Solvent Dependence of n−π* Absorption in Acetone

Indrek Renge*

Institute of Physics, University of Tartu, Riia Street 142, EE51014 Tartu, Estonia

Received: April 13, 2009; Revised Manuscript Received: August 10, 2009

A barely resolved structure can cause considerable loss of precision when locating the maxima of broad spectra. The centers of band envelopes were determined for the acetone n−π* absorption in vapor, pure liquid, and solutions at 293 K. A complementary method of "band-halving" is proposed for accurate measurement of solvent-induced displacements. Solvent shifts span from −280 cm^{-1} in CCl_4 to 465 cm^{-1} in acetonitrile, and further to 1785 cm^{-1} in hydrogen-bonding water, being negligible in *n*-alkanes. In the latter case the dispersive and induction shift components almost cancel mutually. Unbiased values of absolute frequency shifts will provide a reference to quantum chemical calculations, in particular, in nonpolar and weakly polar solvents where much controversy exists. The dipole moment in the excited state ($\mu_e = 1.81 \pm 0.2$ D, $\Delta\mu = -1.81$ D) and polarizability change ($\Delta\alpha = 0.6 \pm 0.2$ Å^3) were estimated. A solvent set where the Onsager model is apparently applicable was used for the determination of μ_e. Remarkably, the bandwidth at half-maximum (fwhm) decreases in liquids, including water (6270 cm^{-1}), as compared to vapor (6680 cm^{-1}).

1. Introduction

Simple carbonyls such as formaldehyde[1−6] and acetone[4−24] have often served as test systems in computer chemical calculations of solvent effects on a n−π* transition. Occasionally, excellent agreement to measured shifts within several tens of wavenumbers has been obtained.[9,10,14,16] This may seem suspicious, because experimental work on absorption spectra of acetone is quite old[25−30] and not always consistent. Finding absolute solvent shifts of acetone is complicated by the fact that the peak positions are poorly defined in the vapor phase and inert solvents as a result of irregular band shape in the maximum region. Hayes and Timmons[29] noticed redistribution of intensities within absorption bands in different liquids but failed to take into account the humpy structure in the peak region, affecting the maximum position. These authors[29] as well as Ito et al.[26] did not report vapor maxima, but with the value of 36100 cm^{-1},[30] the shift reported by different authors for *n*-hexane can be as disparate as −250 cm^{-1},[29] and 390 cm^{-1}.[26] In closely related aliphatic ketones the shifts between the vapor phase and *n*-heptane solution are unexplainably irregular, ranging from −300 cm^{-1} in acetone to 450 cm^{-1} in di-*n*-propyl ketone (Table 1).[30] Therefore, the sign and magnitude of the effect of refractive index, or solvent polarizability remain controversial, both experimentally and in theory.[8,9,11,14,16] In polar environments the band structure is smoothed out, allowing one to locate the maxima more accurately, and leading to more coherent solvent shift data from different sources: 335[28] and 400 cm^{-1} [26,27,29] in acetonitrile, 650,[28] 700,[30] 750,[29] 790,[26] and 940 cm^{-1} [27] in ethanol, and 1700 ± 50 cm^{-1} in water[27−30] (shifts are given versus the vapor maximum at 36100 cm^{-1} [30]).

Because of theoretical and practical relevance, reliable solvent shift data for carbonyl and other n−π* chromophores are highly desirable. Determination of matrix-induced shifts can be difficult for multiphonon bands. The situation is rather different from purely electronic bands, narrow lines, or spectral holes at low temperatures,[33−35] where the 0−0 origin recorded in a cold molecular beam[36−38] can serve as a reference. Shifts of broad vibronic contours are often calculated with respect to vapor spectra, supposing that vibronic coupling parameters are not modified by solvent. In order to define solvent shifts more precisely, the bands' centers of gravity can be used. A complementary method will be proposed, if the complete band cannot be recorded, because of red-shifted self-absorption edge of the solvent.

The applicability of solvent shift equations derived on the basis of Onsager reaction field theory[39−46] will be elucidated from both theoretical and practical points of view. The relative success of solvent shift formulas expressed in terms of refractive index *n* and static permittivity ε functions can be puzzling, because intermolecular interactions are local. Thus, about 90% of solvation energy, due to repulsive−dispersive potential,[35] and even the dipole−dipole interaction,[21,47] is restricted to the first coordination layer surrounding a chromophore. Deviations from the continuous dielectric approach are expected to be particularly severe in the case of a carbonyl entity that is smaller than most solvent molecules. Still the plots of band maxima of many chromophores in *n*-alkanes, versus the Lorentz−Lorenz function of the refractive index, are almost perfectly linear as a result of uniform polarizability density on an atomic scale.[48,49] Moreover, spectral shifts show a smooth functional dependence on ε for a well-defined set of aprotic, monofunctional, aliphatic solvents.[50] Solvatochromic plots can be calibrated with the polarizabilities and dipole moments of the excited states, obtained from Stark shift measurements.[48,50] These considerations, delineated by us earlier,[48−50] will be applied to acetone.

Doubtful experimental data can be very misleading for quantum chemical treatments of solvent shifts. When computing dispersion energy shifts for acetone, Rösch and Zerner[10] have given preference to the model predicting a bathochromic shift of about −400 cm^{-1} in cyclohexane, in accordance with data available to them. Li, Cramer, and Truhlar calculated dispersive shifts about −650 cm^{-1} in common solvents.[16] A similar assumption about considerable bathochromism in nonpolar

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* Phone: +3727-374716. Fax: +3727-383033. E-mail: indrek.renge@ut.ee.

10.1021/jp9033886 CCC: $40.75

TABLE 1: Solvent Shifts of n−π* Absorption Bands in Aliphatic Ketones[a]

ketone[b]/solvent	$-\Sigma E_s^{\circ c}$	*n*-heptane	cyclohexane	Et_2O	CH_2Cl_2	methanol	water
Me_2CO	0	−300 −40 ± 5[d]	−400	−50 180 ± 25[d]	200 325 ± 10[d]	850 941 ± 10[d]	1700 1785 ± 7[d]
MeCOEt	0.27	100	−100	150	600	1000	1100
Et_2CO	0.54	200	0	150	300	800	1450
MeCO-*n*-Pr	0.56	−150	−100	−50	150	1000	1100
n-Pr_2CO	1.12	450	200	400	500	800	1550
n-Bu_2CO	1.18	200	300	250	300	750	1350
i-Pr_2CO	1.7	−50	0	−50	100	400	1000
i-Bu_2CO	2.26	50	0	0	50	550	1450
cyclohexanone	<0?	100	50	250	450	1300	1800

[a] Shifts of maxima between the vapor phase and solvent in cm^{-1}, data from Table 1 in ref 30. [b] Me, methyl; Et, ethyl; Pr, propyll; Bu, butyl. [c] Sum of steric constants of substituents after refs 31 and 32. [d] This work.

environments prompted van Duijnen et al. to devise a method that overestimates dispersive shifts.[11,14] On the contrary, the authors[12] admit that the maximum in cyclohexane solution is shifted by 1200 cm^{-1} (0.15 eV) to the blue. Our value for the partial shift, caused by the London forces will be as small as −140 cm^{-1} for solvents with refractive index $n \sim 1.4$. Rapid advancement of computer chemical calculations of solvent shifts in the 1990s[1−24] in conjunction with uncritical use of old reference data[25−30] has led to an unfavorable state of matters that calls for revision.

