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Theoretical Study on Molecular First-Order Hyperpolarizability for Push–Pull Quinones: The Effects of Donor–Acceptor Pairs and Solvents

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The first-order hyperpolarizabilities ($\beta_{\rm vec}$) of a set of quinonoid derivatives with different donor and acceptor groups in gas-phase and in solution were calculated by the INDO/s method. The variations of $\beta_{\rm vec}$ with respect to the donor–acceptor strength gave an insight into the effects of donor–acceptor pairs and solvation. The mechanism of the solvent and the dependence of the strength of donor–acceptor pairs on $\beta_{\rm vec}$ values are interpreted by a two-level model. The results may provide guides on selecting donor and acceptor groups for synthesizing molecules with desired nonlinear optical (NLO) properties.

Conjugated organic molecules containing donor and acceptor groups are known to have large nonlinear optical responses due to the delocalization of π-electrons.[1,2] Extensive research efforts have already been devoted to the structure-property relationships both in theory and in practice.[3—10] One of the fundamental questions of interest is how the polarizabilities of these molecules vary with the donor–acceptor combinations, the bridge, and the medium. Previous studies[6,10] demonstrated that for a polyene bridge, there is an optimal combination of donor and acceptor groups that will maximize the first-order NLO polarizability (β).

Push–pull quinones, another class of organic π conjugated system with intrinsically large β, have not been extensively investigated for NLO applications. Lalama et al.[11] found that 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)imidazolidine (DCNQI) had an unexpectedly large negative β, and INDO/SCI calculations on the model system 7,7′-diamino-8,8′-dicyanoquinodimethane (DCNQA) supported their observation. As we know, donor and/or acceptor groups induce asymmetry of the electron charge distribution in the quinonoid molecule, and result in large NLO responses, while how donor and/or acceptor groups affect NLO responses for quinonoid molecules is still unknown. Therefore, a more detailed investigation is needed.

Recently, Ravi and Radhakrishnan[12] have observed several quinonoid molecules with large β. They apply an external electric field on the DCNQI molecule to mimic the effects of donor-acceptor pairs and solvents, and study their influence on β. However, the effect produced by an applied electric field may overestimate the effects produced by real donor–acceptor pairs or solvents.[13] So, in this paper, we use a series of donor–acceptor pairs instead of the action of a variable applied field on a definite molecule to induce and to compare the variation of β. Then the effect of solvent on β is also studied because in practice, how β change in different solvents has attracted much attention.[5,6]

Methods of Calculation

1. The Choice of Input Geometry. All calculations of molecular NLO properties should be implemented with an optimal representation of the chromophore structure. Input geometries of different sources have been adopted in some semi-empirical investigations.[9,14—17] As a result, there was evidence that hyperpolarizabilities calculated by ZINDO-SOS formalism in the gas phase[14,15] and in solution[16,17] based on MNDO-optimized geometries are in good agreement with the experimental data.

To confirm this, we have also done INDO/2 calculations on hyperpolarizabilities with AM1- and PM3-optimized geometries for a wide variety of aromatic and polyenic π-electron chromophores. We found analogously that they could all provide comparatively reliable results in comparison to experiments. For our purpose, we would solely adopt AM1-optimized geometries to implement INDO/2 calculations.

2. Calculation Method of Solvent Effect. The calculation of frequency dependent β by ZINDO-SOS formalism adopted in this paper was well discussed in references.[14—17] The solvent-induced β is computed on the basis of Onsager cavity theory,[18] done through the self-consistent reaction field (SCRF) scheme,[19] where transition energies in SOS formalism are adjusted by using the following relationship[16,20]

$$\hbar\Delta\omega_{\rm ng} = A\Delta\mu_{\rm ng}(\mu_{\rm n}+\mu_{\rm g}) + B\Delta\mu_{\rm ng}\mu_{\rm g}, \qquad (1)$$

here $\hbar\Delta\omega_{\rm ng}$ is the difference of transition energies on passing from gas phase to solution, $\mu_{\rm g}$ is the ground state solute dipole moment, $\mu_{\rm n}$ the excited state dipole moment, and $\Delta\mu_{\rm ng}$ represents $\mu_{\rm n}-\mu_{\rm g}$. A and B denote the reaction field factors for ground and excited states, and can be calculated by

