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Analytical Dielectric Spectrum Formula Based on Representative Frequencies

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According to experimental data available for the complex refractive index of particular dielectrics, a dielectric spectrum formula is proposed by the least square fitting technique combined with selected natural frequencies. From the dielectric spectrum formula, the spectra of optical and dielectric constants can be obtained in the whole frequency region. Three dielectrics, water, ethanol, and toluene, are taken as examples. In the region where the experimental data are available, the spectra of the optical constants calculated by the formula are in good agreement with the real refractive spectrum obtained by Kramers-Kronig (K-K) transform and the experimental imaginary refractive spectrum. In the region where no experimental data are available, the extrapolation of our formula can make predictions. The merits of the present treatment are that we are able to get the uniform spectrum formula, without splitting into different frequency sections, and the analytical form of the dielectric spectra will be useful in the theoretical description of solvation dynamics.

Key words: Frequency, Least square fitting technique, Dielectric spectrum, Optical constant, Polarization

I. INTRODUCTION

Many important chemical or physical quantities, such as molar absorption coefficient, complex dielectric constant and complex molar polarizability, can be calculated with complex refractive index [1-6]. Integrated intensities that are used for the analysis of molecular properties can also be calculated indirectly [7-13], so determining complex refractive index accurately and conveniently is very meaningful. The imaginary refractive index can be measured by transmittance spectra [1-14], but unfortunately it is very difficult to get the real refractive index directly from experiments [14]. Generally, this quantity is obtained by the Kramers-Kronig (K-K) transform [1-14] from imaginary refractive indexes, and many researchers have adopted this method.

$$n(\nu_0) = n(\infty) + \frac{2}{\pi} \int_0^{\infty} \frac{\nu k(\nu)}{\nu^2 - \nu_0^2} d\nu$$

The K-K transform usually gives good results, and the errors are estimated to be below 0.5% in most of the experimental frequency region [7]. However this method is not convenient to get the optical constant or dielectric constant for an arbitrary frequency, even

if it falls into the region where experimental measurements can be made. Therefore, an analytical expression for the optical and dielectric constants will be helpful to extract the spectral information at a specified frequency. The development of such an analytical expression for dielectric is the central goal of the present work. With the experimental data of the complex refractive index $\tilde{n}(\nu)$, we make efforts to give the dielectric spectrum formula of some dielectrics in the analytical way using the least square fitting technique combined with the selected natural frequencies. Then the complex dielectric constant $\tilde{\epsilon}(\nu)$ and the complex refractive index are expressed as functions of the wavenumber (ν), so they can be calculated in the whole frequency region. At the same time, the value of χ_j , the j th component of the static polarizability, will provide an indicator for the polarization contribution from the vibration mode j of the dielectric. The dielectric spectrum formulas, optical constant spectrum and dielectric spectrum of water, ethanol and toluene are presented. Moreover, according to the value of χ_j , the relative contributions of different vibration modes to polarization are discussed.

II. METHODS

According to the dielectric theory [15], the complex dielectric constant is given by

$$\tilde{\epsilon}(\omega) = 1 + \frac{N q^2}{\epsilon_0 m} \frac{1}{(\omega_0^2 - \omega^2) - 2i\eta\omega} \quad (1)$$

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where ω and ω_0 are the angular frequencies of the electric field and the natural vibration respectively, η the damping coefficient of unit mass, m the equivalent mass of the vibrator, q the equivalent charge, and N the number of modules per unit volume. In the case of l vibration modes, we have

$$\tilde{\varepsilon}(\omega) = 1 + \sum_{j=1}^l \chi_j \frac{\omega_{0j}^2}{\omega_{0j}^2 - \omega^2 - 2i\eta_j\omega} \quad (2)$$

$$\chi_j = \frac{Nq_j^2}{\varepsilon_0 m_j \omega_{0j}^2} \quad (3)$$

being the static polarizability corresponding to the j th vibration. When $\omega=0$, $\tilde{\varepsilon}(\omega)$ reduces to the static dielectric constant

$$\varepsilon_s = \varepsilon(0) = 1 + \sum_{j=1}^l \chi_j \quad (4)$$

Therefore, the value of χ_j can be an indicator of the contribution from the j th vibration mode to the polarization. Since ω and η [15] have the same dimension, Eq.(2) can be converted to the following form,

