IR STUDIES OF SOLVENT-SOLUTE INTERACTIONS; ESTIMATION OF RAMAN ACTIVE FUNDAMENTAL FREQUENCIES OF ACETYLENE IN SOLUTIONS

Azhar M. Syed

PCSIR Laboratories, Karachi

Specific solvent-solute interactions involving C–H and C≡C groups of acetylene have been studied. Acetylene has two IR active and three Raman active fundamental vibrations. It has become possible to estimate the frequency shifts of Raman active fundamentals by the observation of binary combination bands in a range of solvents.

Key words: Raman active frequencies in solutions.

INTRODUCTION

It has already been investigated that vibrational spectra of liquids and solutions provide evidence for specific interactions between molecules and that these make a major contribution to the frequency shifts observed in passing from the vapour.

The number of instances where specific interactions involving C–H groups have been studied is rather limited. Evidence has come, both from Infra-red and N.M.R. studies that such interactions do occur between chloroform and a number of basic solvents [1] and that, at least for such strong bases as pyridine and triethylamine, they may be termed loosely as hydrogen-bonding. 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. Standford and Gordy [2] in 1941 brought forward evidence for this by showing that the IR spectrum of phenyl acetylenes dissolved in a number of solvents had systematic frequency shifts of the acetylenic C–H stretching vibration of CH_3 OD disssolved in the same solvents.

The study of acetylene itself in solution has a number of advantages. These are: (i) the vibrational spectra of acetylene is very well understood, (ii) acetylene is a highly symmetrical simple molecule and has fundamentals (as well as overtones and combination bonds) which are forbidden in the infra-red spectrum of the free molecule (when solvent-solute interactions occur, there is a possibility of the breakdown of the selection rules and therefore an opportunity for showing up intermolecular effects); and (iii) the symmetry of acetylene is such that the IR active C–H stretching vibration is the only one of its type and is a pure stretching vibration as long as the molecule maintains this symmetry, there is no possibility of this vibration coupling with others and thus of changes in another part of the molecule influencing the frequency of this mode. El-Bermani [3] and Iogansen *et al* [4] have studied the frequency shifts of the two IR active vibrations of acetylene in a range of solvents.

The induced Raman active C≡C stretching vibration in solutions was studied earlier [5]. The present work deals with the accurate estimation of the other two Raman active streching and bending vibrations of acetylene in a range of solvents. This completes the study of frequency shifts of all the fundamental vibrations of acetylene in solution.

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 stated wave number accuracy was ± 0.02 % and reproducibility better than accurancy. From the water vapour spectra, the calibration showed an accuracy of ± 0.05 % cm^{-1}. The spectra of all the solvents used were examined in the region 4000-650 cm^{-1} and compared with the standard spectra.

The acetylene gas was commercial cylinder acetylene dissolved in acetone and was bubbled through concentrated sulphuric acid before use.

Saturated solutions were prepared by bubbling acetylene through the solvent for several hours. Those solvents were selected which gave suitable transmittance in the solvent-solute interaction studies. Compensation of the solvent was achieved by using a variable pathlength cell (Research and Industrial Instruments Co., England).

RESULTS AND DISCUSSION

Table 1 shows the fundamental vibrations along with summation and difference frequencies of acetylene gas reported by Plylar [6] and Bell and Nielson [7]. A survey spectrum of the solvents suggested that solvent absorption was weak enough for $\nu_3+\nu_4$, $\nu_1+\nu_5$ and $\nu_1+\nu_3$ to be observable in a sufficient number of instances for the variation between strongly interacting and comparatively weakly interacting systems to be studied. The solvents selected in the present work were carbonatetrachloride, bromoform, ethyl cyanide, methyl-*n*-propyl ketone and dioxan. Tables 2

and 3 show the frequencies $\nu_1+\nu_5$ and $\nu_3+\nu_4$ with their relation to other observed fundamentals (forbidden and allowed). The observation of the combination frequencies allows access to the Raman active fundamentals for which there are no direct experimental data. In particular there is the question of the Raman active C–H stretching frequency for which no direct evidence has previously been reported from the infrared spectra of solutions. This could be obtained in principle from $\nu_1+\nu_5$ and $\nu_1-\nu_5$ but the latter is a weak band in the gas spectrum. To use $\nu_1+\nu_5$ raises the question of the anharmonicity correction without which consideration gross errors could result in determining ν_1, even though ν_5 is well known.

In the gas the difference between the observed $\nu_1+\nu_5$ and the calculated from ν_1 and ν_5 is quite small (approximately -11 cm^{-1}) but it is not certain that in solution this would be true. It was clearly not possible to test the behaviour of $\nu_1+\nu_5$ from experimental ν_1 and ν_5 values as in no case has any certain value of ν_1 been observed.

