

## EFFECT OF SOLVENT-SOLUTE INTERACTIONS ON C—H AND C≡C STRETCHING VIBRATIONS OF ACETYLENE

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**Abstract.** The antisymmetric C—H and symmetric C≡C stretching vibrations ( $\nu_3$  and  $\nu_2$ ) of acetylene have been studied in solution. Accurate measurements of the frequency of the C≡C stretching vibration which appeared in a range of solvents have shown the involvement of C≡C group into specific interactions similar to the C—H group.

The IR studies of the vibrational spectra of liquids and solutions have proved that in a number of cases specific interactions occur between molecules. These make a major contribution to the frequency shifts observed in passing from the vapour. The investigation of X—H vibrations has been concerned mainly with the systems containing O—H or N—H linkages in situations where strong hydrogen bond interactions occur. In recent years studies have been extended to weaker interactions which, for example, may involve an O—H group and  $\pi$ -electrons of a multiple bond or an aromatic ring. The number of instances where specific interactions involving C—H groups have been studied are very much limited and comparatively little work has been reported. The marked acidity of monosubstituted acetylenes, as shown by their ability to form metallic salts, suggests that the acetylenic C—H linkage should be able to take part in hydrogen bond formation and possibly also in specific interactions of a less clearly defined type.

Gastilovich and his coworkers<sup>1</sup> have investigated acetylene in a range of organic solvents and concluded that hydrogen bond formation occurs and put forward evidence of specific solvent-solute interactions. In the present work, it has been considered that acetylene is a highly symmetrical simple molecule and has fundamentals which are forbidden in the IR spectrum of the free acetylene molecule. When solvent-solute interactions occur there is the possibility of the breakdown of the selection rules and, therefore, an opportunity for showing up intermolecular effects.

### Experimental

Spectra were recorded on a Perkin-Elmer 125 spectrometer which is a double-beam instrument with a limiting resolution of  $0.3 \text{ cm}^{-1}$  at  $2500 \text{ cm}^{-1}$ . It has a stated wave number accuracy of  $\pm 0.02\%$  and reproducibility better than this accuracy.

The spectra of all the solvents used were examined in the region  $4000\text{--}400 \text{ cm}^{-1}$  and compared with published curves. Dimethylsulphoxide (B.D.H.) was dried before use by molecular sieve drying agent.

The acetylene gas was commercial cylinder acetylene (British Oxygen Co.) dissolved in acetone, and to remove traces of moisture and solvent, the gas was bubbled through sulphuric acid (concd) before use. The spectrum at 63 mm pressure in a 10-cm gas-cell was in good agreement with published work.<sup>2,3</sup>

Saturated solutions were prepared by bubbling acetylene through the solvent for several hours. Those solvents were selected which gave suitable transmittance in the region of interest and were equally important for their theoretical background in the solvent-solute interaction studies. Compensation of the solvent was achieved by using variable path-length cell (Research and Industrial Instruments Co., England).

### Results and Discussion

Tables 1 and 2 show the frequencies and frequency shifts of the C—H stretching vibration of acetylene and N—H stretching vibration of pyrrole respectively, in a range of solvents. Solvents selected are such that they cover a wide range of frequency shifts in passing from vapour and are important for the solvent-solute interaction studies. The N—H stretching vibration of pyrrole has already been reported by Bellamy.<sup>4</sup>

Table 3 shows the frequencies and frequency shifts of the weakly appearing Raman active C≡C stretching vibration of acetylene in the same range of solvents. Kiyama *et al.*<sup>5</sup> have studied acetylene vapour in a mixture of hydrogen, nitrogen and argon at 20 atmospheres and observed weak absorption at  $1974 \text{ cm}^{-1}$ , associated with the forbidden C≡C stretching vibration. Similar work has also been reported by Coulon<sup>6</sup> and Welsh<sup>7</sup> for a number of compressed gases and interpreted as being associated with induced dipole absorption which arises during the collisions of pairs of molecules. Van Kranendonk<sup>8</sup> has given a theoretical treatment of the effect in which the induced electric dipole moment arising during collisions between nonpolar molecules is a result of (i) the asymmetric distortion of electronic wave functions by the overlapping of atomic orbitals in the colliding species and (ii) the polarisation of one molecule by the electric quadrupole moment in the other. In a mixture of a polar and nonpolar gas a much more important effect occurs in which the oscillating dipole of the polar molecule induces absorption from the normally forbidden frequency of the nonpolar gas.

Barrow<sup>9</sup> has recently studied acetylene in a mixture of carbon tetrachloride and acetone and concluded that absorption at  $1964 \text{ cm}^{-1}$  is associated with a 1:1 complex between acetylene and ketone, assuming that no absorption is present from acetylene in car-

TABLE 1. IR ACTIVE C—H STRETCHING VIBRATION ( $\nu_3$ ) OF ACETYLENE.

Solvents	C—H Stretching vibration ( $\text{cm}^{-1}$ )	Frequency shift ( $\text{cm}^{-1}$ )	$\frac{\Delta\nu}{\nu} \times 10^3$
Gas	3283 <sup>3</sup>	—	—
Carbon tetrachloride	3260	23	7.0
Bromoform	3249	34	10.0
Ethyl cyanide	3233	50	15.2
Methyl <i>n</i> -propyl ketone	3223	60	18.3
Dimethylsulphoxide	3158	125	38.0

TABLE 2. IR ACTIVE N—H STRETCHING VIBRATION OF PYRROLE.