2. Experimental Section

Solvents of highest purity were purchased from Aldrich and used as received. Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer in wavelength (λ) scale with 1 nm slit width. The spectrum of saturated acetone vapor was measured at 295 K in a 10 cm silica cell (Hellma). Neat acetone was recorded in a cell of 0.01 mm path length. Solvent dependencies were run in 1 mm and 10 mm cells with respect to a matched one filled with neat solvent. The instrument was calibrated with 287.15, 278.2, and 241.15 nm lines of 0.25 M $HoCl_3$ in 0.1 M aqueous HCl,[51] and found reproducible to within 0.01 nm over several months, with systematic error not exceeding 0.15 nm. Data are presented as λ^{-1}, without correction to the refraction of air, equal to 0.0825 nm or −11 cm^{-1} at 280 nm.[52]

3. Results

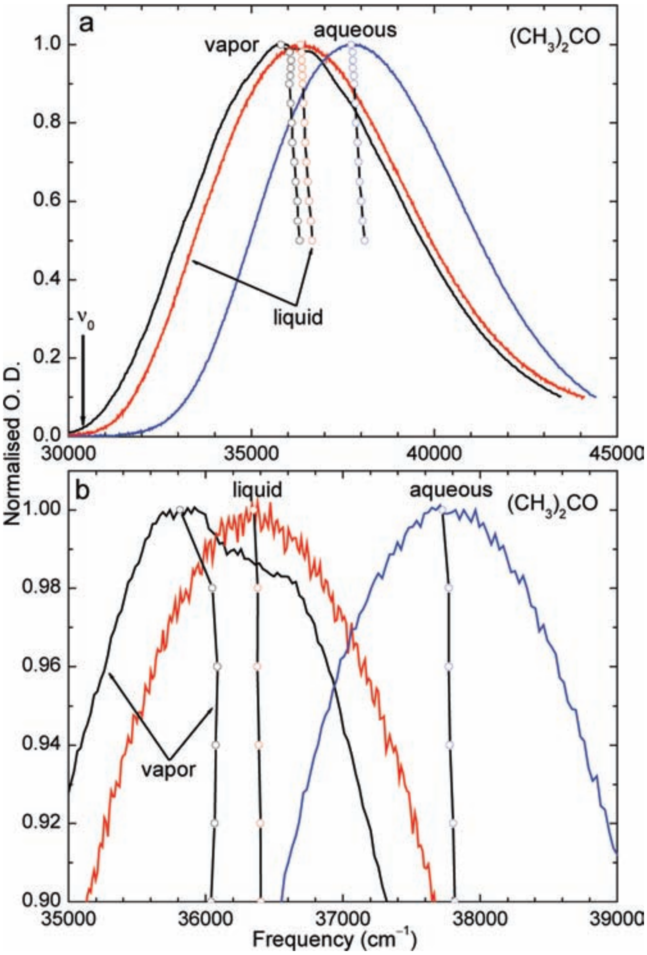

Figure 1. Normalized absorption spectra of acetone in the vapor and pure liquid phase and aqueous solution. Band-halving procedure for estimation of solvent shifts is illustrated. Position of purely electronic 0−0 origin from ref 36 (30435 cm^{-1}) is indicated by arrow.

The forbidden n−π* absorption band of acetone shows barely resolved vibronic structure in the vapor phase (Figure 1). The shoulder appearing on the high frequency side in vapor or alkane solutions is shifted to the opposite flank in CCl_4 (Figure 2). As the vibronic structure is complicated and variable, the deconvolution procedure using component sub-bands with adjustable widths[53] is hardly applicable. It becomes obvious from Figures 1 and 2 that determination of the shifts as small as a few % of the total bandwidth can be difficult. The center of gravity of the whole band ν_{cg} would be preferable to rather ill-defined peak maxima. The high-frequency tail was cut off at 10% height of the spectrum, and the remaining envelope was integrated, yielding ν_{cg} of vapor absorption at 36464 ± 25 cm^{-1} (Table 2). Self-absorption in many solvents prevents recording the whole band down to 230 nm. Therefore, a compromise procedure had to be adopted, consisting of building a frequency dependence of the midpoints of normalized spectra at different heights (Figures 1 and 2a). Fortunately, the bisectrices drawn at the relative heights between 0.5 and 0.9 define the relative band shifts very well, and a linear extrapolation leads to a set of band maxima $\nu_{1/2}$. Absolute solvent shifts $\Delta\nu_{1/2}$ are calculated with respect to vapor, having $\nu_{1/2}$ of 35975 ± 25 cm^{-1} (Table 2). The centers of gravity $\Delta\nu_{cg}$ and $\Delta\nu_{1/2}$ are related linearly with a slope close to unity

$$\Delta\nu_{cg} = (57 \pm 11) + (1.02 \pm 0.02)\Delta\nu_{1/2}, \quad N = 14, \quad R = 0.9975 \quad (1)$$

where N is the number of solvents and R is the regression coefficient.

