

Solvent Dependence of the Intensity of the Absorption Band of Carbon Disulfide at 316 nm

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The integrated intensity of the absorption band of carbon disulfide at about 316 nm has been measured in the gas phase and in sixteen solvents. It is found that the absorption intensity rises steeply with the refractive index of the solvent, whereas the wavenumbers of the absorption maxima exhibit a small red shift. Both results are explained, according to Liptay's theory of solvatochromism, as due to dispersion interactions.

Introduction

The absorption spectrum of gaseous carbon disulfide in the near UV consists of a band system extending from about 380 to 290 nm. This system arises from at least two electronic transitions, a very weak one in the range 380—330 nm, a more intense one in the range 330—290 nm.

The rotational structure of the first transition is relatively simple, and has been analyzed in detail^{1,2}. It turns out that this transition leads to an elec-

tronic state in which the molecule is non linear ($S-C-S=136^\circ$). The second transition exhibits an exceedingly complex and apparently irregular rotational structure¹, which has not yet been analyzed. As regards the vibrational structure, RAMASASTRY³ observed long progressions with a spacing of about 450 cm^{-1} , and concluded that most probably this transition also leads to an excited state in which the molecule is slightly bent.

In solutions only the second transition is observed; it appears as a band extending from about

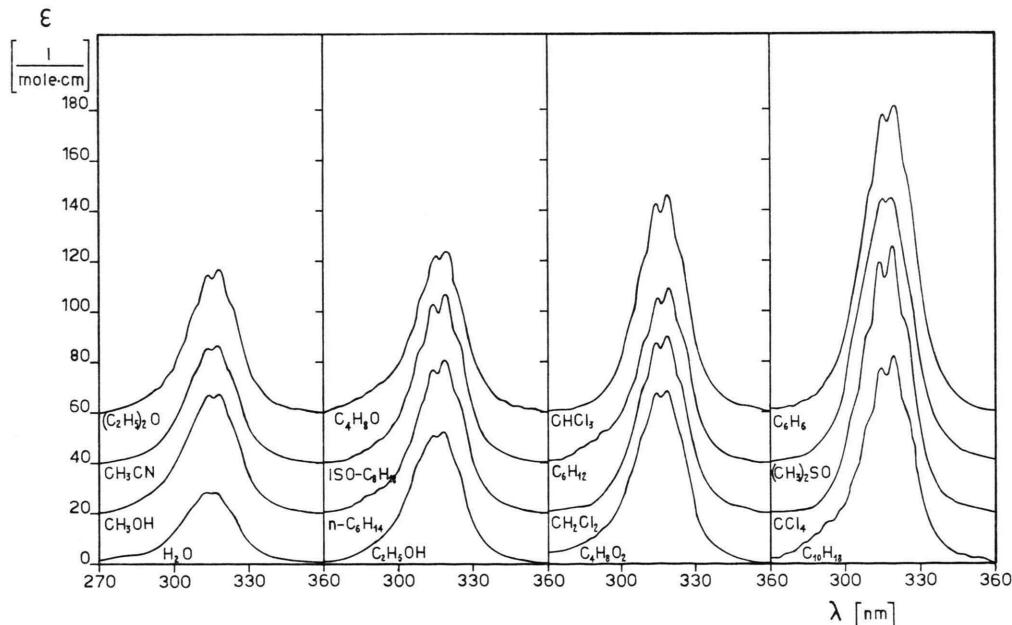


Fig. 1. The absorption band of carbon disulfide in various solvents. (The ordinate scales are displaced by 20 units of ϵ .)

¹ B. KLEMAN, Canad. J. Phys. **41**, 2034 [1963].

² G. HERZBERG, Electronic Spectra of Polyatomic Molecules, Van Nostrand, Princeton 1966, pp. 504 and 601.

³ C. RAMASASTRY, Proc. Natl. Inst. Sci. India **18**, 177 [1952] (C. A. **47**, 2596 [1953]).

360 to 270 nm, showing two maxima of moderate intensity ($\log \epsilon \approx 2$) at about 318 and 314 nm. Besides these maxima, in some solvents there appear distinct traces of vibrational structure, especially on the high frequency side (Fig. 1).

In 1951 TREIBER and KOREN⁴ observed that the intensity of this band depends strongly on the nature of the solvent. In this work we report the results of a study of its integrated intensity in the gas phase and in several solvents of widely different properties.

Experimental

The measurements were carried out by means of a Beckman DK-2A spectrophotometer. The solution spectra were recorded in absorbance; recording range 360–270 nm, speed 9 nm/min, spectral slit-width at the band centre 0.45 nm (45 cm^{-1}).

