Evaluating the Solvent Stark Effect from Temperature-Dependent Solvatochromic Shifts of Anthracene

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The solvent Stark effect on the spectral shifts of anthracene is studied with temperature-dependent solvatochromic measurements. The Stark contribution Δv_{Stark} to the absorption shift Δv_p in polar solvents is measured to be $\Delta v_{Stark} = (53 \pm 35)$ cm^{-1}, in reasonable agreement with dielectric continuum theory esti-mate of 28 cm^{-1}, whereas the major shift $\Delta v_p \sim 300$ cm^{-1} presumably originates from the solute quadrupole. We pay attention to the accurate correction of Δv_p for the nonpolar contribution that is crucial when the shifts are modest in magnitude.

1. Introduction

When a nondipolar polarizable solute like anthracene, perylene or trans-stilbene is immersed in a polar solvent, it is stabilized via interaction with fluctuating solvent electric field ε by energy $E_\alpha = -\alpha\langle \varepsilon^2 \rangle/2$ where α is the solute polarizability, and the averaging is taken over all solvent configurations.[1,2] This stabilization is commonly called the solvent Stark effect.[3–7]

Karlström and Halle[1] applied a fluctuation approach for dielectrics with a spherical cavity of radius a to obtain the following exact result

$$E_\alpha = -\frac{3}{2}RT \cdot \ln[(1 - \alpha_l \chi_l^q)/(1 - \alpha_l \chi_l)] \tag{1}$$

$$\chi_l = \frac{l!(l+1)(\varepsilon-1)}{(l+1)\varepsilon+l}\frac{1}{a^3} \quad \chi_l^q = \frac{l!(l+1)(n^2-1)}{(l+1)n^2+l}\frac{1}{a^3} \tag{2}$$

Here multipolar susceptibilities χ_l, χ_l^q are related to slow (orientational) and fast (quantum, electronic) degrees of freedom of the solvent with dielectric constant ε and refractive index n; $R = 8.31$ J/mol/K is the gas constant and T temperature; $l = 1$ or 2 corresponds to dipolar or quadrupolar solute, or with $l \geq 3$ to higher multipoles. For a nondipolar solute and when $\alpha_l \chi_l^q, \alpha_l \chi_l \ll 1$, one gets

$$E_\alpha = -\frac{3}{2}RT\alpha_1(\chi_1 - \chi_1^q)\ ] = -\frac{3\alpha}{2a^3}RTf_p \tag{3}$$

where $f_p = [2(\varepsilon-1)/(2\varepsilon+1) - 2(n^2-1)/(2n^2+1)]$ is the well-known response in polar solvents.[4] A very similar expression for E_α was also derived by Scaife.[2]

The Stark effect directly results in solvatochromic shifts for absorption

$$\Delta v_{Stark} = -\frac{3}{2}f_p\frac{RT(\alpha_e^{FC} - \alpha_g)}{a^3} = -B_{Stark}f_p \tag{4}$$

where the polarizability difference appears because α differs in ground (g) and excited (e) electronic state of the solute; the superscript FC abbreviates "Franck-Condon" indicating that α_e is taken at ground state (S_0) chromophore geometry.

Hereinafter, we apply the following units: Δv in cm^{-1}, a in Å, α in Å^3, dipole moment μ in D, quadrupole moment Q in DÅ. Energies E and shifts Δv are in eV, kJ/mol or cm^{-1} with the relations between the units

$$1\,\text{eV} = 96.49\,\text{kJ/mol} = 8065\,\text{cm}^{-1} = 1.602\,\text{D}^2/\text{Å}^3,$$
$$1\,\text{D}^2/\text{Å}^3 = 0.624\,\text{eV} = 5032\,\text{cm}^{-1} \tag{5}$$

Just to give an idea of the expected shift (4), one has $3f_p/2 \approx 1$, $(\alpha_e^{FC} - \alpha_g) \sim 15$ Å^3, $a = 5$ Å, $RT = 2.44$ kJ/mol $= 204$ cm^{-1} at $T = 20\,°C$, that predicts quite a small value $\Delta v_{Stark} \sim 20$ cm^{-1}.