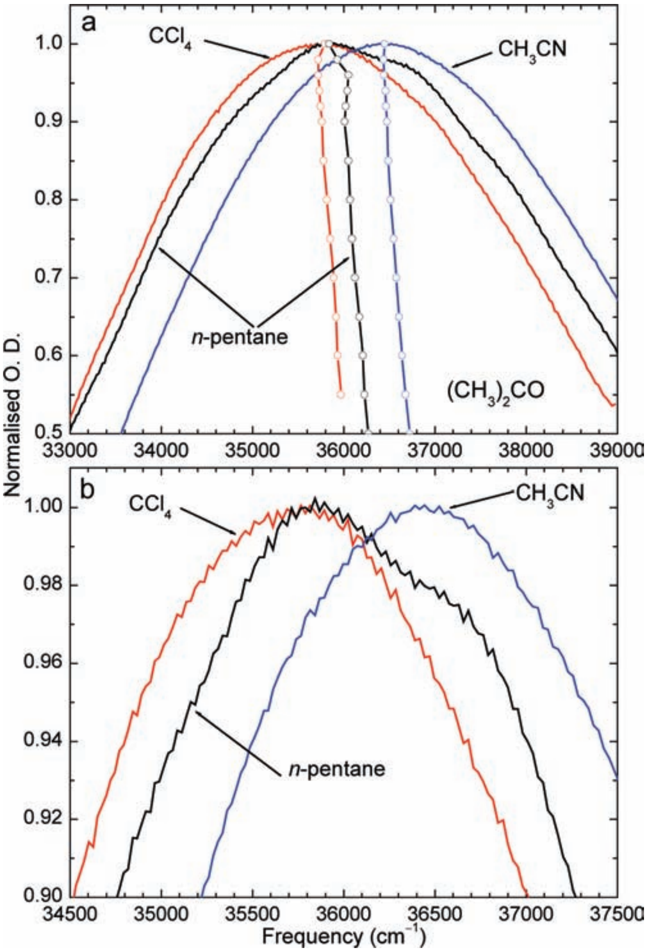

Figure 2. Normalized absorption spectra of acetone showing the solvent dependence of a hidden structure. The band-halving procedure is illustrated.

4. Discussion

4.1. Qualitative Interpretation of n−π* Spectrum in Acetone.

The Vapor Spectrum. For acetone vapor at ambient conditions the maximum $\nu_{1/2}$ (35975 ± 25 cm^{-1}) obtained by band halving is very close to the value ν_{max} reported by Bayliss and Wills-Johnson (36100 cm^{-1}).[30] In ref 30 the vapors of acetone and a number of heavier ketones were measured at 70 °C, and because the thermal shift coefficient between 0 and 400 °C is ∼−1 cm^{-1}/°C,[54] the ν_{max} at the room temperature may be larger by ∼50 cm^{-1}. Earlier, Bayliss has reported the value of 36200 cm^{-1},[25] whereas Herzberg gave the maximum at 36360 cm^{-1}.[57]

With respect to the weak 0−0 origin of the $^1A_2 \leftarrow {}^1A_1$ transition at 30435 cm^{-1}, appearing in fluorescence excitation spectrum in supersonic jet of argon,[36,37] the maximum $\nu_{1/2}$ is shifted by 5540 cm^{-1} to higher frequency. Relative absorption at pure electronic origin, marked with an arrow in Figure 1, is as low as ∼0.025 at the room temperature. Negligible intensity of hot bands (<30435 cm^{-1}) reflects small Franck−Condon factors for the first 10 modes with frequencies less than 500 cm^{-1} (see Table 1 in ref 36). The vibronic spectrum calculated by Liao et al. (Figure 2 in ref 58) seems to possess a too strong origin and carry excessive intensity of the modes below 1000 cm^{-1}.

To elucidate the origin of the humps appearing in absorption contour in vapor and alkanes, a comparison can be made to a less floppy carbonyl, cyclopentanone, showing resolved vibronic peaks at 30908 ± 3, 32126 ± 3, 33346 ± 3, and 34527 ± 10 cm^{-1} (in n-pentane at 293 K, not shown). The average separation between the lines of 1200 ± 20 cm^{-1} corresponds to CO bond stretching that has undergone elongation in the excited state, shifting the frequency of the ground state from 1733 cm^{-1} to 1226 cm^{-1} (in acetone).[58] Therefore, the barely resolved structure in the peak region corresponds to the fourth and fifth harmonics of this mode (5540:1226 = 4.5).

Bandwidth of Acetone Absorption. The n−π* absorption band contour has 6680 ± 20 cm^{-1} of full width at half-maximum (fwhm) in the vapor (Figure 1). As expected, the structure is gradually smoothed out in the liquid phase and disappears in polar solvents. Nevertheless, the band narrows to 6580 cm^{-1} in n-pentane, and further with increasing dielectric constant ε to 6330 cm^{-1} in acetonitrile, and to 6270 cm^{-1} in water (Table 1). The dependence of fwhm on the function $\phi(\varepsilon)$ ($\phi(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2)$) is approximately linear in all solvents (except for CCl$_4$), including protic ones, such as water and methanol (Figure 3)

$$(\mathrm{fwhm})[\mathrm{cm}^{-1}] = (6630 \pm 30) - (327 \pm 47) \times (\varepsilon - 1)/(\varepsilon + 2), \quad N = 23, \quad R = 0.837 \qquad (2)$$

Tentatively, narrowing between the vapor and solution can be attributed to clamping of rotations and even nonplanar vibrations[58] in the environments with high cohesion energy. On the other hand, the loss of structure in polar environments means that inhomogeneous width Γ_{ih} increases. It has been established in a low temperature study that a fluctuating reaction field causes a solvent shift and broadening $\Delta\Gamma_{ih}$ of comparable magnitude.[33] Because the solvent shift in CH$_3$CN is 465 cm^{-1} (see below), total narrowing, ascribable to changes in “phonon” coupling may be as large as 800 cm^{-1} (465 + 350 cm^{-1}), or 12% of the total width in vapor. The width value reported in ref 58 (10588 cm^{-1}) for acetone vapor is exaggerated by a factor of 2. Strangely, Bernasconi, Sprik, and Hutter calculate an inhomogeneous width Γ_{ih} as large as 5000 cm^{-1} (∼0.6 eV) in water[19] that is hardly realistic, bearing in mind the predominately vibronic origin of bandwidth.

4.2. Solvent Shifts.

Simplified Expressions for Solvent Shifts. The interaction energy between the solute and solvent molecules, treated as polarizable dipoles has four terms, namely, dispersion, two types of polarization, and a dipole−dipole component. The spectral shift, emerging as a result of solvation energy difference of the ground and the excited states, is a superposition of these contributions. The solvent properties are described collectively in terms of the refractive index n and dielectric permittivity ε functions, such as $\phi(n^2)$ and $\phi(\varepsilon)$.[40−46] On the other hand, the microscopic solute properties, the scalar polarizability difference $\Delta\alpha$, and dipole moments of the ground state μ_g and the excited state μ_e are included explicitly.