$$\tilde{\varepsilon}(\nu) = 1 + \sum_{j=1}^l \chi_j \frac{\nu_{0j}^2}{\nu_{0j}^2 - \nu^2 - 2i\beta_j\nu} \quad (5)$$

where χ_j , β_j , and ν_{0j} are undetermined parameters and β_j has a meaning similar to η_j . Here ν_{0j} represents the j th vibration frequency of the dielectric. The parameters β_j and ν_{0j} have the same dimension as wavenumber ν which is regarded as the frequency of the external field. We call Eq.(5) the dielectric spectrum formula. We can rewrite the complex dielectric constant as [16]

$$\tilde{\varepsilon}(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu) \quad (6)$$

where $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ are the real and imaginary parts of the complex dielectric constant respectively. Comparing Eq.(6) with Eq.(5), we have

$$\varepsilon'(\nu) = 1 + \sum_{j=1}^l \chi_j \frac{\nu_{0j}^2(\nu_{0j}^2 - \nu^2)}{(\nu_{0j}^2 - \nu^2)^2 + 4\beta_j^2\nu^2} \quad (7)$$

$$\varepsilon''(\nu) = \sum_{j=1}^l \chi_j \frac{2\beta_j\nu\nu_{0j}^2}{(\nu_{0j}^2 - \nu^2)^2 + 4\beta_j^2\nu^2} \quad (8)$$

It is known that the complex dielectric constant is related to the complex refractive index $\tilde{n}(\nu)$ with [16]

$$\tilde{\varepsilon}(\nu) = \tilde{n}^2(\nu) \quad (9)$$

$$\tilde{n}(\nu) = n(\nu) + ik(\nu) \quad (10)$$

where $n(\nu)$ and $k(\nu)$ are the real and imaginary parts of $\tilde{n}(\nu)$ respectively. Combining Eqs.(6), (9), and (10),

it is easy to get

$$n(\nu) = \sqrt{\frac{1}{2} \left[\varepsilon'(\nu) + \sqrt{\varepsilon'(\nu)^2 + \varepsilon''(\nu)} \right]} \quad (11)$$

$$k(\nu) = \frac{\varepsilon''(\nu)}{2n(\nu)} \quad (12)$$

From Eqs.(4), (7), (8), (11), and (12), the relationships between parameters χ_j , β_j , ν_{0j} , and the experimental data $k(\nu)$, $n(\nu)$ and ε_s , can be established in Eq.(13). By taking a certain number of peak frequencies (natural frequencies) from the experimental spectrum of $k(\nu)$ and making use of the least square fitting technique, the minimum of the object function as given by Eq.(13) will give the values of the three parameters

$$O(\chi_j, \beta_j, \nu_{0j}) = \sum_{i=1}^{N_1} \left[\frac{\varepsilon''(\nu_i)}{2n(\nu_i)} - k'(\nu_i) \right]^2 + \sum_{i=1}^{N_2} [n(\nu_i) - n'_{\text{op}}(\nu_i)]^2 + \left(1 + \sum_{j=1}^l \chi_j - \varepsilon_s \right)^2 \quad (13)$$

In Eq.(13), $k'(\nu_i)$ and $n'_{\text{op}}(\nu_i)$ are the frequency-dependent experimental values of $k(\nu)$ and $n(\nu)$ respectively, and N_1 , N_2 , and l are the numbers of $k'(\nu_i)$, $n'_{\text{op}}(\nu_i)$, and the vibrational modes respectively. Please note that $n'_{\text{op}}(\nu_i)$ only takes values in the optical frequency region.

At the beginning of fitting, the peak frequency must be taken as the initial value of parameter ν_{0j} . In the low frequency region where the values of ν are close to zero, ν_{0j} represents the rotational frequency. In the far-infrared or infrared region, ν_{0j} corresponds to the intermolecular or intramolecular vibrations. In those regions, the peak positions of $k(\nu)$ are readily determined and usually a natural frequency is taken from a peak. If the peak is very weak, it may be neglected. But, in the ultraviolet region, the $k(\nu)$ spectrum exhibits a flat feature and ν_{0j} corresponds to electronic mode, with more spectrum lines appearing, so several natural frequencies may be taken from a peak. We choose a few representative frequencies within the ultraviolet region, according to the experimental $k(\nu)$ spectrum. If $k(\nu)$ spectrum is not available in the low frequency region or in ultraviolet region, the initial value of ν_{0j} should be presumed. We know that there are a great number of natural vibrations in condensed matter. If we take a sufficiently large number of natural frequencies, the dielectric spectrum formula can be fitted to a form of enough accuracy in the region where experimental data of $k(\nu)$ are available. However, we have to find a balance between the accuracy and the number of natural frequencies. In our experience, tens of representative frequencies can give