Cells of thicknesses 1 and 0.1 cm were used, according to the transparency of solvents (for water, cells of 5 cm were employed because of the low solubility of carbon disulfide).

Carbon disulfide was a reagent-grade product (Erba RP). Solvents were spectrophotometric-grade products (Erba RS), except dimethylsulfoxide and decalin (Erba RP). The latter contained aromatic impurities, which were removed by treatment with dilute H_2SO_4 , followed by washing with dilute NaOH and water, drying on drierite and repeated fractionating under reduced pressure.

In order to avoid evaporation losses, the required amount of carbon disulfide was introduced into a volumetric flask filled with solvent by means of a microsyringe through a plug fitted with a gasket of silicone rubber. This method yielded very reproducible and accurate results, confirmed by checking the fulfilment of Beer's law.

Because of the limited resolving power of our spectrometer, we employed for the measurement of the gas-phase intensity the method of BOURGIN^{5, 6}. This consists in determining the value of the absorption area:

$$\frac{1}{C l} \int_{\text{band}} (1 - T) d\tilde{\nu}$$

(where C : concentration, l : cell thickness, T : transmittance) at various concentrations, and extrapolating to zero concentration (Fig. 2).

As the absorption area does not depend on the slit function, the nature of the extrapolation depends only on the form of the band, and not on the resolving power of the spectrometer.

During these measurements the scanning speed was 45 nm/min and the spectral slit width at the band

centre 1.5 nm (150 cm^{-1}). Carbon disulfide was introduced into the cell (thickness 1 cm, volume 3.55 cm^3) by means of a microsyringe, following the same technique used for the preparation of solutions. As carbon disulfide vapour is slowly adsorbed by silicone rubber, the measurement was repeated at intervals of about two minutes, and the absorption areas thus determined were extrapolated to zero time.

Results and Discussion

The results are collected in Table 1 (see also Fig. 1). It is at once evident that the intensity increases rapidly and rather regularly with the refractive index of the solvent, whereas the polarity of the latter does not seem to exert any appreciable systematic effect.

Such a behaviour is to be contrasted with the trend of the frequencies of both maxima, which change only slightly with the refractive index of the solvent. This change seems entirely explainable in terms of dispersion interactions: in fact, increasing the refractive index causes a small red shift, as usually observed (Fig. 3). LIPTAY^{7, 8} has derived the following equation for the wavenumber shift of an electronic absorption band:

$$\tilde{\nu}_{\text{sol}} - \tilde{\nu}_{\text{gas}} = - \frac{(\mu_e - \mu_g) F_{\text{RM}}}{h c} - \frac{2(n^2 - 1)}{a^3(2n^2 + 1)} D \quad (1)$$

where μ_e and μ_g are the dipole moments of the molecule in the excited and ground states respectively, F_{RM} is the arithmetic mean of the reaction fields acting upon the molecule in the ground state and in the Franck-Condon excited state, n is the refractive index of the solution, a is the radius of the spherical cavity occupied by the molecule inside the solvent according to the ONSAGER's dielectric model⁹, and D is a term describing the effect of the dispersion interactions on the position of the band.

F_{RM} depends on the dipole moments of the molecule in the ground state and in the Franck-Condon excited state; for CS_2 , $\mu_g = 0$, $\mu_e = 0$ too (because in the Franck-Condon state the coordinates of the nuclei are the same as in the ground state), and therefore $F_{\text{RM}} = 0$. Thus $\tilde{\nu}_{\text{sol}}$ should vary linearly with $(n^2 - 1)/(2n^2 + 1)$. Such a behaviour is experimentally verified (within the usual limits of accuracy of a model treating the solvent as a continuous dielectric medium); from the slopes of the

⁴ E. TREIBER and H. KOREN, Monatsh. **82**, 1109 [1951].

⁵ D. G. BOURGIN, Phys. Rev. **29**, 794 [1927].

⁶ D. A. RAMSAY, J. Amer. Chem. Soc. **74**, 72 [1952].

⁷ W. LIPTAY, Z. Naturforsch. **20a**, 1441 [1965].

⁸ W. LIPTAY, Angew. Chem. (Internat. Edit.) **8**, 177 [1969].

⁹ L. ONSAGER, J. Amer. Chem. Soc. **58**, 1486 [1936].