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$$A = \frac{1}{a^3}\frac{n^2-1}{2n^2+1}, \quad B = \frac{2}{a^3}\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}, \tag{2}$$

here, ε and n_D stand for the dielectric constant and refractive index of the solvent, and a represents the cavity radius. In our study, carbon tetrachloride (CCl_4) ($\varepsilon = 2.24$, $n_D = 1.4601$) and acetone ($\varepsilon = 20.7$, $n_D = 1.3588$) are used as solvents.

In our calculations, 130 low-lying singly excited configurations are used as the basis set that was conventionally proposed to gain reliable β values.[15,16] After all 27 β_{ijk} components are obtained, the specific one, β_{vec} measurable via EFISH (electric-field-induced-second-harmonic generation) experiments[5] can be computed by

$$\beta_{vec}(-2\omega;\omega,\omega) = \sum_{j=1}^{3} \mu_i\beta_i / \parallel \mu \parallel, \tag{3}$$

where μ_i is the i th dipole component, $\|\mu\|$ is the norm of the dipole moment, and β_i is evaluated according to

$$\beta_i = \sum_j \beta_{ijj}. \tag{4}$$

The Strength of Donor–Acceptor Pairs

First, the strength of donor (or acceptor) groups should be well characterized. According to our previous work,[10] δ_D (or δ_A) is a good parameter to characterize the effectiveness of donor (or acceptor) groups. Here, δ_D and δ_A are calculated by AM1 scheme, in which δ_D stands for the energy difference between the calculated HOMO (highest occupied molecular orbital) of the donor-substituted-hexatriene as a model compound and that of hexatriene. Similarly, we have $\delta_A = E(\text{LUMO})_A - E(\text{LUMO})_P$ where $E(\text{LUMO})_A$ represents the lowest unoccupied orbital energy of the acceptor-substituted hexatriene.

In Table 1, ten donor groups numbered from D_1 to D_{10} with significantly separated δ_D values are listed in descending order. Similarly, acceptor groups numbered from A_1 to A_{13} are also selected with their δ_A tabulated. Then, we define δ_{DA} to be $\delta_D - \delta_A$ and use it to represent the strength of the donor–acceptor pair.

Upon adopting different combinations of these donor and acceptor groups, various push–pull chromophores are obtained. In Table 2, 20 selected donor–acceptor pairs are numbered one by one with δ_{DA} divided into nine sets in descending order with respect to the donor effectiveness, and within each set they are also arranged in decreasing order of acceptor effectiveness. The strongest pair symbolized by D_1–A_1 has the largest value of $\delta_{DA} = 4.46$ eV, while the least one $\delta_{DA} = 0$ eV refers to the unsubstituted species.

Table 1. Values of δ_D and δ_A for Donor and Acceptor Groups

	Donor	δ_D/eV		Acceptor	δ_A/eV
D_1	$NH(CH_2)_3NH$	1.26	A_2	$(SO_2Cl)_2$	−2.90
D_2	$(NH_2)_2$	1.05	A_3	$(SO_2F)_2$	−2.45
D_3	$O(CH_2)_3NH$	1.01	A_5	$(SO_2CN)_2$	−2.44
D_4	$NH(CH_2)_4$	0.97	A_5	SO_2CF_3	−1.92
D_5	$NH(CH_2)_2NH$	0.91	A_6	SO_2Cl	−1.89
D_6	$(Me)_2N$	0.91	A_7	$(CO_2H)_2$	−1.57
D_7	NH_2	0.81	A_8	$(CN)_2$	−1.39
D_8	MeO	0.45	A_9	NO_2	−1.34
D_9	Me	0.19	A_{10}	NO	−1.04
D_{10}	H	0.00	A_{11}	CHO	−0.79
			A_{12}	F	−0.26
	Acceptor	δ_A/eV	A_{13}	H	0.00
A_1	$(SO_2CF_3)_2$	−3.20			

Table 2. δ_{DA}, the Dipole Moments (μ) of 20 Donor–Acceptor Substituted Quinones in Gas Phase and in Solution (δ_{DA} and μ are in the units of eV and Debye).