The solute−solvent distance in the ground state equilibrium a, referred to either as (Onsager) cavity radius or as the interaction radius, is assumed to be the same in both states. The Onsager radius is found for neat liquids as $(4/3\pi N)^{-1/3}$, where N is concentration in number per volume units (eq 4.5 in ref 39). Apart from the approximate nature of the spherical cavity approximation itself, a lacks a clear definition in the case of solutions. A study of dispersive solvent shifts versus the polarizability differences $\Delta\alpha$ from electrochromism, for centrosymmetric chromophores in nonpolar solvents, has led to a conclusion that the solute radius cubed a^3 (in Å^3 units) is numerically close to molecular weight M_W.[48]

TABLE 2: Solvent Dependence of Acetone n−π* Absorption Band at 293 K[a]

no	solvent	ε	n^2	ν_{cg} (cm^{-1})	$\nu_{1/2}$ (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	fwhm (cm^{-1})
1	vapor	1	1	36464	35975	0	6678
	nonpolar solvents						
2	perfluoro-*n*-octane	1.7	1.69	36645	36130	155 ± 15	6575
3	*n*-pentane	1.84	1.844	36416	35950	−25 ± 5	6579
4	*n*-hexane	1.89	1.891	(36398)	35940	−35 ± 5	~6577
5	*n*-heptane	1.94	1.927	(36393)	35935	−40 ± 5	6542
6	*n*-decane	1.978	1.991	(36398)	35920	−55 ± 5	6550
7	*n*-hexadecane	2.046	2.056	(36425)	35950	−25 ± 5	6582
8	carbon tetrachloride	2.3	2.132	(36354)	35695	−280 ± 10	6165
9	dioxane	2.2189	2.022	(36685)	36280	305 ± 20	6448
	polar solvents						
10	tetraethoxysilane	2.5	1.910	36513	36104	129 ± 30	6452
11	diethyl ether	4.42	1.828	36508	36155	180 ± 25	6427
12	methyl acetate	6.94	1.852	(36712)	36308	333 ± 10	6377
13	tetrahydrofuran	7.47	1.980	(36649)	36272	297 ± 10	6482
14	*sec*-butyl chloride	8.564	1.949	36584	36132	157 ± 10	6473
15	dichloromethane	9.02	2.028	36723	36300	325 ± 10	6341
16	*cis*-dichloroethylene	9.5	2.088	(36667)	36170	195 ± 10	6281
17	*tert*-butyl chloride	9.663	1.918	36571	36120	145 ± 10	6472
18	1,2-dichlorethane	10.74	2.088	36683	36280	305 ± 20	6322
19	acetone, neat	21.36	1.847	36842	36373	398 ± 5	6475
20	acetonitrile	36	1.806	36847	36440	465 ± 10	6331
21	dimethyl sulfoxide	46.71	2.187	(36767)	36350	375 ± 10	~6222
22	propylene carbonate	62.93	2.019	36787	36393	418 ± 10	6303
	protic solvents						
23	methanol	33.52	1.766	37317	36916	941 ± 10	6437
24	water	80.37	1.777	38168	37760	1785 ± 7	6271

[a] ε, dielectric permittivity (from ref 55); n, refractive index for Na D line (from ref 56); ν_{cg}, frequency at the center of gravity of the band, values in parentheses are calculated from eq 1; $\nu_{1/2}$, band maximum extrapolated from the bisectrices of absorption bands; $\Delta\nu_{1/2}$, shift versus the vapor phase; fwhm, full width at half-maximum.

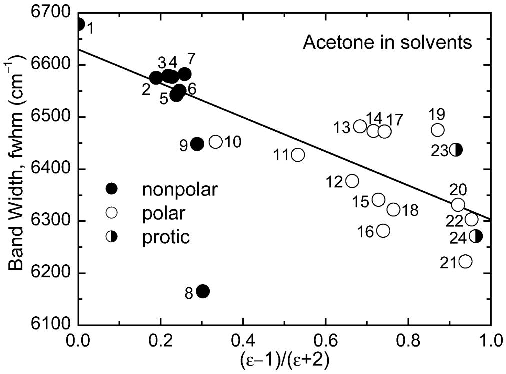

Figure 3. Dependence of full width at half-maximum of acetone absorption band on dielectric permittivity. Numbers correspond to data in Table 2.

Therefore, the dispersive $\Delta\nu_{disp}$ and induction $\Delta\nu_{ind}$ components of solvents shifts, depending only on $\phi(n^2)$ were written as[33,59]

$$\Delta\nu_{disp}\,(\mathrm{cm}^{-1}) = (-5.5 \times 10^4)\Delta\alpha M_w^{-1}\phi(n^2) \tag{3}$$

$$\Delta\nu_{ind}\,(\mathrm{cm}^{-1}) = (6.3 \times 10^3)(\mu_g{}^2 - \mu_e{}^2)M_w^{-1}\phi(n^2) \tag{4}$$

where μ_g and μ_e are in Debye units (1D = 3.336×10^{-30} C m), $\phi(n^2) = (n^2 - 1)/(n^2 + 2)$.

The Lorentz−Lorenz function $\phi(n^2)$ is known to describe the polarizability very well over a broad range of densities, from diluted gases to condensed phase under pressure up to several of kilobar.[60] The applicability of eqs 3 and 4 is improved by the fact that the polarizability density for atoms encountered in common solvents is nearly constant[48] (see below).

As for the ε dependence of solvent shifts in polar liquids ($\varepsilon > n^2$, see Table 2) the solvent cavity field is expected to polarize the solute, producing a shift $\Delta\nu_{pol}$.[61] An empirical expression has been suggested for $\Delta\nu_{pol}$[33]

$$\Delta\nu_{pol}\,(\mathrm{cm}^{-1}) = (-2.7 \times 10^3)\Delta\alpha M_w^{-1}[\phi(\varepsilon) - \phi(n^2)] \tag{5}$$

Finally, the interaction between permanent dipoles translates into internal electrochromic shift in the reaction field created by solute dipole. On the basis of Onsager's reaction field concept,[39] Bakhshiev,[43,59] and his predecessors[40−42] have established for the dipolar solvent shift

$$\Delta\nu_{dip} = [2(2n^2 + 1)/(n^2 + 2)] \times [\mu_g(\mu_e - \mu_g\cos\gamma)/4\pi\varepsilon_0 hca^3][\phi(\varepsilon) - \phi(n^2)] \tag{6}$$

Since $2(2n^2 + 1)/(n^2 + 2) \sim 2.5$ in most solvents, and $a^3 \sim M_W$ as above, one obtains an empirical expression for the dipolar solvent shift[33,50]

$$\Delta\nu_{dip}\,(\mathrm{cm}^{-1}) = (1.26 \times 10^4)\mu_g(\mu_g - \mu_e\cos\gamma)M_w^{-1} \times [\phi(\varepsilon) - \phi(n^2)] \tag{7}$$

where γ is the angle between the solute dipole moments in different states.