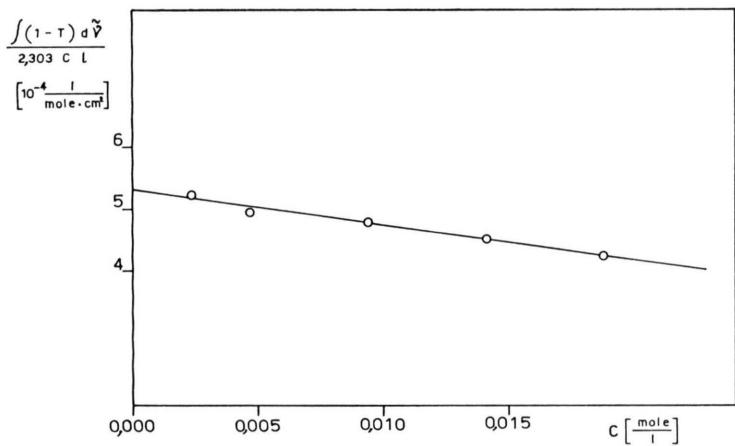


Fig. 2. Determination of the gas-phase intensity by the method of Bourgin.

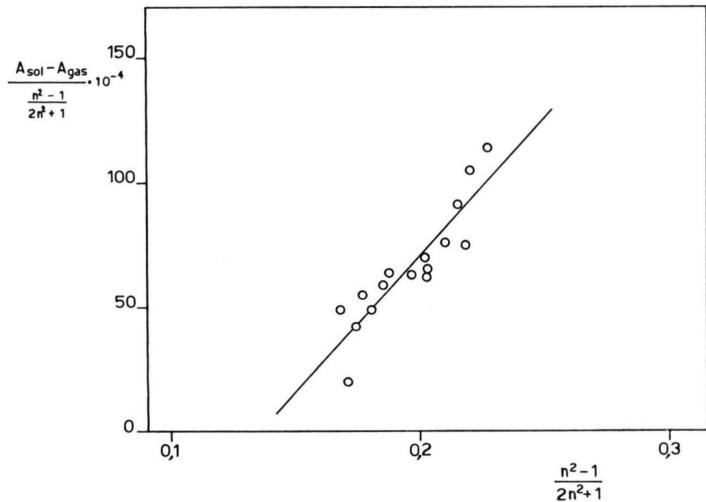


Fig. 4. Dependence of the integrated intensity on the refractive index of the solvent.

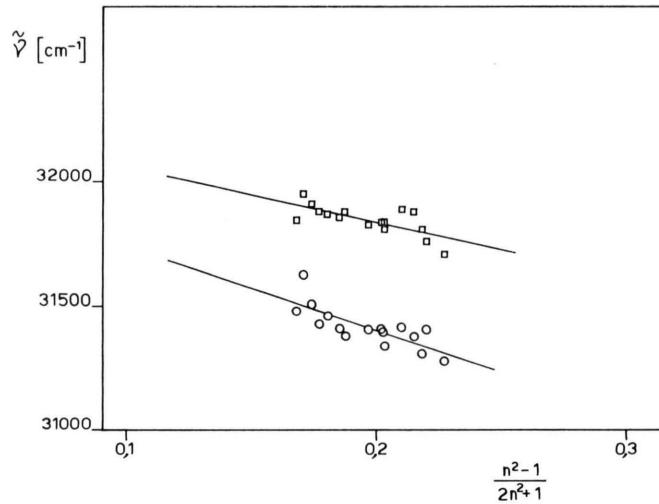


Fig. 3. Dependence of the wavenumbers of the absorption maxima on the refractive index of the solvent.

Table 1.

Solvent	$n_{\text{D}}^{25^{\circ}}$	$\tilde{\nu}_1$ [cm ⁻¹]	$\tilde{\nu}_2$ [cm ⁻¹]	A [mole ⁻¹ l · cm ⁻²]
Vapour	—	—	—	$5,3 \cdot 10^4$
Methanol	1,326	31850	31480	$13,5 \cdot 10^4$
Water	1,333	31950	31630	$8,7 \cdot 10^4$
Acetonitrile	1,342	31910	31510	$12,6 \cdot 10^4$
Diethyl ether	1,350	31880	31430	$15,0 \cdot 10^4$
Ethanol	1,359	31870	31460	$14,1 \cdot 10^4$
n-Hexane	1,372	31860	31410	$16,2 \cdot 10^4$
Iso-octane	1,389	31880	31380	$17,3 \cdot 10^4$
Tetrahydrofuran	1,404	31830	31410	$17,7 \cdot 10^4$
Dioxan	1,420	31840	31410	$19,4 \cdot 10^4$
Methylene chloride	1,422	31840	31400	$17,8 \cdot 10^4$
Cyclohexane	1,424	31810	31340	$18,6 \cdot 10^4$
Chloroform	1,444	31890	31420	$21,3 \cdot 10^4$
Carbon tetrachloride	1,459	31880	31380	$24,8 \cdot 10^4$
Decalin	1,471	31810	31310	$21,7 \cdot 10^4$
Dimethylsulfoxide	1,475	31760	31410	$28,3 \cdot 10^4$
Benzene	1,498	31710	31280	$31,2 \cdot 10^4$

$\tilde{\nu}_1$, $\tilde{\nu}_2$: wavenumbers of absorption maxima; $A = \int \varepsilon d\tilde{\nu}$; $\varepsilon = 1/C l \cdot \log(1/T)$.

straight lines of Fig. 3 one obtains for D/a^3 a value of about 1400 cm^{-1} , fully reasonable for a weak band⁷.