No.	D	A	δ_{DA}	μ in gas	μ in CCl_4	μ in acetone
1	D_1	A_1	4.46	29.1	30.6	32.2
2		A_2	4.16	28.1	29.9	31.7
3		A_{13}	2.80	16.4	19.8	25.1
4	D_2	A_2	4.25	27.7	29.2	30.6
5		A_{10}	2.62	15.6	14.2	23.7
6	D_3	A_2	3.91	25.8	28.2	30.7
7	D_4	A_4	3.41	23.1	25.4	27.9
8		A_{12}	2.36	13.3	16.2	20.7
9	D_5	A_1	4.11	27.3	29.0	30.7
10	D_6	A_2	3.81	26.6	25.9	30.8
11		A_4	3.36	22.6	25.2	28.1
12	D_7	A_5	3.25	20.1	22.6	25.5
13		A_{10}	2.38	13.8	13.3	21.8
14		A_{13}	2.15	11.9	15.2	18.8
15	D_8	A_{12}	1.84	10.0	12.0	15.4
16		A_{14}	1.49	7.5	9.3	12.5
17	D_9	A_{14}	1.23	6.2	7.6	10.1
18		A_{16}	0.45	2.5	2.8	3.3
19	D_{10}	A_{15}	0.79	5.9	7.3	9.7
20		A_{17}	0.00	0.0	0.0	0.0

The strength defined by δ_{DA} is consistent with dipole the moments obtained from INDO/2 calculations. As indicated in Table 2, dipole moments of 20 donor–acceptor substituted quinones vary monotonously with the increasing δ_{DA} from 0 to the largest positive value either in idealized gas state or in solution, provided solvation has increased the dipole moments for all species in solvent, for example the calculated data in acetone are shown in the last column of Table 2.

β_{vec}, from the Gas Phase to Solution

The values of β_{vec} for 20 substituted hexatrienes tabulated in Table 2 have been calculated at an incident laser frequency of $\hbar\omega = 0.0$ eV in the gas phase and in solution (CCl_4 and acetone as solvents), respectively. The calculated β_{vec} are plotted with respect to δ_{DA} in Figs. 1(a), (b), and (c), providing information about how the first-order hyperpolarizabilities change with the donor–acceptor pair strength and solvation. Unlike the substituted polyenes,[5,6] most quinones have a negative β_{vec}. As we know, the chromophores with β_{vec} in either a positive or a negative sense are of interest for NLO activity, such as poled polymer application.[6,11]

In the gas phase, molecules with $\delta_{DA} = 0$ eV have zero β. This corresponds to the case of unsubstituted quinones. For one-sided donor- (acceptor-) substituted quinones, of which δ_{DA} fall in the range of 0 to 1.5 eV, only a minor NLO increase will occur in these molecules. For example, β_{vec}

