \oint_{|z|=1} \sum_{n=0}^{\infty} \frac{(\beta \mu E)^n (z+z^{-1})^{n+1}}{2^{n+1} n! z} idz}{\oint_{|z|=1} \sum_{n=0}^{\infty} \frac{(\beta \mu E)^n (z+z^{-1})^n}{2^n n! z} idz} \quad (14)$$

The integrals are determined by the residues in the area $|z| = 1$. It is easily observed that the odd point is $z = 0$, and the integrals are given as

$$\langle \mu \rangle = \frac{\sum_{n=0}^{\infty} \frac{(\beta \mu E/2)^{2n+1} C_{2n+2}^{n+1}}{(2n+1)!}}{\sum_{n=0}^{\infty} \frac{(\beta \mu E/2)^{2n} C_{2n}^n}{(2n)!}} = \frac{\mu I_1(\beta \mu E)}{I_0(\beta \mu E)} \quad (15)$$

where $I_n(z)$ represents the Bessel function, which is the solution for the differential equation

$$z^2 y'' + zy' - (z^2 + n^2) y = 0 \quad (16)$$

Expanding (15) in power series of μ , we obtain

$$\langle \mu \rangle = \frac{1}{2} \beta \mu^2 E - \frac{1}{16} \mu^4 (\beta^3 E^3) + \frac{1}{96} \beta^5 \mu^6 E^5 + o(\mu^7) \quad (17)$$

Taking the first term, we get

$$\langle \mu \rangle = \frac{\mu^2 E}{2kT} \quad (18)$$

which can be interpreted as the polarization of the system induced by the electric field.

For a system involving no mutual interaction, the molar polarizability can be given as

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho} \quad (19)$$

where M represents the molar mass, ρ the density of a substance. For very dilute solution, we can assume that the mutual interaction is very low. Considering that the dielectric constant as well as the density of the solution is linearly perturbed by the molar ratio of the solute,

$$\begin{cases} \varepsilon = \varepsilon_1(1 + \phi x_2) \\ \rho = \rho_1(1 + \psi x_2) \end{cases} \quad (20)$$

where ε, ρ stand for the dielectric constant and the density of the solution, and ε_1, ρ_1 for those of the solvent, and x_2 the molar ratio of the solute. Thus we have the molar polarizability of the solute in the infinite dilute solution

$$P_2^\infty = \frac{3\phi\varepsilon_1}{(\varepsilon_1 + 2)^2} \frac{M_1}{\rho_1} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \frac{M_2 - \psi M_1}{\rho_1} \quad (21)$$

In a electric field of high frequency, the dielectric constant of a transparent substance is determined by, neglecting difference of magnetic permeability,

$$\varepsilon = n^2 \quad (22)$$

where n is the refraction index. Thus

$$R_2^\infty = \frac{6n_1^2 M_1 \gamma}{(n_1 + 2)^2 \rho_1} + \frac{n_1^2 - 1}{n_1^2 + 2} \frac{M_2 - \psi M_1}{\rho_1} \quad (23)$$

where γ is the correction of first order of the refraction rate in series of molar ratio of solute. Assuming that the polarizability caused by eternal dipole moment does not contribute in a electric field of high frequency, we get

$$\mu/\text{deb} = \frac{3}{2} \sqrt{\frac{k}{\pi N_A}} \sqrt{(P_2^\infty - R_2^\infty)T} \times 10^{18} \quad (24)$$

TABLE I. Physical constants measured of ethyl acetate - cyclohexane solutions in different molar ratio of ethyl acetate

x	0	0.0522283	0.104286	0.159063	0.208204	0.291448
n	1.4234	1.4199	1.4164	1.4127	1.4097	1.4047
$\rho/\text{kg/m}^3$	868.116	870.102	872.576	874.769	876.701	881.51
ε	1.6327	1.78344	1.91083	2.03397	2.08068	2.31847

TABLE II. Result of calculation for ethyl acetate, where 'N/A' represents the failure to obtain stable structure.

dipole moment				
	gas		solution	
Structure	trans	cis	trans	cis
B3LYP	2.106818	4.625914	2.34267	5.221142
M06	2.071554	4.495996	N/A	N/A
M06-2X	2.058394	4.648344	2.285849	5.225078
Polarizability				
B3LYP	59.44233	59.77567	65.79000	66.23267
M06	58.56267	58.86867	N/A	N/A
M06-2X	57.36500	57.62100	63.41333	63.76300

II. METHODS AND PROCEDURES

A series of different molar ratio of ethyl acetate - cyclohexane solutions are obtained through weight measuring, each of which is subjected to refraction rate measurement using Abbe refractometer thermo-stabilized at 25 °C. The density is measured using density bottle. The dielectric constant is measured using small capacitance meter.

III. RESULTS AND ANALYSIS

Data obtained is shown in Table.I. The fitting result is

$$\begin{cases} \rho = 45.2279x + 867.817 & R^2 = 0.993958 \\ n = 1.42322 - 0.0644092x & R^2 = 0.999163 \\ \varepsilon = 2.33502x + 1.71614 & R^2 = 0.988258 \end{cases} \quad (25)$$

which leads to

$$\begin{cases} P_2^\infty = 6.96051 \times 10^{-5} \text{ m}^3/\text{mol} \\ R_2^\infty = 2.36925 \times 10^{-5} \text{ m}^3/\text{mol} \end{cases} \quad (26)$$

thus

$$\mu = 1.50 \text{ D} \quad (27)$$

which is smaller than that from the reference (1.78 D).

The deviation arises from several factors, including measurement errors that exist in the method, as can be seen from the mismatches of the data for pure cyclohexane. Several approximations for the deduction of the relation between dipole moment and external electric field are also responsible for the deficiency, as is given in the Introduction section. Further, some assumptions are still

questionable, including the validity of linear perturbation between physical constants and molar ratio, as well as the neglected margin effect of the capacitance. Thermostats may also fail to provide stabilized temperature due to non-zero gradient of temperature that can not be eliminated, as is discussed in former reports.

Calculation by Gaussian 16 is concluded in Table.II. The calculated dipole moment is much larger than that from the reference, which might be attributed to neglect of thermodynamic distribution. The vibrations of the bonds as well as interactions of ethyl acetate with solvents will result in a distributed occupation of energy states, each of which contributes differently to the dipole moment. Also the fact that density functional theory methods are still unable to give chemical accuracy still cast shades on the credibility of the result. Derivations of dipole moment in computational chemistry is based on

energy perspective, while experimental dipole moment is defined from charge distribution - such a difference might also result in the inconsistency of the results.

IV. CONCLUSION

Starting from derivations of the relation between dipole moment and electric field, the dipole moment of ethyl acetate is investigated from both experimental and computational methods, which fail to provide consistent result with the reference. Main reasons include the unsatisfying approximations and assumptions in the experimental method and neglect of thermodynamic effect in computational method.