However, the closely related combination between the IR active C–H stretching (ν_3) and the Raman active C≡C-H bending (ν_4) did provide an important guide as in some instances ν_4 was observed in the IR spectrum of the solutions. In particular a value of ν_4 was available for methyl-*n*-propylketone (seet Table 2) as well as ν_3 and $\nu_3+\nu_4$. In the gas phase the difference between the observed value of $\nu_3+\nu_4$ and the value calculated from the observed frequencies ν_3 and ν_4 is -12cm^{-1}. This is very similar to the corresponding difference from $\nu_1+\nu_5$. In methyl-*n*-propyl ketone the difference between the observed values for ν_3V_4 and those calculated form the sum of ν_3 and ν_4 is $-$ -6cm^{-1} (Table 3) and is thus even smaller than that for the gas.

This observation leads to the conclusion not only that $\nu_3+\nu_4$ may be used in conjunction with the observed value

Table 1. Acetylene gas frequencies

Vibration	Symmetry type	Approx. description	Activity	Frequency (cm^{-1})
ν_4	πg	C≡C-H Bending	Raman	612.88
ν_5	πu	C≡C-H Bending	I.R.	730.29
ν_2	Σ_g^+	-C≡C- Stretching	Raman	1973.99
ν_1-ν_5	πu	—	I.R.	2643.69
ν_3-ν_4	πu	—	I.R.	2670.33
ν_3	Σ_u^+	C-H Stretching	I.R.	3281.92
ν_1	Σ_g^+	C-H Stretching	Raman	3372.83
ν_3+ν_4	πu	—	I.R.	3882.85
ν_1+ν_5	πu	—	I.R.	4092.37

Table 2. ν_5, $(\nu_1+\nu_5)$ and $(\nu_1-\nu_5)$ frequencies of acetylene in organic solvents.

Solvent	Observed frequencies (cm^{-1})			Calculated frequencies (cm^{-1})		
	ν_5	$\nu_1+\nu_5$	$\nu_1 \nu_5$	ν_1	ν_5	$\nu_1+\nu_5$
Carbon tetrachloride	—	4077	2613	3345[+]	732[+]	(4077)
Bromoform	739	4071	2598	3337[+] 3334[+]	737[+]	4076[++] (4071)
Ethyl cyanide	755	4082	—	3327	—	—
Methyl-*n*-propylketone	764	4082	—	3318	—	—
Dioxan	767	4080	—	3313	—	—

+ Calculated from $(\nu_1+\nu_5)$ and $(\nu_1-\nu_5)$
++ Calculated from ν_5 (observed) and ν_1 (calculated)

Table 3. ν_3, ν_4, $(\nu_3+\nu_4)$ and $(\nu_3-\nu_4)$ frequencies of acetylene in organic solvents

Solvents	Observed frequencies cm^{-1}				Calculated frequencies cm^{-1}		
	ν_3	ν_4	$\nu_3+\nu_4$	$\nu_3-\nu_4$	ν_3	ν_4	$\nu_3+\nu_4$
Carbon tetrachloride	3260	–	3868	2647	3258[+]	610[+]	(3868)
Bromoform	3249	–	3860	2634	3247[+]	613[+]	(3860)
						615[++]	3864
Ethyl cyanide	3233	640(b)	3866	–	–	633[+]	3873
Methyl-*n*-propylketone	3223	631	3860	–	3229[⊕]	637[*]	3866
Dioxan	3209	–	3858	–	–	649[*]	–

+ Calculated from $(\nu_3+\nu_4)$ and $(\nu_3-\nu_4)$ ⊕ Calculated from ν_4 and $(\nu_3+\nu_4)$
* Calculated from ν_3 and $(\nu_3+\nu_4)$ ++ Calculated from ν_3 and $(\nu_3-\nu_4)$

Table 4. All the fundamental frequencies of acetylene in organic solvents

Solvents	ν_1	ν_2	ν_3	ν_4	ν_5 cm^{-1}
Carbon tetrachloride	3345	1963	3260	613	734
Bromoform	3337	1959	3249	615	739
Ethyl cyanide	3327	1957	3233	633	755
Methyl *n*-propylketone	3318	1956	3223	637	764
Dioxan	3313	–	3209	649	767

of ν_3 to estimate ν_4 in known cases, but also that a similar situation is true for $\nu_1+\nu_5$ in conjunction with ν_5. Calculation of ν_1 and ν_4 bands on this conclusion have been made and are presented in Tables 2 and 3. Comparison with calculated and observed values, where possible, are also given in the same tables, and are in good agreement.

Table 4 shows all the fundamental frequencies of acetylene in a range of solvents.

REFERENCES

1. Pimental and McClellan, *The Hydrogen Bond* (Freeman and Co., 1960).
2. B.S.C. Standford and W. Gordy, J. Am. Chem. Soc., **63**, 1094 (1941).
3. M.F. El-Bermani, M.Sc. Thesis, Univ. Birmingham (1964).
4. A.V. Iogansen and G.A. Kurkchi, Opt. and Spectros., **13**, 267 (1962).
5. A.M. Syed, Pakistan J. Sci. Ind. Res., **16**, 230 (1973).
6. E.K. Plyler, J. Opt. Soc. Amer., **53**, 589 (1963).
7. E.E. Bell and H.H. Nielson, Jr. Chem. Phys., **18**, 1382 (1950).