In the late 1960s Baur and Nicol[8] suggested a *different* expression for the Stark shift, $\Delta v_{Stark} \sim \varepsilon(\varepsilon-1)/(2\varepsilon+1)$ which gives for $\varepsilon > 10$ a much larger shift than that by Eq. (4). Furthermore, they tried to ascribe the *full* observed shift from nondipolar solutes in polar solvents entirely to the Stark contribution, and even obtained a support from other workers.[9] However, Ghoneim and Suppan[3] experimentally demonstrated an inconsistency in their approach, and instead proposed quadrupolar or higher multipolar nature of the aforementioned shifts.

Since then, to the best of our knowledge, there were no attempts to quantify the Stark contribution to the solvatochromic shifts experimentally.

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The aim of the present paper is to determine the weak Stark contribution to temperature-dependent solvatochromic shifts of the absorption spectra of anthracene.

In addition, we propose a simple method for correcting the shifts for the nonpolar contribution, the correction being crucial when the shifts are modest in magnitude.

The paper is organized as follows. In section 2.1 we overview the theory of solvatochromic shifts and introduce the correction procedure, section 2.2 describes our calculations, followed by section 2.3 for the experimental results and discussion.

2. Results and Discussion

2.1 Solvatochromic Shifts

For a dipolar solute a classical theory[4,10–14] expresses absorption shifts Δv as the sum of nonpolar Δv_n and polar Δv_p contribution

$$\Delta v = \Delta v_n + \Delta v_p = -\frac{f_n}{2a^3}$$
$$\left[\left((\mu_e^{FC})^2 - \mu_g^2\right) + C(\alpha_e^{FC} - \alpha_g)\right] - \frac{f_p}{a^3}\mu_g(\mu_e^{FC} - \mu_g)$$

(6)

$$f_n = 2(n^2-1)/(2n^2+1), \quad f_p = [2(\varepsilon-1)/(2\varepsilon+1)$$
$$-2(n^2-1)/(2n^2+1)]$$

(7)

Here f_n, f_p is already familiar nonpolar and polar solvent response, μ, α is the solute dipole moment and polarizability, and the products of the dipole moments are to be understood as scalar products. The nonpolar part Δv_n is proportional to f_n and consists of inductive (the first term) and dispersive contribution.[4] The semiempirical constant C is often expressed via solute (I) and solvent (I') ionization potential, $C = 2II'/(I+I')$ and usually is in the range of 10 eV = 80000 cm^{-1}. This gives an estimate of 4000 cm^{-1} for the dispersive term, and with $\mu_g = 5$ D, $\mu_e = 10$ D an estimate of 1500 cm^{-1} for the inductive term. Regarding the polar part Δv_p, it is proportional to f_p and represents the dipolar shift in polar solvents. With the above $\mu_g = 5$ D, $\mu_e = 10$ D, the dipolar shift Δv_p reaches 1000 cm^{-1}.

When like in our case, the solute dipoles vanish, $\mu_g \approx \mu_e \approx 0$, the shifts Δv are strongly dominated by the dispersive contribution, which exceeds the expected Stark shift by two orders of magnitude.

Baur and Nicol[8] and Gerhold and Miller[9] plotted experimental shifts Δv against the calculated shifts given by a sum of Δv_n and their Stark term $\Delta v_{Stark} \sim \varepsilon(\varepsilon-1)/(2\varepsilon+1)\cdot RT(\alpha_e^{FC} - \alpha_g)/a^3$. It is however quite clear, that small (in percentages) errors in the huge dispersive contribution Δv_n may completely mask the effect of interest.

