

INFRARED STUDIES OF SOLVENT-SOLUTE INTERACTIONS; DEUTERIUM SUBSTITUTED DERIVATIVES OF ACETYLENE IN SOLUTION

AZIHAR MAHMOOD SYED

PCSIR Laboratories Complex, Karachi, Pakistan

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The Buckingham's theory deals with the effects of solvents on deuterated vibrations of the solute as compared to the normal IR group frequencies. Acetylene and its deuterium substituted derivatives have been studied taking the relative frequency shifts and band-half widths of C-H and C-D vibrations.

Key words : Solvent-solute interaction, Deuterated-acetylene.

Introduction

A quantum mechanical treatment of solvent-solute interaction has been given by Buckingham [1], using the basic KBM model of diatomic oscillator. The theory predicts that for two isotopic species A and B.

$$(\Delta\nu/\nu)_A = (\Delta\nu/\nu)_B$$

The second isotopic relationship deduced from the theory concerns the band-half-widths. On the assumption that the widths of the infrared absorption bands of dissolved molecules are dominated by fluctuations in the solvent environment, the relationship is that

$$(\Delta\nu_{1/2}/\nu)_A = (\Delta\nu_{1/2}/\nu)_B$$

For diatomic molecules such as HCl and DCl the above theory has been found to be in agreement with experiment. For polyatomic molecules, Caldwell *et al.* [2] tested the Buckingham's theory on HCN and DCN molecules. The relative frequency shifts of the C-H and C-D stretching modes, disagreed with the predictions.

It has been an important aim of the present work to make further tests of the isotopic relationships for relative frequency shifts and band-half-widths on C-H and C-D stretching modes of a polyatomic acetylene molecule. The infrared active C-H stretching mode of acetylene is particularly suitable for this investigation as the mode can be approximated as a diatomic oscillator. The anti-

symmetrical C-H stretching vibration of acetylene, ν_3 is the only one of its symmetry type (Σ_u^+) and as long as the symmetry is maintained in solution, this vibration cannot interact with any other mode.

Experimental

Spectra were recorded on a Perkin-Elmer 125 spectrophotometer which is a double beam instrument with a limiting resolution of 0.3 cm^{-1} at 2500 cm^{-1} . The wave number accuracy is $\pm 0.5 \text{ cm}^{-1}$ and reproducibility better than the accuracy. The calibration was checked by water vapour spectra using the instrument on single beam and comparing with standard Tables [3].

Preparation of the deuterated acetylene. Dideo-teroacetylene was prepared by the action of heavy water on calcium carbide.

Results and Discussion

The vapour phase vibration frequencies of deuterioacetylene and acetylene gas have been reported by Tally *et al.* [4] and Plyler [5] respectively. The measurements in solutions have been confined to the frequency shifts and band-half-widths of infrared active stretching mode (ν_3). Table 1 shows the frequency shifts of ν_3 for C_2H_2 and C_2D_2 in a range of organic solvents.

In general no severe problems were met in measuring ν_3 even though its frequency was quite close to the

TABLE 1. FREQUENCIES AND FREQUENCY SHIFTS FOR ν_3 OF C_2H_2 AND C_2D_2 IN ORGANIC SOLVENTS.

Solvents	C_2H_2		C_2D_2		$\frac{\Delta\nu_3\text{H}}{\Delta\nu_3\text{D}}$
	$\nu_3 \text{ cm}^{-1}$	$\nu_3 \text{ cm}^{-1}$	$\nu_3 \text{ cm}^{-1}$	$\nu_3 \text{ cm}^{-1}$	
Gas	3283	-	2439	-	-
Carbondisulphide	3257	26	2418	21	1.24
Carbontetrachloride	2560	23	2422	17	1.35
Benzene	3246	37	2410	29	1.28
Acetone	3216	67	2389	50	1.34
Dioxan	3209	74	2383	56	1.32
Dimethylsulphoxide	3128	125	2341	98	1.28

atmospheric carbondioxide absorption centred at 2350 cm^{-1} . The gas phase value of ν_3 has been quoted as 3283 cm^{-1} , for C_2H_2 [5] and as 2439 cm^{-1} for C_2D_2 [4].

If Buckingham's [1] theory is strictly obeyed the ratio of $\Delta\nu$ for acetylene to that of dideuteroacetylene should be 1.35, taking observed values of ν_g for these species. The ratio $\Delta\nu_{\text{H}}/\Delta\nu_{\text{D}}$ (Table 1), is found to vary between 1.24 and 1.35. No significance can be attached either to this variation or to the fact that the mean value of 1.30 lies a little below the predicted value. The reason for this is that the value of the ratio is quite sensitive to the measured frequency shifts, particularly when these are small. The frequency measurements are considered accurate to $\pm 0.5\text{ cm}^{-1}$. The conclusion is that, the agreement with Buckingham's prediction regarding the isotopic substitution is as close as can be expected in these experimental circumstances.

TABLE 2. BAND-HALF-WIDTHS ($\Delta\nu_{1/2}$) OF ν_3 FOR C_2H_2 AND C_2D_2 IN ORGANIC SOLVENTS.

Solvents	C_2H_2 $\Delta\nu_{1/2}\text{ cm}^{-1}$	C_2D_2 $\Delta\nu_{1/2}\text{ cm}^{-1}$	$\frac{(\Delta\nu_{1/2})_{\text{H}}}{(\Delta\nu_{1/2})_{\text{D}}}$
Carbondisulphide	27	22	1.23
Carbontetrachloride	23	18	1.28
Benzene	22	17	1.29
Acetone	43	33	1.30
Dioxan	47	38	1.23
Dimethylsulphoxide	59	47	1.25

A comparison between the band-half-widths for ν_3 of C_2H_2 and C_2D_2 is shown in Table 2. It can be seen that the half-widths for the deuterio compound are markedly lower than for acetylene. Also the results lead to set of values of $(\Delta\nu_{1/2})_{\text{H}} / (\Delta\nu_{1/2})_{\text{D}}$ which vary over the narrow range from 1.23 to 1.29 in spite of a large variation in the individual half-widths.

In Buckingham's treatment of absorption line shapes in isotopically substituted species the basic deduction is that the ratio of the second moments should be equal to that of the vibration frequencies. If there is a simple direct relationship between second moment and band-half-widths (as there is for example for a Gaussian band shape), then $\Delta\nu_{1/2} / \nu$ remains invariant on isotopic substitution. For ν_3 of acetylene this requires $(\Delta\nu_{1/2})_{\text{H}} / (\Delta\nu_{1/2})_{\text{D}}$ to be 1.35, which is the same value as for the frequency shifts. The results as shown in Table 2 are sufficiently close to the prediction to suggest that Buckingham's treatment is at least a good first approximation.

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