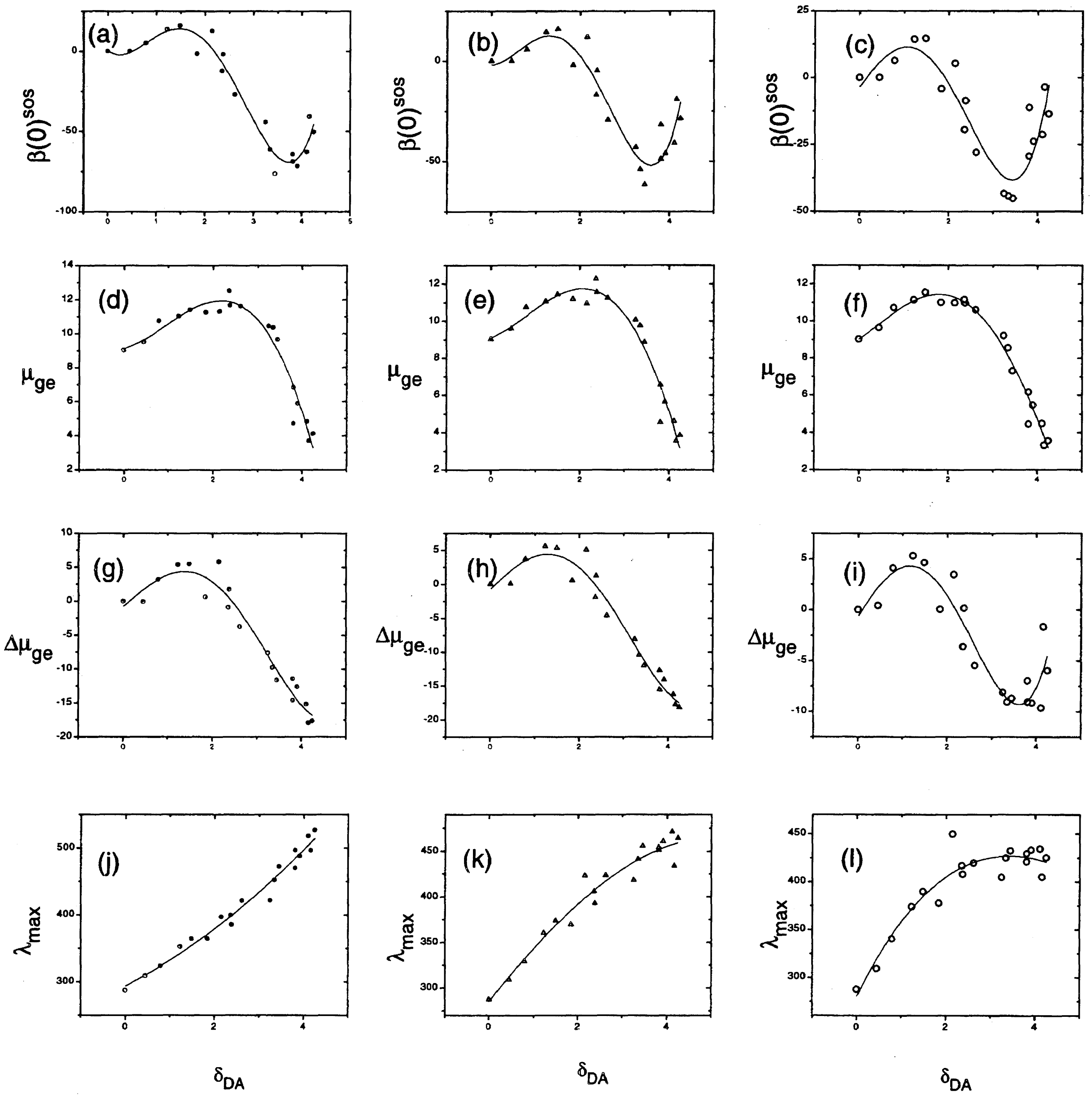

Fig. 1. The calculated $\beta(0)^{\mathrm{SOS}}$ in the gas phase (a), CCl_4 (b), and in acetone solvent (c) versus δ_{DA}. And the calculated μ_{ge} in the gas phase (d), CCl_4 (e), and in acetone solvent (f) versus δ_{DA}. And the calculated $\Delta\mu_{\mathrm{ge}}$ in the gas phase (g), CCl_4 (h), and in acetone solvent (i) versus δ_{DA}. And the calculated $\lambda_{\max}$ in the gas phase (j), CCl_4 (k), and in acetone solvent (l) versus δ_{DA}.

values for molecules $MeCHC(CH)_4CCHNO$ (**17** in Table 2, $\delta_{\mathrm{DA}} = 1.23$ eV) and $MeOCHC(CH)_4CCHNO$ (**16**, $\delta_{\mathrm{DA}} = 1.49$ eV) are only 13.7 and 16.0×10^{-30} $\mathrm{cm^5\,esu^{-1}}$.