Solvents	N—H Stretching vibration ( $\text{cm}^{-1}$ )	Frequency shift ( $\text{cm}^{-1}$ )	$\frac{\Delta\nu}{\nu} \times 10^3$
Vapour	3530	—	—
Carbon tetrachloride	3500	30	8.9
Bromoform	3478	52	16.4
Ethyl cyanide	3414	116	34.1
Methyl <i>n</i> -propyl ketone	3375	155	43.9
Dimethylsulphoxide	3195	335	94.9

TABLE 3. RAMAN ACTIVE  $\text{C} \equiv \text{C}$  STRETCHING VIBRATION ( $\nu_2$ ) OF ACETYLENE.

Solvents	$\text{C} \equiv \text{C}$ Stretching vibration ( $\text{cm}^{-1}$ )	Frequency shift ( $\text{cm}^{-1}$ )	$\frac{\Delta\nu}{\nu} \times 10^3$
Gas	1974 <sup>2</sup>	—	—
Carbon tetrachloride	1963	11	5.5
Bromoform	1959	15	7.6
Ethyl cyanide	1957	17	8.6
Methyl <i>n</i> -propyl ketone	1956	18	9.1
Dimethylsulphoxide	1954	29	14.6

bon tetrachloride alone. In the present study, the appearance of absorption at  $1973 \text{ cm}^{-1}$  in carbon tetrachloride and at  $1950 \text{ cm}^{-1}$  in acetone, contradicts the above results.

Several theories have been put forward regarding the solvent-solute interactions, taking into account the polar, nonpolar and hydrogen bonding solvents. These include the dielectric, refractive index and local association properties. Bellamy and his coworkers<sup>4</sup> have supported the local association theory by examining the plot of relative frequency shifts for the X—H vibration against the N—H vibration of pyrrole. It has been considered in the present work that local association effects are of major importance and that a simple, linear and symmetrical polyatomic molecule like acetylene is very suitable for such studies.

Figure 1a shows a plot of  $\frac{\Delta\nu}{\nu}$  for the C—H stretching vibration of acetylene against  $\frac{\Delta\nu}{\nu}$  for the N—H stretching vibration of pyrrole. Fig. 1b shows a similar plot for the Raman active  $\text{C} \equiv \text{C}$  stretching vibration of acetylene in the same range of solvents. For both the vibrations, the plots are linear and weak interacting as well as strong hydrogen bonding solvents lie on the respective straight lines showing evidence of specific solvent-solute interactions. A

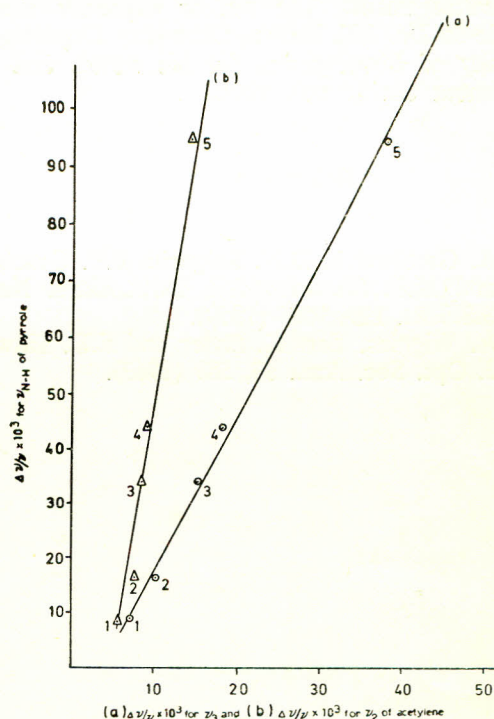


Fig. 1

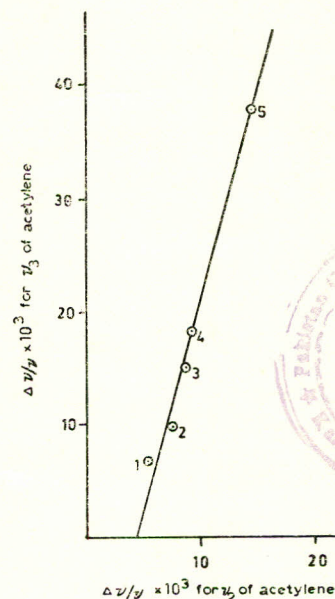


Fig. 2

Figs. 1(a,b) and 2. (1) Carbon tetrachloride, (2) bromoform (3) ethyl cyanide, (4) methyl *n*-propyl ketone, (5) dimethylsulphoxide.

further check has been made by plotting  $\frac{\Delta\nu}{\nu}$  for the C—H stretching vibration against  $\frac{\Delta\nu}{\nu}$  for the  $\text{C} \equiv \text{C}$  stretching vibration of acetylene, giving again a straight line (Fig. 2). Variation of the slope for the two vibrations (Fig. 1) may suggest the degree of interaction. The  $\text{C} \equiv \text{C}$  group being a donor of  $\pi$ -electrons is affected less than the C—H group, but the nature of the interactions are similar.

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