an acceptable accuracy for our problem. That is to say, we only use a small number of frequencies in the fitting. We can imagine that the more the natural frequencies are adopted, the higher the fitting precision is. Of course, the initial values of β_j and χ_j have to be set too. We roughly take the value of $\beta_j = \nu_{0j}$ but the value of χ_j is proportional to the peak value of $k(\nu)$ at ν_{0j} . In the region where experimental data are not available, they are also presumed by intuition. In fitting, we at first keep ν_{0j} invariant but adjust β_j and χ_j . After iterations, the values of β_j and χ_j will be considerably modified, and may be quite different from the initial values. At the same time, the value of object function in Eq.(13) becomes very small. Finally we let all three parameters ν_{0j} , β_j , and χ_j change and the iterative process continues until the value of $O(\chi_j, \beta_j, \nu_{0j})$ converges to a threshold. The fitting shows that the change of ν_{0j} is small and the converged values of β_j and χ_j are insensitive to their initial values with a given set of ν_{0j} .

Adopting the above method, three solvents, water, ethanol, and toluene, are taken as examples. From the experimental data at $T=25^\circ\text{C}$, their dielectric spectrum formulas, the fitted curves of refractive index spectrum and the dielectric spectrum were worked out.

III. RESULTS AND DISCUSSION

A. Water

The ε_s of water is 78.2977 at $T=25^\circ\text{C}$. From the data of Ref.[<http://www.philiplaven.com/Segelstein.txt>], 1261 digital points of $k'(\nu)$ were picked out in the range from $\nu=1.8837 \times 10^{-2}$ to $1.8837 \times 10^5 \text{ cm}^{-1}$. Meanwhile, 151 digital points of $n'_{\text{op}}(\nu)$ are obtained in the optical frequency region of 1.4285×10^4 - $2.5 \times 10^4 \text{ cm}^{-1}$ [17]. In practice, we have found that a very limited number of representative frequencies can give excellent fitting results for the dielectric spectra. In the case of water, according to $k(\nu)$ spectrum of water and the method mentioned above, 13 natural frequencies are taken in the whole region. We apply Eq.(13) to this case, and the three parameters χ_j , β_j , and ν_{0j} are fitted and listed in Table I.

Making use of the parameters given in Table I, we can calculate $\varepsilon'(\nu)$, $\varepsilon''(\nu)$, $n(\nu)$, and $k(\nu)$ of water with Eqs.(7)-(12). The obtained $n(\nu)$ and $k(\nu)$ are plotted in Fig.1. In contrast, the results of $n(\nu)$ obtained by Kramers-Kronig transform and the experimental data $k'(\nu)$ (Ref.[<http://www.philiplaven.com/Segelstein.txt>]), and $n'_{\text{op}}(\nu)$ [17] are also shown. The results of $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ of water from the present work are plotted in Fig.2.

In the fitting process, the determination of parameter χ_j requires particular attention. The important information, which is the relative contributions from different forced vibrations to polarization in the presence of external electric field, can be judged approxi-

TABLE I Fitted values of χ_j , β_j , and ν_{0j} in dielectric spectrum formula of water at 25°C .

j	ν_{0j}	β_j/cm^{-1}	χ_j/cm^{-1}
1	6.1	57.63	72.6308
2	127.5	487.34	1.8396
3	176.4	182.28	1.2497
4	542.7	334.23	0.5908
5	705.3	229.18	0.1529
6	1641.4	90.63	0.0170
7	3298.9	201.75	0.0402
8	3446.6	178.84	0.0233
9	66002.8	4287.45	0.0340
10	87321.5	15348.30	0.1155
11	108948.0	24027.20	0.2592
12	140332.0	37724.60	0.2314
13	199107.0	71176.40	0.1302