We therefore apply below a different approach. First, we note that both Δv_n and Δv_p contribute to the shift Δv in polar solvents. On the other hand in nonpolar solvents, Δv_p vanishes completely since $\varepsilon = n^2$ and $f_p = 0$, and hence Δv_n can be fully determined with a set of nonpolar solvents only

$$\Delta v_n = -\frac{f_n}{2a^3}C(\alpha_e^{FC} - \alpha_g) \equiv -B_n f_n$$

(8)

with the slope B_n being calculated from a linear fit of Δv_n against f_n. Having this result at hand one can get rid of the nonpolar contribution to Δv

$$\Delta v_p = \Delta v - \Delta v_n = \Delta v + B_n(f_n - f_{pe})$$

(9)

In our case Δv_p does not contain the dipolar part, but presumably contains Stark Δv_{Stark} and quadrupolar[3] Δv_Q part

$$\Delta v_p = -\frac{RT(\alpha_e^{FC} - \alpha_g)}{a^3}f_p - \frac{2Q_{gi}(Q_{ei}^{FC} - Q_{gi})}{3a^5}f_Q$$
$$\equiv -B_{Stark}f_p - B_Q f_Q$$

(10)

where the traceless quadrupole tensors Q are according to Buckingham[15] and their products should be understood as the double inner products. The quadrupolar response $f_Q = [3(\varepsilon-1)/(3\varepsilon+2)-3(n^2-1)/(3n^2+2)]$ is slightly different from f_p, but in the realm of more common solvents, where $1.4 < n^2 < 2.6$ (from perfluoroalkanes to CS$_2$) and $n^2 \leq \varepsilon < 111$ (formamide) f_Q deviates from f_p by at most 6%, the highest discrepancy to be expected for extreme cases, perfluoroalkanes and compounds with high ε and n^2. Therefore, one can safely substitute f_p to obtain

$$\Delta v_p = -\left[\frac{2Q_g(Q_e^{FC} - Q_g)}{3a^5} + \frac{RT(\alpha_e^{FC} - \alpha_g)}{a^3}\right]f_p$$
$$\equiv -[B_Q + B_{Stark}]f_p$$

(11)

In experiment the polar shifts Δv_p from nondipolar chromophores are in *no* case negligible and reach 300 cm^{-1} for anthracene, stilbene or diphenylbutadiene. We believe, following Suppan,[3] that these shifts originate from quadrupolar[15] or higher multipolar contribution, as shall be discussed in detail in our forthcoming article.

Regarding the Stark contribution, although it is much smaller in magnitude, it can be derived from temperature-dependent shifts $\Delta v_p(T)$.

A further very helpful comparison is between Stark $B_{Stark} = RT(\alpha_e^{FC} - \alpha_g)/a^3$ and nonpolar $B_n = C(\alpha_e^{FC} - \alpha_g)/2a^3$ slope. As seen, the both depend on the solute parameters in a similar fashion. This allows one to exclude the solute radius a (not well-defined in the continuum dielectric theory) and to express B_{Stark} through the well-measured quantity B_n that provides an improved estimate for the Stark shift. With $(\alpha_e^{FC} - \alpha_g) = 16.5$ Å^3,[16–18] and taking $I = 7.4$ eV for anthracene, $I' = 10.4$ eV for n-pentane, one calculates $C = 69740$ cm^{-1}. And with our experimental $B_n = 3150$ cm^{-1} (see Figure 2) this gives at T = 293 K

$$B_{Stark}/B_n = 3RT/C \approx 0.0088, \quad B_{Stark} = 28 \text{ cm}^{-1}$$

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2.2 Calculations

Vacuum static polarizabilities for S_0 and S_n states are computed with two approaches. The first uses the CC2 approximation of coupled-cluster theory with a aug-cc-pVTZ basis set,[19] and corresponding auxiliary basis set[20] using the ricc2 module of the Turbomole program package version 7.0.2.[21] The second approach involves the RI-XMCQDPT2 quasi-degenerate perturbation theory[22] implemented in the Firefly V8.2 software[23] which is partly based on the GAMESS(US) package.[24] The perturbation corrections are applied on top of the CASSCF (14e,14o)/aug-cc-pwCVTZ reference where the active space encompasses all the 14 π-orbitals. To suppress the intruder state effects, the intruder-state-avoidance (ISA) parameter is set 0.02 a.u.

The anthracene polarizabilities have already been calculated.[16–18] Pavlovich[16] considered the temperature-dependent shifts of absorption in frozen glassy alcohols where the Stark effect and the dispersive contribution were added up. Mathies and Albrecht[17] performed electric field perturbation spectroscopy in a frozen medium, and Bendkowsky et al.[18] measured the quadratic Stark effect in jet-cooled molecules.