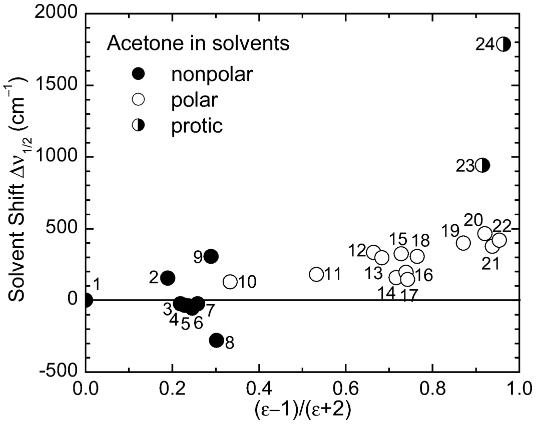

Figure 4. Dependence of solvent shifts of acetone absorption bands on dielectric permittivity. Numbers correspond to data in Table 2.

The substitution $a^3 = M_W$, initially derived for dispersive interaction,[48] proved reliable also for the dipole−dipole interaction (eq 7). No extra calibration to dipole moments was needed, since the slope of eq 7 is close to that calculated with μ_g and μ_e, taken from independent sources, for several solvatochromic indicators.[50]

One may ask whether the induction shift component (eq 4) is affected by the presence of a strong permanent reaction field.[62] Recently, it has been established that the slope of the net $\phi(n^2)$ dependence (i.e., the sum of slopes of eq 3 and 4) for polar dyes is the same in both nonpolar *n*-alkanes and highly polar solvents.[50] Thus, the suppression of induction shift in polar media, emphasized by Brady and Carr,[62] does not manifest itself. Consequently, the separation of shifts caused by of n and ε, although doubtful in terms of Onsager theory, is justified empirically (see below for a discussion).

Nonpolar Solvents. Dielectric permittivity of nonpolar liquids is solely due to electronic polarization, as far as the Maxwell relation ($\varepsilon = n^2$) is obeyed (Table 2). The transition energy $\nu_{\max}$ can be plotted versus the Lorentz−Lorenz function $\phi(n^2)$, or the identical Clausius−Mossotti function $\phi(\varepsilon)$ (Figure 4, filled circles)

$$\nu_{\max} = \nu_0 + p\phi(n^2) \qquad (8)$$

Nearly perfect linearity of eq 8 in *n*-alkanes, with correlation coefficients usually exceeding 0.99, has often been exploited for estimation of $\Delta\alpha$ (eq 3) and the transition frequency in the free chromophores ν_0.[48−50] Bathochromic shift of acetone absorption in a set of hydrocarbons from *n*-pentane to *n*-hexadecane is almost negligible, ranging between −25 ± 5 and −55 ± 5 cm^{-1} (Table 2). Rather obviously, if the dipole moment of the chromophore diminishes in the upper state, dispersive and induction shifts may cancel (eqs 3 and 4):

$$p = (-5.5 \times 10^4)\Delta\alpha M_w^{-1} + (6.3 \times 10^3)({\mu_g}^2 - {\mu_e}^2)M_w^{-1} \qquad (9)$$

Provided that dipole moments are known from Stark or solvatochromic studies, the polarizability difference can be calculated from the slope of solvatochromic plot p (eq 8)[48,50]

$$\Delta\alpha(\text{Å}^3) = (-1.82 \times 10^{-5})pM_w + 0.11({\mu_g}^2 - {\mu_e}^2) \qquad (10)$$

The dipole moments of acetone in the ground state (2.88 ± 0.03 D, ref 52, pp 9−52) and the excited state (1.81 ± 0.2 D, see next section), and $p = 0$ cm^{-1}, yield a polarizability increase by 0.6 ± 0.2 Å^3, or about 10% of the ground state value (α_g = 6.4 Å^3).[52] The only α_e value we could find in literature[63] is very large, 16.3 Å^3, giving $\Delta\alpha$ equal to ~10 Å^3. Near tripling of polarizability in the excited state is improbable for a forbidden transition and follows from erroneous bathochromic shifts in nonpolar solvents,[25] utilized by Abe.[63]

Remarkable deviations from the $\phi(n^2)$ dependence occur in nonpolar liquids other than *n*-alkanes. The so-called dioxane and perfluoro effects, as well as the tetrachloromethane anomaly, well documented in solvatochromic studies,[49,64,65] are very pronounced in acetone (Figure 4). The behavior of perfluorinated solvents and CCl$_4$ may be rationalized in terms of polarizability density, defined as a ratio of group polarizability after Vogel[66] α_{gp} to van der Waals radius r_w (after Bondi)[67] cubed. In aliphatic compounds the atoms H, C, N, and O possess very similar $\alpha_{gp}/{r_w}^3$ values of 0.24, 0.21, 0.25−0.29, and 0.20, respectively. Notice the closeness of $\alpha_{gp}/{r_w}^3$ to the Lorentz−Lorenz function $\phi(n^2)$ of common solvents. The polarizability densities of F and Cl atoms are very different, amounting to 0.10 and 0.43, respectively. As a consequence, dispersive shifts are less than those predicted in perfluorinated solvents but overestimated for CCl$_4$, brominated (for Br $\alpha_{gp}/{r_w}^3 = 0.55$), and iodine containing ($\alpha_{gp}/{r_w}^3 = 0.71$) liquids, and CS$_2$ ($\alpha_{gp}/{r_w}^3$ for S is 0.54)).

Acetone has a large dipole moment ($\mu_g = 2.88 \pm 0.03$ D)[52] capable of orienting solvent bond dipoles, thus creating reaction fields of multipolar origin that can be responsible for additional hypsochromism. Large blue shifts in dioxane ($\Delta\nu_{1/2}$ = 305 cm^{-1}), and probably in part in C$_8$F$_{18}$ ($\Delta\nu_{1/2}$ = 155 cm^{-1}) can be due to a reaction field created by local dipole moments. To summarize, nonpolar solvents can produce deviations from the correlation lines drawn for a homogeneous set of *n*-alkanes for various reasons, because of either different effective interaction radii (branched alkanes),[68] nonuniform density of polarizability (perfluoroalkanes, CCl$_4$),[49,65] or reaction fields created by charge distributions in multipolar molecules (benzene, dioxane).[64,69]

Polar Solvents. The remaining two interactions between polarizable dipoles depend on solvent dipole density, characterized by static permittivity ε. The polarizing effect of a cavity field has been investigated for centrosymmetric chromophores (eq 5)[61] but remains controversial.[69] Because the polarizability change on n−π* transition is only 10%, the Stark effect of the cavity field is expected to be small and will not be treated here.