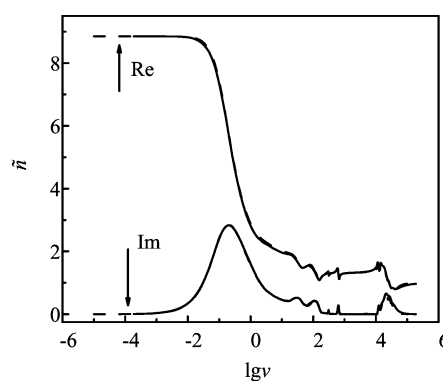


FIG. 1 Optical constant of water. Dashed curves: fitted $k(\nu)$ and $n(\nu)$, solid curves: original $k(\nu)$ and $n(\nu)$ from Ref.[<http://www.philiplaven.com/Segelstein.txt>] and Ref.[17], dot-dashed curve: original $n'_{\text{op}}(\nu)$.

mately in terms of χ_j , as is mentioned above in Section II. From Table I, the natural frequency ν_{01} falls in the region of the rotational frequency of a single water molecule, which is responsible for the orientational polarization. Summing over the values of χ_j in whole region gives a value of $\sum_{j=1}^{13} \chi_j = 77.3046$, and the ratio $\chi_1 / \sum_{j=1}^{13} \chi_j = 0.9395$. This reflects the fact that orientational polarization is dominant for polar solvents. Moreover, it seems that the natural frequencies ν_{02} - ν_{05} should be responsible for the intermolecular vibrations, such as, the hydrogen bond between the water molecules. We can see that ν_{02} - ν_{05} fall in the far-infrared region. The ratio $\sum_{j=2}^5 \chi_j / \sum_{j=1}^{13} \chi_j$ takes a value of 0.053017, which indicates a very small contribution from the intermolecular vibrations to the whole polarization. Obviously, the natural frequencies ν_{06} - ν_{08} mea-

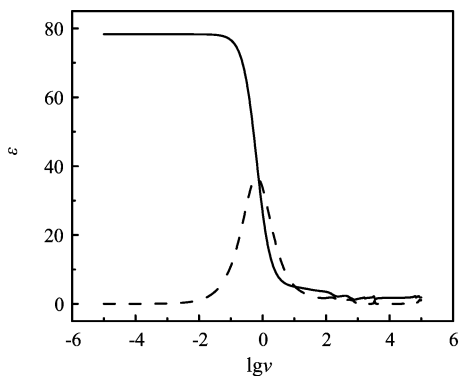


FIG. 2 Dielectric spectrum of water. Solid curve: $\varepsilon'(\nu)$, dashed curve: $\varepsilon''(\nu)$.

sure the three characteristic vibration frequencies of water molecule. Although also in the infrared region, the sum of χ_6 - χ_8 accounts for an even smaller proportion among the total polarizability when we have a look at the ratio of $\sum_{j=6}^8 \chi_j / \sum_{j=1}^{13} \chi_j = 0.00104$. This means that the intramolecular vibrations contribute less to the infrared polarization than the intermolecular vibrations of water. Such phenomena have been found in some solid dielectrics. For example, in the case of ice, Bertie reported that about three-quarters of the infrared contribution to the refractive index are caused by the translational lattice vibrations and about 15% by the rotational vibrations, while the O-H stretching that absorbs very strongly contributes a relatively small part [18].

Moreover, it is seen that the intermolecular and intramolecular vibrations of water contribute in total a fraction of 0.054057 to the static dielectric constant. We can thus safely separate the polarization into only two parts, orientational and electronic, ignoring the "atomic polarization", for the polar solvents. But for the crystal case, the orientational motions should be negligible owing to the rigid structure. Hence the static dielectric constant will be expected to have a small value. In such cases, the contribution fraction from the atomic polarization should not be neglected.

The natural frequencies ν_{09} - ν_{013} are the vibration frequencies due to the electron motion, which correspond to electron polarization. The sum of $\sum_{j=9}^{13} \chi_j$ gives a value of 0.7703. This predicts an optical dielectric constant of 1.7703 at 25 °C, if we take the analogue of Eq.(4) and consider only the electronic polarization.