Our XMCQDPT2 and RI-CC2 computations confirm the first absorbing excited state to be indeed S_1 dominated by the HOMO→LUMO excitation. At the CASSCF level it emerges incorrectly as S_3. The second (after S_1) bright absorbing state turns out to be S_6 which is almost degenerate with S_5 at the XMCQDPT2 level. It involves a mixture of several single excitations. Taking into account that the task of accurate description of the higher-lying excited states would require at least further augmentation of the basis set, the XMCQDPT2 calculations were primarily focused at the task of more accurate description of the S_0 and S_1 states. In view of that, we use the CASSCF reference averaged over the five lowest singlet roots and include 13 states in the XMCQDPT2 model space. Resulting vertical gas-phase excitation energies of 3.39 eV for $S_0 \rightarrow S_1$ and 4.88 eV for $S_0 \rightarrow S_6$ are in a good agreement with the experiment.

The calculated polarizabilities are given in Table 1 (x is the long axis of the anthracene molecule, y is the short one, and z – the perpendicular one). As seen $\Delta\alpha$ for $S_0 \rightarrow S_1$ equals 15.9 Å³, in agreement with both the present experiment (see below) and the earlier estimates.[16–18] A very close result was previously obtained in the relaxed RI-CC2/aug-cc-pVTZ calculations.[25] At the same time, considering the S_0 and S_1 states separately, our values in Table 1 are lower than the previous CCSD(T) estimates for S_0[26] (interestingly, the discrepancy is almost entirely associated with α_{xx}) and than the above RI-CC2 data for S_1.[25])

Unfortunately there is an understandable lack of reliable polarizability benchmarks even for the ground state of anthracene, as can be seen from a survey of the previous condensed-phase experimental data.[18]

The XMCQDPT2 polarizability of the S_6 state is considerably underestimated. This obviously results from the coupling to S_5 which is placed by the calculation only a few meV below S_6. Thus, an accurate computational treatment of S_6 requires very precise energies of the other states and possibly even an explicit consideration of the relevant vibronic levels. Our present RI-CC2 data are however qualitatively correct, suggesting a 40% increase in the polarizability from S_1 to S_6.

2.3. Experimental Shifts and Discussion

Absorption spectra of anthracene in solution are recorded at $T = 10, 20, 30, 40, 50°C$ with 0.02 nm step both in the visible ($S_0 \rightarrow S_1$) and in the UV ($S_0 \rightarrow S_6$). Anthracene is chosen as the probe because its narrow sub-bands (see Figure 1) allow for high accuracy ± 1 cm^{-1} of the spectral shifts in the visible. The nonpolar and polar solvents used are collected in Table 2 (see ref. 27 for the full solvent properties).

Typical $S_0 \rightarrow S_1$ absorption spectra of anthracene are displayed in Figure 1. They consist of well resolved vibronic bands, with the 0–0 band peaked at 26650 cm^{-1} in n-pentane. The spectra in nonpolar (top) and polar (bottom) solvents are shifted relative to n-pentane for best coincidence in the red part, including the 0–0 and 0–1 band. We estimate the accuracy
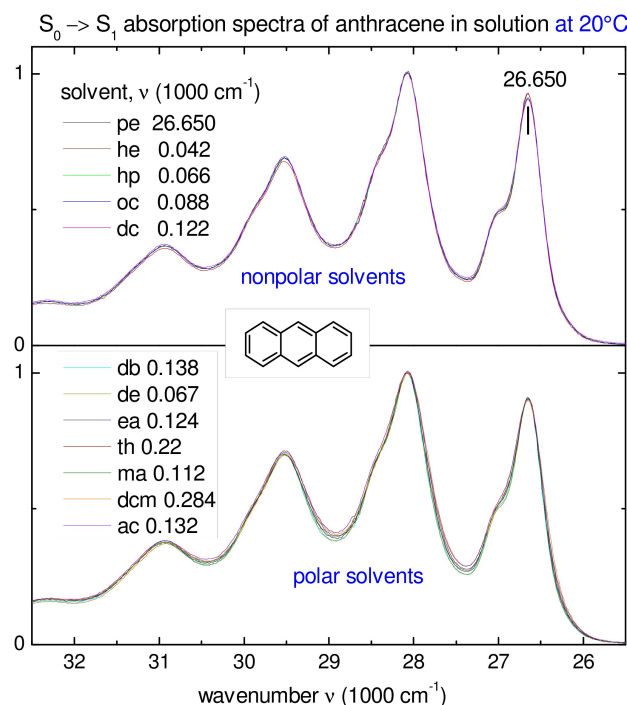
Figure 1. $S_0 \rightarrow S_1$ absorption spectra of anthracene at 20°C in nonpolar and polar solvents, shifted for best coincidence with those in n-pentane. The shifts are indicated in units of 1000 cm^{-1}, the accuracy of the shifts is estimated ± 1 cm^{-1}. Full solvent names are given in Table 2.