In the interval of $1.5 < \delta_{\mathrm{DA}} < 4.2$ eV, β decreases with increasing donor–acceptor strength and reaches a negative peak at $\delta_{\mathrm{DA}} \approx 3.85$ eV. For instance, $O(CH_2)_3NHCC(CH)_4CC(SO_2Cl)_2$ (**6**) and $Me_2NCHC(CH)_4CC(SO_2Cl)_2$ (**10**) have large β_{vec} values of -71.8 and -68.9×10^{-30} $\mathrm{cm^5\,esu^{-1}}$, indicating that β_{vec} can be significantly increased by introducing an additional donor and/or acceptor substituent at the terminuses of the quinoid chain. According to our calculated results, the molecules with δ_{DA} falling into 3.2 to 4.1 eV may be the most suitable to provide candidates for large NLO responses. As the strength of donor-acceptor pairs increase further ($\delta_{\mathrm{DA}} > 4.2$ eV), the β_{vec} curve goes up.

Up to now, we have investigated the variation of β_{vec} versus the strength of the donor–acceptor pair in the gas phase. The solvent-induced β_{vec} in CCl_4 and in acetone solution are also calculated and plotted versus δ_{DA} in Figs. 1(b) and (c). As can be seen from Fig. 1, a similar trends occur in solution, i.e., β_{vec} increase to a peak value, then decrease through zero to become negative, finally β_{vec} increase.

However, curves are pushed down, then up in such a manner that β_{vec} decrease absolutely with their peak being shifted to the weaker donor-acceptor substituted species on passing from gas phase to solution. In the gas phase, the largest

$\beta_{\rm vec}$ (about 16×10^{-30} cm^5 esu^{-1}) appears at $\delta_{\rm DA}\approx1.50$ eV, while in CCl$_4$ solution, the peak of $\beta_{\rm vec}$ (about 13×10^{-30} cm^5 esu^{-1}) moves to a slightly smaller $\delta_{\rm DA}$ of 1.36 eV due to CCl$_4$ being relatively nonpolar. The peak of $\beta_{\rm vec}$ is further shifted to $\delta_{\rm DA}\approx1.15$ eV in acetone solution (about 10×10^{-30} cm^5 esu^{-1}) because the acetone solvent is of a polarity with larger dielectric constant. Similarly, on passing from gas phase to acetone solution, the region of negative peak $\beta_{\rm vec}$ is also shifted from $\delta_{\rm DA}\approx3.85$ through 3.60 to 3.45 eV. However, values of $|\beta_{\rm vec}|$ decrease from 71 through 50 to 38×10^{-30} cm^5 esu^{-1}. This implies, that, although it favors the relatively weaker donor–acceptor substituted chromophores to gain a larger first-order hyperpolarizability, polar media weaken the NLO response.

Two-Level Interpretation

We have simply described the variation of $\beta_{\rm vec}$ versus the strength of donor–acceptor pairs ($\delta_{\rm DA}$) in passing from gas phase to solvents. It is useful to discuss the mechanism of the solvent effect and the dependence of $\delta_{\rm DA}$ on $\beta_{\rm vec}$ values. In this section, the information on the two-level parameters, such as the transition energies ($E_{\rm ge}\propto1/\lambda_{\rm max}$), changes in dipole moment following excitation ($\Delta\mu_{\rm ge}$), and the dipole integrals associated with the transition ($\mu_{\rm ge}$) are provided and plotted versus $\delta_{\rm DA}$ in Figs.1(d)—(l).