B. Ethanol

The static dielectric constant of ethanol at $T=25$ °C is $\varepsilon_s=24.3$. The digital points of $k'(\nu)$ are available in two regions: 371 points in the infrared region of

TABLE II Fitted Values of χ_j , β_j , and ν_{0j} in the dielectric spectrum formula of ethanol at 25°C.

j	ν_{0j}	β_j/cm^{-1}	χ_j/cm^{-1}
1	0.5	24.73	20.9874
2	16.3	380.97	1.4492
3	912.2	28.06	0.0008
4	942.6	26.68	0.0079
5	1084.5	13.69	0.0056
6	1095.2	4.77	0.0029
7	1113.3	10.45	0.0063
8	1166.4	24.44	0.0212
9	1189.5	13.56	0.0084
10	1450.9	18.26	0.0013
11	1466.6	41.08	0.0042
12	2820.2	25.11	0.0016
13	2890.4	126.58	0.0145
14	2926.9	22.95	0.0003
15	2990.6	39.32	0.0016
16	58400.0	23948.82	0.7795

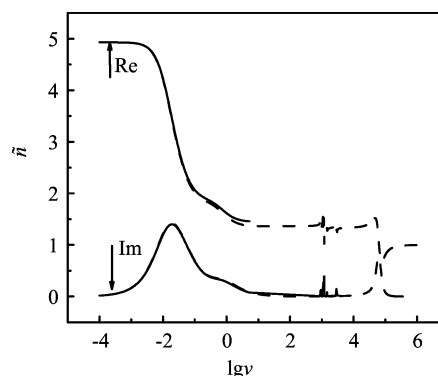


FIG. 3 Optical constant of ethanol. Dashed curves: fitted $k(\nu)$ and $n(\nu)$, solid curves: original $k(\nu)$ and $n(\nu)$ from Refs.[19,20], dot-dashed curve: original $n'_{op}(\nu)$.

$848 < \nu < 3544.9 \text{ cm}^{-1}$ [http://202.127.145.134/scdb/irs/IRS_Draw.asp?ID=15307.1] and 237 points in the low frequency region (10^{-4} - 5.25 cm^{-1}) [19]. Moreover, 151 digital points of $n'_{op}(\nu)$ are adopted in the optical frequency region of 1.4285×10^4 - $2.5 \times 10^4 \text{ cm}^{-1}$ [20]. In this case, we make use of the method introduced in Sec. II, and adopt 16 natural frequencies. With Eq.(13), the three parameters χ_j , β_j , and ν_{0j} were fitted and are presented in Table II.

In a similar way, the $\varepsilon'(\nu)$, $\varepsilon''(\nu)$, $n(\nu)$, and $k(\nu)$ of ethanol can be calculated by Eqs. (7), (8), (11) and (12) with these parameters given in Table II. $n(\nu)$ and $k(\nu)$ are plotted in Fig.3. For comparison, the results of $n(\nu)$ obtained by Kramers-Kronig (K-K) transform [19] and the experimental data $k'(\nu)$ [19] and $n'_{op}(\nu)$ [20] are also shown in the same figure. The results for $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ of ethanol by the present work are plotted in

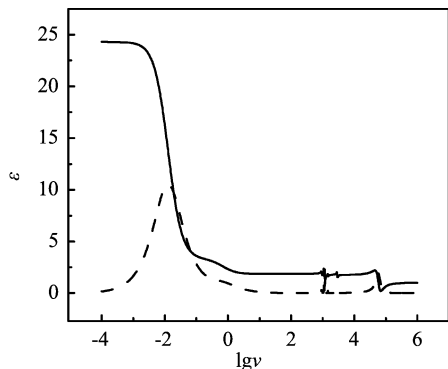


FIG. 4 Dielectric spectrum of ethanol. Solid curve: $\varepsilon'(\nu)$, dashed curve: $\varepsilon''(\nu)$.

Fig.4 .

From Table II, a similar analysis as water can be made for ethanol. Seen from the ratio of $\chi_1 / \sum_{j=1}^{16} \chi_j = 0.9077$, the orientational polarization is still dominant. Furthermore, we see that the vibration frequency of $j=2$ is much lower than the other vibration frequencies ($j=3-15$) in the whole infrared region, so this frequency should also be classified as the orientational mode. In our fittings, although only one representative frequency, $\nu_{0,16} = 58400 \text{ cm}^{-1}$ is taken for the high-frequency vibrations because of the lack of experiment data, it still produces a rational fitting for the optical dielectric constant, that is, $\varepsilon_{\text{op}} = 1 + \chi_{16} = 1.7795$. In order to get better fitting result, it is necessary and reasonable for the presumption of one or two initial ν_{0j} , if $k(\nu)$ spectrum in ultraviolet region is not available.