Table 1. Anthracene Polarizabilities [Å³].				
	α_{xx}	α_{yy}	α_{zz}	α
S_0	34.2	24.1	12.8	23.7
S_1	77.7	28.0	13.1	39.6
S_6	90.7	22.8	12.8	42.1
$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$.				

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Table 2. Solvent Properties[27] at T = 25 °C.

	Solvent	ε	$d\varepsilon/dT/\varepsilon$ x1000	n	dn/dT x1000
1	2-methyl-butane (tm)	1.84	–	1.3537	–
2	n-pentane (pe)	1.84	2.0	1.3547	0.552
3	n-hexane (he)	1.88	1.9	1.3723	0.52
4	n-heptane (hp)	1.92	1.68	1.3851	0.506
5	n-octane (oc)	1.95	1.54	1.3951	0.476
6	n-decane (dc)	1.99	1.5	1.4097	0.444
7	n-dodecane (dd)	2.00	–	1.4195	–
8	n-hexadecane (hd)	2.05	0.65	1.4325	–
9	cyclohexane (ch)	2.02	1.82	1.4235	0.538
10	di-n-butylether (db)	3.08	–	1.3968	0.45
11	di-n-propylether (dp)	3.39	–	1.381	
12	di-n-ethylether (de)	4.2	5.0	1.3495	0.56
13	ethylacetate (ea)	6.02	5.7	1.3698	0.49
14	tetrahydrofurane (th)	7.58	3.94	1.405	0.44
15	methylacetate (ma)	6.68	7.6	1.3589	0.50
16	acetonitrile (ac)	35.94	4.16	1.341	0.496
17	dichlorometane (dcm)	8.93	8.5	1.421	0.60
18	dimethylsulfoxide (ds)	46.7	–	1.4783	

of such determined shifts to be ± 1 cm^{-1}. The shifts are indicated in units 1000 cm^{-1}. Similarly, shifted UV spectra for the bright $S_0 \rightarrow S_6$ electronic transition are displayed in Figure S1, Supporting Information (SI).

Figure 2 shows plots $\Delta v_n(f_n)$ and $\Delta v_p(f_p)$ for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_6$ band of anthracene (top and middle frame), and for the $S_0 \rightarrow S_1$ band of highly polar dye C153.

Let us consider the $S_0 \rightarrow S_1$ band of anthracene first. Non-polar shifts Δv_n (top left) show a nice linear behavior along n-hydrocarbons, from n-pentane to n-hexadecane. Note that 2-methylbutane (tm) and cyclohexane (ch) apparently deviate from the linear fit. The deviation is systematic and is also observed with other solvatochromic probes.

Switching to polar solvents at right of Figure 2, one sees that directly measured shifts Δv (black squares) reveal strong scatter that prevents from a satisfactory fit. As discussed above, this scatter is mainly due to the nonpolar contribution $\Delta v_n = B_n f_n$. The subtraction (9) eliminates that contribution from Δv and results in Δv_p shown by the open squares. These allow now for a good linear fit with slope $B_p = (272 \pm 13)$ cm^{-1}.