According to the two-level model[3] (Eq. 5) as well as Fig. 1, the reason for the variations of $\beta_{\rm vec}$ could be interpreted well.

$$\beta_{\rm vec}\propto\Delta\mu\cdot{\mu_{\rm ge}}^2/{E_{\rm ge}}^2\propto\Delta\mu\cdot{\mu_{\rm ge}}^2\cdot{\lambda_{\rm max}}^2 \qquad (5)$$

In the gas phase, $\mu_{\rm ge}$ increases at first, reaches its peak value (11.9 D) at $\delta_{\rm DA}=2.16$ eV and then decreases rapidly, at $\delta_{\rm DA}=4.46$ eV it reaches about 3.3 D (see Fig. 1(d)). $\Delta\mu$ increases at first and reaches its peak value (about 4.4 D at $\delta_{\rm DA}=1.37$ eV) then decreases, through zero and becomes negative ($\Delta\mu=-16.8$ D at $\delta_{\rm DA}=4.46$ eV) (see Fig. 1(g)). While the maximal absorption ($\lambda_{\rm max}$) increases monotonically with the increasing $\delta_{\rm DA}$ (see Fig. 1(j)).

In the interval of $\delta_{\rm DA}=0.0$ to 2.0 eV, $\Delta\mu$, $\mu_{\rm ge}$ and $\lambda_{\rm max}$ are all positive, so $\beta_{\rm vec}$ take the positive sign. Considering the two-level model (Eq. 5), the peak of $\beta_{\rm vec}$ is located at $\delta_{\rm DA}\approx1.50$ eV, being dependent on the peaks of $\Delta\mu$, $\mu_{\rm ge}$, and $\lambda_{\rm max}$ curves. In the interval of $\delta_{\rm DA}=2.0$ to 3.85 eV, $\Delta\mu$ becomes to be negative, while the absolute values of $\Delta\mu$ increase. In addition, $\lambda_{\rm max}$ also increases. These factors leads to the increased $|\beta_{\rm vec}|$. As the donor–acceptor strength increases further, though $\Delta\mu$ and $\lambda_{\rm max}$ remain the previous variation trends, the values of $\mu_{\rm ge}$ drop sharply and fall to only 3.3 D at $\delta_{\rm DA}=4.46$ eV, offsetting the contributions on $\beta_{\rm vec}$ from $\Delta\mu$ and $\lambda_{\rm max}$, thus the $\beta_{\rm vec}$ curve goes up.

In the presence of CCl$_4$ solvent (Figs. 1(e), (h), and (k)), besides the decreased $\mu_{\rm ge}$, the blue shift of $\lambda_{\rm max}$ also leads to a rise of $\beta_{\rm vec}$. In a polar solvent, such as acetone, $\mu_{\rm ge}$ takes a similar trend as in the gas phase and in CCl$_4$ solvent, however $\lambda_{\rm max}$ blue-shifts obviously. Moreover, $\Delta\mu$ curve reaches its negative peak ($-$ 9.3 D) and then goes up, but the absolute values are much less than those in the gas phase (Fig. 1(i)). All these factors lead to a significant increase of $\beta_{\rm vec}$.

Donor–Acceptor Pairs And Two-Level Parameters

The above section describes the variation of β versus the strength of donor–acceptor pairs by using the two-level model. In this section, the reason of variation in $E_{\rm ge}$, $\mu_{\rm ge}$, and $\Delta\mu$ for the strength of donor and acceptor groups is discussed.

1. $\boldsymbol{\delta_{\rm DA}}$ and the Transition Energies. For most push–pull polyenes, the ground state dipole moments are larger than those of excited state, so the excited state will be stabilized in polar solvents, the absorption spectrum is red-shifted.[5] On the contrary, the absorption spectrum is blue-shifted in the case of push–pull quinones. As we know, for π-organic chromophores, the principal excited state is primarily composed of a HOMO–LUMO excitation.[7,24] Thus, analyzing the interaction between HOMO and LUMO may help us get a further understanding in the variation trend of transition energies. In Fig. 2, the changes in HOMO–LUMO gaps from the gas phase to acetone solvent (denoted as HOMO–LUMO$_{\rm (gas-acetone)}$) are plotted versus $\delta_{\rm DA}$. All the calculated HOMO–LUMO$_{\rm (gas-acetone)}$ are positive, indicating the increase in the transition energies and consequently, the blue shift of $\lambda_{\rm max}$.