C. Toluene

In the case of toluene, the static permittivity is $\varepsilon_s = 2.3792$ at 25°C . From the data of Ref.[21], 15692 points of $k'(\nu)$ are picked out in the range from 434 cm^{-1} to 8000 cm^{-1} , and those absorptions with the value of $k'(\nu)$ smaller than 0.0015 are neglected. Thus only 2922 points which are in the region of $434-4000 \text{ cm}^{-1}$ were used. On the other hand, 151 digital points of $n'_{\text{op}}(\nu)$ are obtained in the optical frequency region ($1.4285 \times 10^4 - 2.5 \times 10^4 \text{ cm}^{-1}$) [20]. Similar to water and ethanol, we adopt 18 natural frequencies in the case of toluene. With Eq.(13), the three parameters χ_j , β_j , and ν_{0j} were calculated and these are presented in Table III.

Through parallel manipulation, the ε' , ε'' , $n(\nu)$, and $k(\nu)$ of toluene can be determined by using Eqs.(7), (8), (11), and (12). The curves of $n(\nu)$ (see Eq.(11)) and $k(\nu)$ (see Eq.(12)) against the frequency are plotted in Fig.5, which allows comparison with the values of $n(\nu)$ obtained by Kramers-Kronig transform [21] and the experimental $k'(\nu)$ [21] and $n'_{\text{op}}(\nu)$ [20]. The

TABLE III Fitted values of χ_j , β_j , and ν_{0j} in the dielectric spectrum formula of toluene at 25°C .

J	ν_{0j}	β_j/cm^{-1}	χ_j/cm^{-1}
1	0.1	4.60	0.1886
2	464.0	4.05	0.0075
3	521.1	2.77	0.0001
4	694.1	4.56	0.0073
5	728.1	6.63	0.0204
6	895.6	5.74	0.0001
7	1029.9	5.79	0.0005
8	1043.7	13.94	0.0004
9	1080.9	8.39	0.0006
10	1379.2	6.31	0.0001
11	1459.9	29.15	0.0014
12	1495.4	4.63	0.0009
13	1604.2	5.45	0.0003
14	2921.9	18.94	0.0002
15	3027.0	15.61	0.0004
16	3061.1	12.61	0.0001
17	42107.4	16172.60	0.4618
18	99988.4	30005.30	0.6884

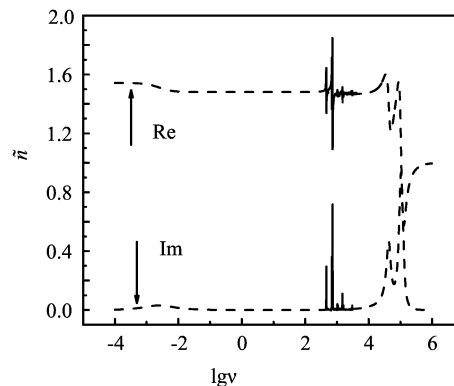


FIG. 5 Optical constant of toluene. Dashed curves: fitted $k(\nu)$ and $n(\nu)$; solid curves: original $k(\nu)$ and $n(\nu)$ from reference (see the text); dot-dashed curve: original $n'_{\text{op}}(\nu)$ which coincides with the fitted $n(\nu)$ curve.

results for $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ of toluene by the present work are plotted in Fig.6. From Table III we get $\sum_{j=17}^{18} \chi_j / \sum_{j=1}^{18} \chi_j = 0.83394$. This implies, unlike the polar solvents discussed above, the electronic polarization contributes the dominant part to the overall polarization. By taking the analogue of Eq.(4), the optical dielectric constant turns out to be $1 + \sum_{j=17}^{18} \chi_j = 2.1502$. This value is very close to the experimental value of 2.232 at 25°C .

Let us consider the case that ν falls in the far infrared region. Based on this presumption, only the atomic and

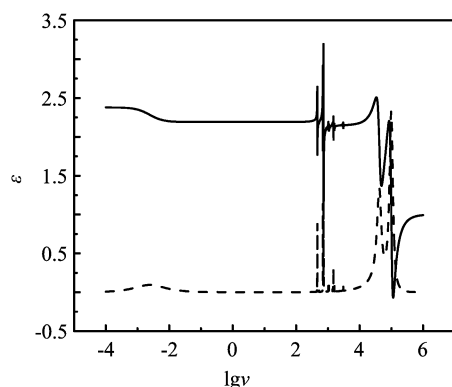


FIG. 6 Dielectric spectra of toluene. Solid curve: ϵ' , dashed curve: ϵ'' .