The ε dependence of solvent shifts can be more precisely ascertained for aprotic, monofunctional solvents, such as ethers, esters, (mono)halogenides, ketones, nitriles, nitroalkanes, amides, and DMSO, containing either a short linear alkyl chain up to C$_4$, or an aliphatic cycle, attached to a single functionality.[50] Before eq 7 is applied, the refractive index dependent shift components (dispersion and induction) are to be subtracted from the experimental frequency $\nu_{\max}$, by using the slope p of eq 8, as follows

$$\nu_{\max}' = \nu_{\max} - p\phi(n^2) \qquad (11)$$

However, for acetone $p \sim 0$ cm^{-1}, and eq 7 can be applied without correction (Figure 5)

$$\Delta\nu_{1/2} = (-25 \pm 11) + (668 \pm 27)[\phi(\varepsilon) - \phi(n^2)], \quad N = 13, \quad R = 0.9914 \qquad (12)$$

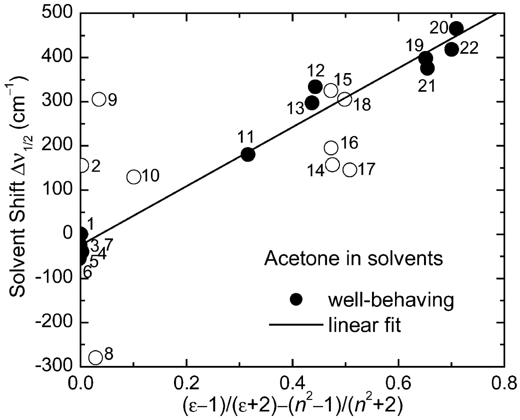

Figure 5. Dependence of solvent shifts of acetone on dipolarity function. Filled symbols correspond to aprotic, aliphatic, monofunctional solvents, effectively obeying classical solvent shift theory.

Protic solvents methanol and water, nonpolar CCl_4, n-C_8F_{18}, and dioxane, polyfunctional $Si(OEt)_4$ and CH_2Cl_2, olefinic *cis*-$C_2H_2Cl_2$, and branched chlorobutanes were removed from the correlation, although CH_2Cl_2 and CH_2ClCH_2Cl do not actually deviate (Figure 5).

By using the slope of eq 12 of 668 cm^{-1}, the ground state dipole moment $\mu_g = 2.88 \pm 0.03$ D,[52] and M_W of acetone 58.08, one obtains from eq 7 for the excited state dipole moment: $\mu_e = 1.81 \pm 0.2$ D. Perhaps accidentally, a nearly identical value was obtained by Abe ($\mu_e = 1.84$ D),[63] using McRae theory,[42] and a small set of data from ref 26. Abe's own method has yielded a smaller value ($\mu_e = 0.86$ D). The dipole moment change of $\Delta\mu \sim 1$ D is fairly characteristic for carbonyl compounds, such as formaldehyde ($\mu_g = 2.332 \pm 0.002$ D,[52] $\mu_e = 1.56 \pm 0.07$ D[70]). Dipole moment difference calculated on a DZP basis set is larger ($\mu_g = 3.36$ D, $\mu_e = 1.48$ D, $\Delta\mu = 1.88$ D), and so is the computed hypsochromism of electrostatic origin[14] (see next section). Another computation by the CASSCF method, considered reliable by Li et al.,[71] has yielded $\mu_e = 2.27$ D (and $\mu_g = 2.90$ D, $\Delta\mu = 0.63$ D).[72] The dipole moments in formulas based on dielectric theory (eqs 4 and 7) refer to gas phase and that of the excited state corresponds to a nonrelaxed molecule. Further theoretical, as well as electro- and solvatochromic studies on both absorption and fluorescence are required to establish the dipole moment differences between the equilibrated and the Franck−Condon states, and the solvent enhancement factors of dipoles.

4.3. Theoretical Implications. ***Theory of Continuous Dielectrics.*** The equations of solvatochromism, based on theory of continuous dielectric liquids,[40−46] hide several controversies that have passed largely unnoticed. The orientational component of the reaction field vanishes in nondipolar solvents, and if $\varepsilon = n^2$, the respective solvent shift $\Delta\nu_{dip}$ is reduced to zero (eq 7). Therefore, the dielectric function has been expressed as a difference between two identical relations of ε and n^2: $\phi(\varepsilon) - \phi(n^2)$.[40−44,46] In the high permittivity limit $\phi(\varepsilon)$ approaches unity, and the difference is solely dependent on refractive index. As noticed already by Brady and Carr,[62] and discussed later by others,[17,73] this is clearly misleading, because the orientational reaction field is a function of solvent dipole density, not of n^2. Such separation of susceptibilities for the low and optical frequencies does not actually follow from the Onsager reaction field R formula for a neat liquid, composed of polarizable point dipoles (eq 4.31 in ref 39 or eq 3.14 in ref 74):

$$R = (8\pi N/9)[(\varepsilon - 1)(n^2 + 2)/(2\varepsilon + n^2)]\mu \qquad (13)$$

where N is concentration (number density) of particles per volume, $N = dN_A/M_W$, where d is density, N_A is Avogadro's number, and μ is dipole moment.

Undoubtedly, the difference $\phi(\varepsilon) - \phi(n^2)$ has been inspired by the Debye equation that is valid only for diluted dipoles in gases or for liquids with very small dipoles, such as toluene, i.e., if ε is either close to unity or only slightly exceeds n^2 (ref 74, Chapter IX). Therefore, $\phi(\varepsilon) - \phi(n^2)$ should be replaced by another function that, if not theoretically relevant, at least behaves correctly at the limits of both low and high ε. The simplest way to subtract electronic polarizability is as follows: $(\varepsilon - n^2)/(\varepsilon - n^2 + c')$, where c' is an empirical parameter. Experimentally, the value of c' is often close to 4 ± 1,[75] and because $n^2 \sim 2$ for most solvents, $(\varepsilon - n^2)/(\varepsilon - 2)$ will be an acceptable form. For acetone, the plots vs $\phi(\varepsilon) - \phi(n^2)$ (Figure 5, eq 12) and $(\varepsilon - n^2)/(\varepsilon + 2)$ have very similar correlation coefficients (Figure 6)

$$\Delta\nu_{1/2} = (-23 \pm 14) + (504 \pm 25)(\varepsilon - n^2)/(\varepsilon + 2), \quad N = 13, \quad R = 0.987 \qquad (14)$$

Out of the four contributions to solvent shifts calculated from eqs 3−7, the dispersion deserves a comment. Because the dispersive effect arises in the closest layer of solvent molecules,[35,76] the repulsive contribution to solvent shift could be prominent (see ref 49). The attractive and repulsive part can be separated, if the distance (r) dependence of intermolecular potential is written as a sum of two contributions, e.g., in the Lennard-Jones form as $\varepsilon[(\sigma/r)^{12} - 2(\sigma/r)^6]$, where ε is the depth of potential well and σ is the equilibrium distance. At the equilibrium position ($r = \sigma$) the attractive to repulsive energy ratio is equal to −2. If σ is the same in the excited state, the same ratio would apply to solvent shift. Therefore, the "pure" dispersive shift would be two times larger than that calculated from eq 3. However, the contribution of the two branches of interaction energy to solvent shift depends critically on the horizontal shift of potentials (see Figure 4a in ref 34), and there is no reason to assume a lack of such shift between different states. As for acetone, the shift of the excited state is unknown, and the partitioning to attractive and repulsive energies remains a future task for both experiment and theory.