2. $\boldsymbol{\delta_{\rm DA}}$ and $\boldsymbol{\Delta\mu}$. As in our previous work,[10b] we have studied the electron densities of the ground state and excited state in both gas phase and solution. In gas phase (see Fig. 1(g)), in the interval of $\delta_{\rm DA}=0$ to 1.5 eV, the increasing strength of donor–acceptor pairs will lead to more and more charge transferring from donor to acceptor group during the excitation, increasing the asymmetry of electronic distribution in the excited state. This results in a positive $\Delta\mu$. As the strength of donor–acceptor pairs increase further, more and more change is transferred from acceptor to donor group, leading to the decreased asymmetry of electronic distribution in the excited state, then, $\Delta\mu<0$. And Fig. 2 indicates that

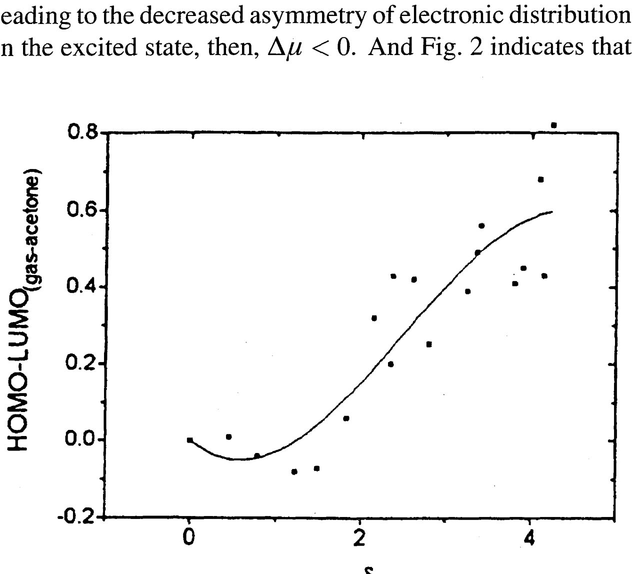

Fig. 2. The changes in HOMO–LUMO gaps from the gas phase to acetone solvent (denoted as HOMO–LUMO$_{\rm (gas-acetone)}$) versus $\delta_{\rm DA}$.

polar solvents stabilize the charge-separated state, so a polar medium favors the excited state of molecules substituted by weak donor–acceptor pairs, leading to the decreased dipole moments of the excited state, therefore $\Delta\mu_{ge}$ decrease from gas phase to solution. While for strong donor–acceptor substituted molecule, for example, $\delta_{DA} > 2.5$ eV, the ground state will be stabilized more in the presence of solvent, resulting in an increased $\Delta\mu$.

3. δ_{DA} and μ_{ge}. The transition dipole moment, μ_{ge}, is directly related to the oscillator strength f_{ge} and the transition energy $1/E_{ge}$, i.e. $\mu_{ge} \propto f_{ge}/E_{ge}$. When $\delta_{DA} < 2.5$ eV, increasing the strength of donor–acceptor pairs will increase the magnitude of charge transfer oscillator strength, resulting a increasing transition dipole moment. As the strength of donor and/or acceptor groups increase further, the electron transition becomes more and more difficult due to the strong coupling between the donor and acceptor groups, thus decreases the charge transfer oscillator strength and consequently decreases μ_{ge}. In polar medium, μ_{ge} obey the similar variation trend, but a polar medium favors the comparative weak donor–acceptor substituted quinones to gain a larger μ_{ge}.

Conclusions

INDO/2 calculations on the molecular first-order hyperpolarizabilities (β_{vec}) were done for push–pull quinones. The variations of β_{vec} in the gas phase and in solution versus the strength of donor–acceptor pairs are shown diagrammatically, giving an insight into the effects of donor–acceptor pairs and solvation. The results may provide us a simple scheme for selecting donor and acceptor groups for synthesizing molecules with desired NLO properties. In addition, one can predict or estimate the value of β_{vec} for unknown donor–acceptor substituted quinones simply by the parameter δ_{DA}. According to our calculated results, a polar medium favors the relatively weaker donor-acceptor substituted chromophores to gain a larger first-order hyperpolarizability, but it weakens the NLO response.

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