Returning now to the solvent dependence of the intensity, we have found that it also can be explained, in the frame of Liptay's theory, as due simply to dispersion interactions. In fact, Liptay has derived the following expression for the transition moment of a dissolved molecule^{8, 10}:

$$\mu_{\text{ge}}^{\text{sol}} = \mu_{\text{ge}}^{\text{gas}} + a_{\text{ge}} F_{\text{RM}} + \frac{2(n^2-1)}{a^3(2n^2+1)} W_{\text{ge}} \quad (2)$$

where a_{ge} is the so-called "transition polarizability", and W_{ge} is a vector describing the effect of the dispersion interactions on the transition moment. The expression of W_{ge} is very complicated [see Eqs. (47) and (61) of Ref. ¹⁰], but it depends mainly on the dissolved molecule, and only slightly on the solvent. In our case ($F_{\text{RM}}=0$):

$$|\mu_{\text{ge}}^{\text{sol}}|^2 = |\mu_{\text{ge}}^{\text{gas}}|^2 + \frac{4(n^2-1)}{a^3(2n^2+1)} \mu_{\text{ge}}^{\text{gas}} \cdot W_{\text{ge}} + \left[\frac{2(n^2-1)}{a^3(2n^2+1)} \right]^2 |W_{\text{ge}}|^2 \quad (3)$$

$$\text{and since } A = \frac{8\pi^3 N_A \tilde{\nu}_{\text{eg}}}{2303 \cdot 3 h c} |\mu_{\text{ge}}|^2 = C |\mu_{\text{ge}}|^2 \quad (4)$$

$$\text{we obtain } \frac{A_{\text{sol}} - A_{\text{gas}}}{(n^2-1)/(2n^2+1)} = \frac{4C}{a^3} \mu_{\text{ge}}^{\text{gas}} \cdot W_{\text{ge}} + \frac{4C}{a^6} |W_{\text{ge}}|^2 \frac{n^2-1}{2n^2+1}. \quad (5)$$

Assuming W_{ge} to be independent on the solvent, a plot of the left-hand side of Eq. (5) vs. $(n^2-1)/(2n^2+1)$ should be linear. This is confirmed by the graph of Fig. 4. From a least-squares inter-

¹⁰ W. LIPTAY, Z. Naturforsch. **21a**, 1605 [1966].

polation it follows:

$$\frac{4C}{a^3} \mu_{\text{ge}}^{\text{gas}} \cdot W_{\text{ge}} = -151 \cdot 10^4 \text{ mole}^{-1} \text{ l cm}^{-2},$$

$$\frac{4C}{a^6} |W_{\text{ge}}|^2 = 111 \cdot 10^5 \text{ mole}^{-1} \text{ l cm}^{-2}.$$

On symmetry grounds, the vector μ_{ge} must lie along the molecular axis or perpendicular to it; the same is true for the vector W_{ge} . Since the scalar product $\mu_{\text{ge}} \cdot W_{\text{ge}}$ is different from zero and negative, the two vectors cannot be mutually perpendicular and must lie in opposite directions [this follows also from Eq. (47) of Ref. ¹⁰].

We can check the above interpretation by calculating A_{gas} from the coefficients of Eq. (5). Indeed:

$$\frac{1}{4} \frac{[4C |\mu_{\text{ge}}| |W_{\text{ge}}|/a^3]^2}{4C |W_{\text{ge}}|^2/a^6} = C |\mu_{\text{ge}}|^2 = A_{\text{gas}}. \quad (6)$$

Replacing the values calculated above we obtain:

$$A_{\text{gas}} = \frac{1}{4} (151 \cdot 10^4)^2 / 111 \cdot 10^5 = 5.1 \cdot 10^4 \text{ mole}^{-1} \text{ l cm}^{-2}$$

a value which compares very well with the experimental one of $5.3 \cdot 10^4$.

Now, supposing to increase smoothly the refractive index starting from the gas-phase value of unity, the intensity first decreases, becomes zero for $n = \sim 1.12$, then increases and eventually becomes greater than A_{gas} . This is a consequence of the change of sign of the transition moment, as is clear from Eq. (2). It would be interesting to find an absorption band, the intensity of which becomes zero for an accessible value of the refractive index.

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