Quantum Chemical Calculations. Solvent shifts were computed by Grozema and van Duijnen with their direct reaction field method that is a hybrid quantum mechanics molecular mechanics (QM/MM) procedure, modeling point charges, radii, and polarizabilities of each atom.[14] A comparison of shifts computed in Dunning's polarized double-ζ basis set (DZP) from Table 4 in ref 14 to our $\Delta\nu_{1/2}$ values reveals excellent coincidence for CCl_4 and CH_3CN within a couple of cm^{-1} (Table 3). The following discussion shows that this perfect agreement must be accidental.

Dispersive and electrostatic partial shifts from quantum chemistry[14] can also be compared with those calculated from empirical expressions, (eqs 3 and 7), using $\Delta\alpha = 0.6$ Å^3, $\mu_g = 2.88$ D, $\mu_e = 1.81$ D, and $M_W = 58.08$, as above (Table 3). Surprisingly, dispersive shifts $\Delta\nu_{disp}$ from QM are very large and not correlated with refractive index. Thus, CCl_4 shows the smallest (−342 cm^{-1}) and methanol the largest $\Delta\nu_{disp}$ (−1469 cm^{-1}). According to authors,[11,14] the large radius of the Cl atom is responsible for the small dispersive effect in CCl_4. Quite the contrary, the large observed negative shift in CCl_4 is rationalized

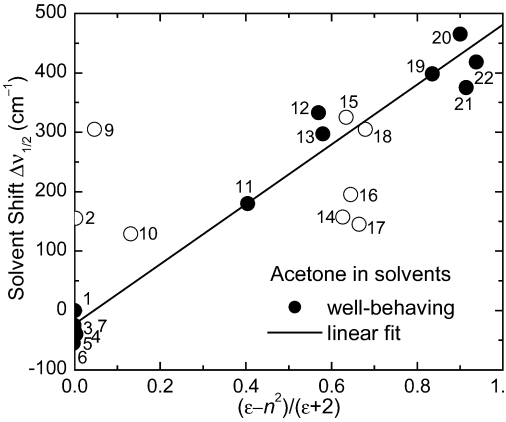

Figure 6. Dependence of acetone absorption shifts on empirical solvent dipolarity function. Filled symbols correspond to a well-behaving set of aprotic, aliphatic, monofunctional solvents.

TABLE 3: Comparison of Solvent Shifts of Acetone n−π* Absorption Band with Quantum Chemical Results from Reference 14[a]

solvent	$\Delta\nu_{1/2}$ (cm^{-1})	$\Delta\nu^b$ (cm^{-1})	$\Delta\nu_{disp}$ (cm^{-1})	$\Delta\nu_{disp}{}^b$ (cm^{-1})	$\Delta\nu_{dip}$ (cm^{-1})	$\Delta\nu_{el}{}^b$ (cm^{-1})
n-hexane	−35 ± 5	−953[c]	−130	−1146[c]	(0)	−29[c]
carbon tetrachloride	−280 ± 10	−278	−156	−342	(0)	−3
dioxane	305 ± 20	54	−144	−1268	(0)	1208
acetonitrile	465 ± 10	478	−120	−1267	470	1588
methanol	941 ± 10	729	−116	−1469	(472)	2127
water	1785 ± 7	1493	−117	−1204	(502)	2503

[a] $\Delta\nu_{1/2}$, experimental shift versus the vapor phase (Table 2); $\Delta\nu$, calculated solvent shift; $\Delta\nu_{disp}$, dispersive shift from eq 3; $\Delta\nu_{dip}$, shift by dipolar reaction field from eq 7; $\Delta\nu_{el}$, electrostatic shift. [b] Calculation, from Table 4 in ref 14. [c] Calculated for cyclohexane.

by us as a result of high polarizability density of Cl atom (see section 4.2). Moreover, the calculated full shift in cyclohexane (−953 cm^{-1}) is far too large, as compared to nearly negligible shifts $\Delta\nu_{1/2}$ in alkanes. It seems that the dispersive stabilization of the excited state is grossly overemphasized in the explicit solvent model.[14]

The dipolar reaction field component $\Delta\nu_{dip}$ (eq 7) can be related with electrostatic contribution $\Delta\nu_{el}$ in ref 14 (Table 3). Because for dioxane $\varepsilon \sim n^2$, the dielectric theory fails to predict a shift, but the local dipole contribution is reflected in calculated $\Delta\nu_{el}$ as large as 1208 cm^{-1}. Since the dispersive effect is overestimated, a too small value (54 cm^{-1}) is obtained for total shift, as compared to experimental $\Delta\nu_{1/2}$ (305 cm^{-1}). Specific solvation is not taken into account in the dielectric model, and the results for methanol and water are placed in parentheses. The observed shift $\Delta\nu_{1/2}$ of 480 cm^{-1} between acetonitrile and methanol, and further up to 1320 cm^{-1} for water, due to hydrogen bonding, are better reproduced in the computation (540 and 920 cm^{-1}, respectively).

Components of solvatochromic shifts have also been calculated and compared to experiment by Li, Cramer, and Truhlar[16] (Table 3 in ref 16). Perfect correspondence of calculated shifts for CCl_4 and ether (−447 and −84 cm^{-1}) to experimental data, available to authors (−440 and −65 cm^{-1}) is misleading, the correct shifts being −280 ± 10 and 180 ± 25 cm^{-1}, respectively. Unfortunately, their approach to dispersive and the H-bonding effect is purely empirical. Moreover, it is based on a single-point calibration, assuming a linear dependence of the dispersive shift on Bayliss function of refractive index $((n^2-1)/(n^2+1/2))$ for cyclohexane, and that of H-bonding induced shift on an empirical hydrogen bond acidity parameter of the solvent, for methanol, respectively. Bearing in mind the "anomalies" in the $\phi(n^2)$ dependencies, discussed above, the use of a dielectric continuum approach is not productive in this context. On the contrary, it tends to cover up interesting details of intermolecular solute−solvent interactions in nonpolar systems, instead of exposing their microscopic mechanisms.