For comparison, the bottom frame of Figure 2 shows the shifts from highly polar C153.[28] While its nonpolar slope $B_n = 5180$ cm^{-1} is comparable with that for anthracene, the polar slope $B_p = 2800$ cm^{-1} is by factor 10 larger, in which case the f_n contribution to Δv can be safely neglected.

Next, the experimental ratio $B_p/B_n \sim 0.1$ is about 10 times larger than $B_{Stark}/B_n = 0.009$ estimated by Eq. (12). That is, the solvent Stark effect is expected to contribute about 10% of the observed shift Δv_p in polar solvents.
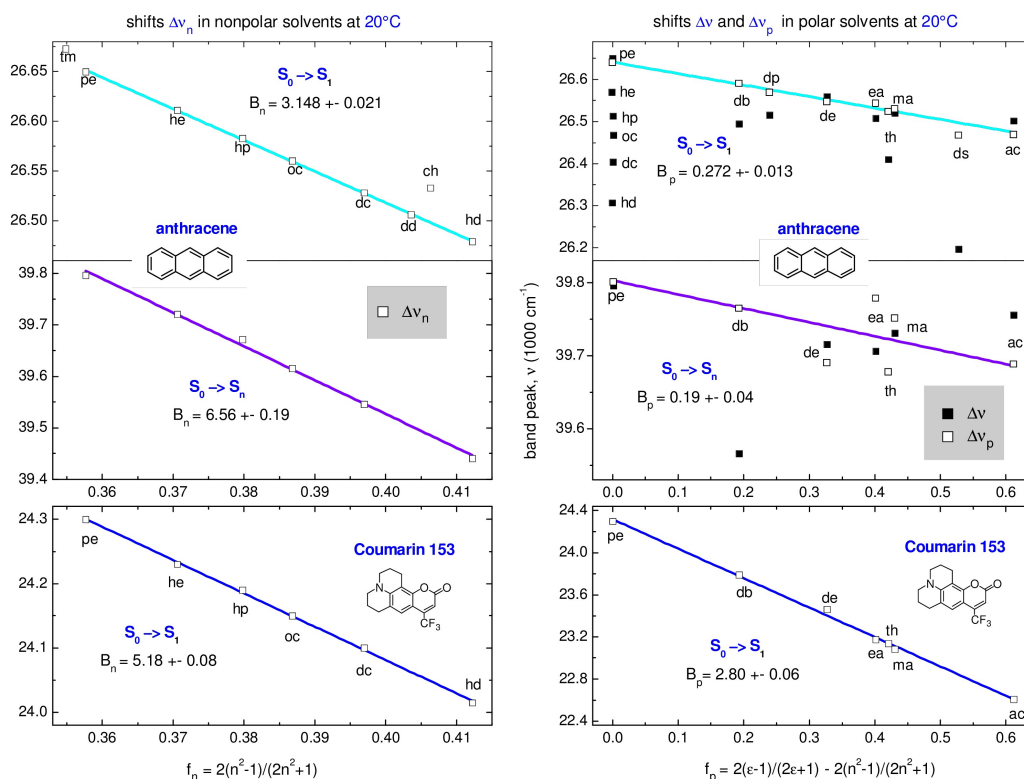
Figure 2. Solvatochromic shifts of anthracene in nonpolar solvents (Δv_n at left), and in polar solvents (Δv, Δv_p at right) for $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_n$ absorption (n = 6 from our