TABLE IV Optical and atomic-electronic dielectric constants estimated for water, ethanol and toluene at 25°C from the dielectric spectra formula fitted.

Medium	$\epsilon_{\text{atom-op}}$	ϵ_{op}
Water	5.6669	1.7703
Ethanol	1.8634 ^a	1.7795
Toluene	2.19016	2.1502

^a $\nu_{02}=16 \text{ cm}^{-1}$ more likely belongs to the orientational frequency, so χ_2 is classified to the orientational.

electronic polarizations happen. Thus we can predict an atomic-electronic dielectric constant [22] according to the fitted χ_j and taking the analogue of Eq.(4), *i.e.*,

$$\epsilon_{\text{atom-op}} = 1 + \sum_J^{\text{atom,op}} \chi_j \quad (14)$$

where the sign “atom, op” means that we only count χ_j that falls within regions of the vibrational and electronic frequency, with the orientational contribution excluded. The results for the three media mentioned above have been listed in Table IV. Quite different from the case of polar solvents such as water or methanol above, the apolar solvent *e.g.* toluene here will undergo a negligible orientational polarization, owing to the small permanent dipole of the molecule. Therefore, the continuum model behaves worse for apolar solvents.

Figures 1, 3, and 5 show that the results obtained with least square fitting technique combined with a small number of natural frequencies are fundamentally in agreement with original experiment results and the results by integrating method (K-K transform). This shows that the values of parameters are credible. With these parameters fitted, the dielectric spectrum can be expressed in a uniform analytical form as shown by Eqs.(5), (7), and (8), in the whole frequency region.

The differences for $n(\nu)$ from the present approach and from the K-K transform are found to be smaller than 0.01 in the region where experimental data are

available. We attribute the errors rising from our fitting to the following reasons. The first cause is probably the natural frequencies we take. Factually some very weak absorption peaks were neglected in our fitting, and strong absorption peaks were mainly taken into account. The second reason is probably that there is not enough experimental data.

IV. CONCLUSION

After the construction of the analytical dielectric spectrum formula of some dielectrics, $\epsilon'(\nu)$, $n(\nu)$, $\epsilon''(\nu)$, and $k(\nu)$ of the specific dielectric can be calculated by using Eqs. (7), (8), (11), and (12) in the whole region. In the region where the experimental data are available, our dielectric spectrum formula gives reliable results. In the region where the experimental absorption data are unavailable, our fitting is still valuable. For example, in the case of toluene, only the experimental data in the range of $434\text{--}4000 \text{ cm}^{-1}$ are adopted, while our fitted results are still applicable in the region of $4000\text{--}8000 \text{ cm}^{-1}$, and the values of $n(\nu)$ and $k(\nu)$ from our dielectric spectrum formula are still consistent with the values of original $n(\nu)$ and $k(\nu)$, as can be seen from Fig.5. So our dielectric spectrum formula can estimate the values of $\epsilon'(\nu)$, $\epsilon''(\nu)$, $n(\nu)$, and $k(\nu)$ in the regions where no experimental data is available. Although the prediction looks reasonable qualitatively, the accurate evaluation for these predictions can not be performed, due to the lack of experimental data.

Using some experimental data of complex refractive index, we propose a dielectric spectrum formula with least square fitting technique combined with a small number of natural frequencies in this work. The analytical dielectric spectrum formulas of water, ethanol, and toluene are constructed, and the optical constants and the dielectric spectra were acquired in the whole frequency region. Applying this approach to a specific dielectric, the analytical dielectric spectra formula can be obtained if its correlative experimental data are available. This method is expected valid for the solid matter, in which the orientational contribution will be negligibly small because of the rigid structure of the crystal.

With the analytical dielectric spectra formula, the dielectric constant of the dielectric in alternate electric field can be calculated conveniently, so our procedure may provide a tool for the dielectric properties and some related research, for example, the time-dependent Stokes shift. A merit of our method is that we can calculate the dielectric properties in the whole frequency region, without the splitting of the formula into several sections. Another merit is that we may attribute the specific static polarizability component to specific response frequency of the dielectric. In this way, the atomic-electronic and the optical dielectric constants can be calculated approximately as given in Table IV.

The relative contributions of different vibration modes to polarization, that is, the origins of polarization can also be analyzed. In future research, we will try to apply the fitted analytical dielectric spectra formula to the solvation dynamics.

V. ACKNOWLEDGMENTS

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