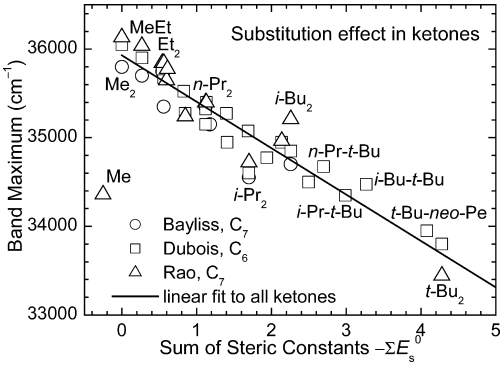

Figure 7. Dependence of absorption maxima of aliphatic ketones in *n*-hexane (C_6) (from refs 28 and 30) and *n*-heptane (C_7) (from ref 77) solutions on steric constants of substituents after Palm (ref 32). Acetaldehyde (Me) deviates to much lower frequencies. Substituents: Me, methyl; Et, ethyl; *n*-Pr, *n*-propyl; *i*-Pr, *iso*-propyl; *t*-Bu, *tert*-butyl.

Obviously, the explicit, polarizable solvent models[11,14] have a greater potential than conventional continuum approaches, however sophisticated, in reproducing solvatochromic behavior. From an experimentalist's point of view, theory has been moderately successful in treating electrostatic and hydrogen bonding effects. Since the Onsager theory fails to take into account self-association of solvents by means of H-bonding, most computer calculations deal exclusively with water,[1−3,5,6,13,15,18−24] where the vapor-to-bulk shift is well established in the case of acetone (1700 ± 50 cm^{-1}),[27−30] reproduced in this work (1785 ± 7 cm^{-1}). Results pertaining to nonaqueous systems remain less definitive,[4,7−12,14,16,17] mainly because of inconsistencies in experimental data.[25−30] In order to obtain proper parametrization for dispersive−repulsive potentials, a closer comparison to measurements under substantial pressure is needed.

4.4. Substituent and Solvent Effects in Higher Aliphatic Ketones. The absorption maxima in aliphatic ketones shift bathochromically with increasing the bulkiness and branching of alkyl substituents.[28,30,77] The spectral shift between acetone and di-*tert*-butyl ketone in hexane solution amounts to −2250 cm^{-1} (Table 1(b) in ref 28). A remarkable correlation can be established between ν_{max} and the sum of steric constants of substituents after Taft and Palm,[31,32,78] $-\Sigma E_s{}^\circ$ (Figure 7)

$$\nu_{max}(C_6,C_7) = (35931 \pm 50) + (524 \pm 27)\sum E_s{}^\circ, \quad N = 43, \quad R = 0.948. \quad (15)$$

It follows from eq 15 that bulky substituents stabilize the excited state relative to the ground state. This may seem surprising, bearing in mind that the negative dispersive shift and the positive induction shift (due to a diminishing dipole) cancel almost exactly in *n*-alkane solvents (see section 4.2). Treating the influence of substituents as internal solvent effect with respect to the carbonyl group, one may suspect that the effective radii for these two interactions differ. In the case of bulky groups, the short-range dispersion produces a strong red shift that is not fully compensated by long-reaching polarization (induction), since the latter feels the polarizability averaged over a larger volume. Incidentally, the steric constants $-E_s°$ (Table 1), defined on the basis of logarithms of the rate constants for hydrolysis reactions of esters, nicely describe the combined effect of both the volume (polarizability) of aliphatic groups, and their proximity to chromophore. However, aldehydes have much lower transition energies than those predicted from the negligible steric influence of hydrogen atom (for acetaldehyde $-\Sigma E_s° = -0.25$, Figure 7).

Shorter interaction radius for the dispersive shift can also be responsible for anomalous behavior in perfluorinated solvents and CCl_4, as discussed above. Because of very different polarizability densities α_{gp}/r_w^3, the red shift is suppressed in n-C_8F_{18}, and enhanced in CCl_4, as compared to alkanes (Table 2, Figure 4) (see Section 4.2).

Solvent shifts tend to diminish with increasing $-\Sigma E_s°$, because the access to the chromophore is progressively restricted by bulky substituents (Table 1).[28,30,77] However, a sign change of solvent shifts (relative to maximum in hexane, Table 1b in ref 28) with increasing bulkiness of substituents, observed in polar aprotic solvents, such as ether, tetrahydrofuran, acetonitrile,[28] and hexametapol,[79] is not expected. Although we did not check the spectra of higher ketones, it is highly probable that, owing to smearing out of spectral structure in polar surroundings, a ~ -300 cm^{-1} pseudoshift will occur, as in the case of acetone (Figure 2). The hypsochromic reaction field and polarization components are suppressed in crowded ketones, and the negative apparent shift prevails. The centers of gravity and the band-halving procedure can be suggested as methods of choice for eliminating spurious shifts.

5. Conclusions

A simple method of "band-halving" has been introduced for reliable determination of solvent shifts for poorly defined maxima of broad, humpy spectral envelopes. Absolute shifts between the vapor phase and solutions are reported for acetone (Table 2), a popular model chromophore for computer chemical calculations.[4−24] Inconsistencies in the shift data, existing in older literature for less polar environments,[25−30] have been corrected for. The dipole moment and polarizability of the excited state were estimated from empirically calibrated solvent shift equations. Aprotic, aliphatic, monofunctional solvents apparently obey better the Onsager theory, enabling one to increase the precision of the solvatochromic method.[48,50]

There is little theoretical justification to widely accepted expressions for induction and dipolar reaction field effects[40−44,59] that cannot be deduced from the Onsager equation for neat polar liquids.[39,74] Instead, a simple empirical expression is proposed that is valid at both low and high polarity limits (eq 14, Figure 6).

Aliphatic substituents with increasing bulkiness cause a progressive red shift of n−π* absorption in ketones[28,30,77] that shows a good correlation with steric constants[31,32,78] (eq 15, Figure 7). The effect can be rationalized, if the dispersion and induction with respect to substituents, regarded as "internal solvent", have different interaction radii.

Large scatter of data points on plots versus some dielectric function, usually regarded as a nuisance, offers excellent opportunities to probe fine details of intermolecular interactions. Qualitatively, solvation energy changes can be explained in terms of electric charges and polarizability densities, as well as electron and proton donating or accepting properties of solute and solvent molecules. Quantum chemistry and molecular modeling is in a position of forming a computational basis to such mechanistic understanding. Careful measurements, in conjunction with judicious use of dielectric functions and flexible QM/MM/MC (quantum mechanics, molecular mechanics, Monte Carlo) computations[1−24] would undoubtedly result in a greatly improved understanding of spectral solvent shift mechanisms on the microscopic level, not only in the special case of acetone but also for impurity spectra in general.

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JP9033886