calculations). The shifts from highly polar C153 are shown for comparison at the bottom. Nonpolar and polar slopes B_n, B_p from linear fits are given as inserts. For anthracene, a big scatter of directly measured shifts Δv (black squares) in polar solvents is due to the nonpolar contribution Δv_n (the point for tetrahydrofuran is out of the range). Its subtraction results in Δv_p (open squares) which allow a much better fit than with original Δv shown in Figure S3 (see Supporting Information). The solvents are listed in Table 1.
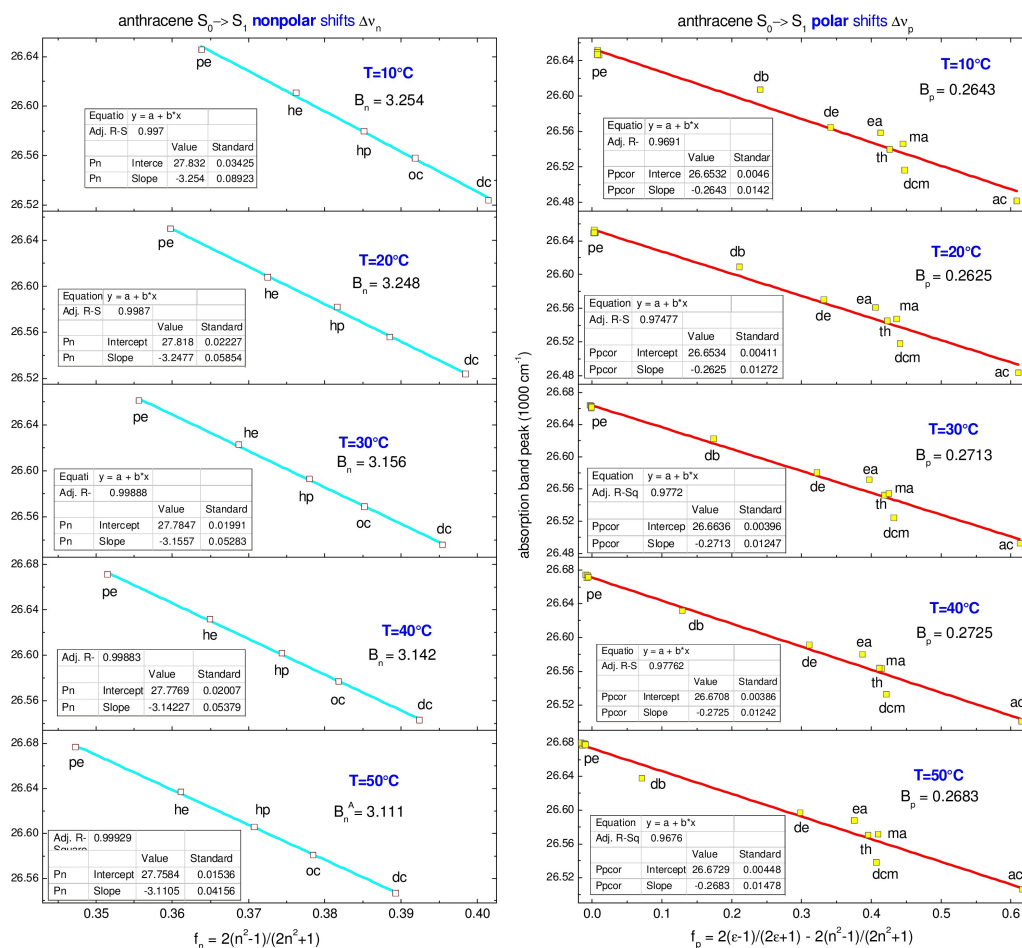
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Figure 3. Temperature-dependent nonpolar $\Delta v_n(T)$ and polar $\Delta v_p(T)$ shifts for the $S_0 \rightarrow S_1$ band of anthracene.
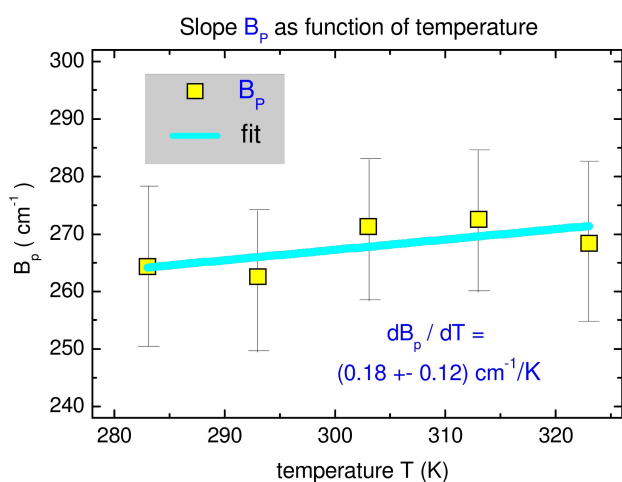

Figure 4. Temperature dependence of polar slope $B_p(T)$. Despite large error bars, the fit gives $dB_p/dT = (0.18 \pm 0.12)$ cm^{-1}/K, in agreement with dielectric continuum theory, $dB_{Stark}/dT = 0.096$ cm^{-1}/K (Eq. (12)). This corresponds to $B_{Stark} = (53 \pm 35)$ cm^{-1} at T = 293 K. Directly measured shifts $\Delta v(T)$, without subtracting the nonpolar contribution, result in $dB_p/dT = (-0.07 \pm 0.14)$ cm^{-1}/K (Figure S4), implying no apparent temperature dependence. Hence the subtraction of the nonpolar contribution is crucial when the shifts in polar solvents are modest in magnitude.

Consider now the shifts of the $S_0 \rightarrow S_n$ band (n = 6 from our calculations) displayed in the middle frames of Figure 2. Here the nonpolar slope $B_n = (6560 \pm 190)$ cm^{-1} is twice steeper than that for the $S_0 \rightarrow S_1$ transition, in approximate agreement with the calculated higher polarizability in S_n (compared to S_1, see Table 1). Turning to the polar slope $B_p = (190 \pm 40)$ cm^{-1}, we note that it is 1.5 times *smaller* than that for the $S_0 \rightarrow S_1$ transition, contrary to what is expected if the slope would depend on the polarizability. Hence the polar and nonpolar shifts in anthracene are of different nature, consistent with the above assumption that Δv_p originate mainly from the solute quadrupole (rather than from the solute polarizability).

To isolate the Stark shift Δv_{Stark} we measure the $S_0 \rightarrow S_1$ absorption spectra of anthracene at different temperatures. The results are presented in Figure 3 with nonpolar shifts $\Delta v_n(T)$ shown at left and polar shifts $\Delta v_p(T)$ at right, the corresponding slopes B_n, B_p being indicated as inserts.

Figure 4 summarizes our results on the temperature-dependent shifts. Here the slope $B_p(T)$ is shown as function of temperature. Despite large error bars, the fit gives $dB_p/dT = (0.18 \pm 0.12)$ cm^{-1}/K, in good agreement with $dB_{Stark}/dT =$

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0.096 cm^{-1}/K (Eq. (12)) estimated by the dielectric continuum theory. We therefore ascribe the temperature dependence in Figure 4 to the Stark contribution that corresponds to $B_{Stark} = (53 \pm 35)$ cm^{-1} at T=293 K.

It is worth noting that *directly* measured shifts $\Delta v(T)$, without subtracting the nonpolar contribution, result in dB_p/dT=(-0.07 ± 0.14) cm^{-1}/K (see Figure S4), that means in fact no actual temperature dependence. Thus, the subtraction of the nonpolar contribution is crucial when the polar shifts are modest in magnitude.

3. Conclusion

In summary, we derived the Stark shift of the $S_0 \rightarrow S_1$ band of anthracene from temperature-dependent solvatochromic absorption shifts. The obtained derivative of the Stark slope dB_{Stark}/dT=(0.18 ± 0.12) cm^{-1}/K corresponds to $B_{Stark}=(53 \pm 35)$ cm^{-1} at T=293 K, that constitutes approximately 10–20% of the full slope B_p in polar solvents observed for anthracene and many other nondipolar chromophores. The measured Stark shift is in good agreement with the estimate from dielectric continuum theory.

To calculate the true shifts Δv_p in polar solvents, it is necessary to subtract from directly measured shifts Δv the nonpolar contribution which can be precisely determined by solvatochromic measurements in nonpolar solvents. The subtraction is especially necessary when the shifts Δv_p are modest in magnitude that is usually the case for nondipolar or weakly polar chromophores.

Experimental Section

Absorption spectra of anthracene in solution are recorded at $T=10$, 20, 30, 40, 50°C, by spectrometer Cary 300 (Varian) with 0.2 nm step.

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