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The Raman spectrum of propynal

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Abstract—The Raman spectrum of propynal as a vapour and dissolved in various solvents were recorded. These data and the observed polarization measurements were in accordance with the fundamental frequencies assigned to the ground state of this molecule. The vibrational modes of propynal were compared with those previously reported for the halopropynals.

INTRODUCTION

The structurally simplest conjugated aldehyde, propynal (H—C≡C—CHO), has been thoroughly studied by a number of spectroscopic techniques, including microwave [1, 2], i.r. [3, 4], Raman [4], ultraviolet [5–7], i.r.–i.r. [8] and i.r. microwave [9] double resonance. Also, normal coordinate analyses of propynal in the ground and electronically excited states have been reported [7, 10].

Propynal has become a model compound among complex polyatomic molecules for assignments of the excited electronic states transitions [5, 6]. In the ground state the molecule is close to a prolate, symmetric top. Because of the very high value of one rotational constant ($\sim 2.25\,\mathrm{cm}^{-1}$) the a' modes give rise to well resolved K-structure in the i.r. vapour spectra [3].

The Raman spectrum of propynal was previously recorded by mercury excitation of the liquid [4]. The uncertain polarization measurements obtained by photographic recording led to assignments in which two of the three a'' modes were misinterpreted, but later reassigned on the basis of the near u.v. spectra [5]. Since we had propynal of high purity available as an intermediate for preparing halogenated propynes, we felt it would be of interest to reinvestigate the Raman spectra.

EXPERIMENTAL

Propynal was prepared from propargyl alcohol by oxidation with chromic acid by standard procedures [11]. The product was purified by repeated fractional distillation in a column and the purity checked by gas chromatographic analysis.

The Raman spectra were recorded with a Coderg model T 800 spectrometer, excited by a Spectra Physics model 170-03 argon ion laser. The vapour was studied at a pressure of *ca.* 100 torr at ambient temperature in a cubic vapour cell of stainless steel. Solutions of propynal in CCl_4, C_6H_6 and CS_2 were prepared by distilling the solute into the solvents on a vacuum line, and the solutions (*ca.* 20%) were investigated in sealed cells. It was observed that the blue (4880 Å) argon line caused rapid polymerisation of propynal, whereas the compound was moderately stable when irradiated with the green (5145 Å) line. If the vapour cell was irradiated with more than 1.5 watt laser energy a dark deposit of polymerized material was formed on the cell windows. The solutions were reasonably stable for a few hours if the laser output was held below *ca.* 80 mW.

RESULTS AND DISCUSSION

The wave numbers of the Raman bands observed in this study in the vapour phase as well as in C_6H_6, CCl_4 and CS_2 solutions are listed in Table 1. They are compared with the Raman data of King and Moule [4] measured at $-20°\mathrm{C}$, and the revised assignments of Brand *et al.* [5], supported by later ultraviolet studies of propynal [7, 8].

As apparent from Table 1 the present Raman spectral data are in excellent agreement with the accepted assignments [5]. For the sake of brevity we shall limit the discussion to the instances where our Raman results disagree with the earlier data [4].

In the low frequency region Raman bands of the vapour were observed at 259 and 208 cm^{-1} of which the latter was definitely polarized. They were accordingly attributed to the ν_{12} and ν_9 modes, respectively, contrary to the earlier work in which the polarization ratios were reversed [4]. A very weak, diffuse, depolarized Raman band at 710 cm^{-1} was previously attributed to both the fundamentals ν_7 and ν_{10} [4]. Instead, we observed very weak vapour bands 659 and 794 cm^{-1} and the solution spectra revealed them to

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Table 1. Raman spectral data for propynal

Vapour	Solution C_6H_6	CCl_4	CS_2	Liquid*	Description	
3324 *m,P*†	3280 *w,P*	3280 *w*	3288 *w,P*	3381 *w,P*	ν_1	*a′*
		3068 *vw*	3061 *vw*		$\nu_4 + \nu_5$	*A′*
2862 *s,P*	2872 *s,P*	2868 *s,P*	2860 *s,P*	2856 *s,P*	ν_2	*a′*
2747 *w*	2746 *w,P*	2745 *m,P*	2743 *w,P*		$2\nu_5$	*A′*
		2625 *vw*			$\nu_4 + \nu_6$	*A′*
2115 *vs,P*	2098 *vs,P*	2100 *vs,P*	2101 *vs,P*	2080 *m,P*	ν_3	*a′*
2109 *s*					hot	
2103 *m*					bands	
2098 *w*						
	2055 *w,P*	2055 *w,P*			$\nu_5 + \nu_7$	*A′*
		2007 *vw*			$\nu_5 + \nu_8$	*A′*
1701 *vs,P*	1675 *vs,P*	1672 *vs,P*	1678 *vs,P*	1658	ν_4	*a′*
		1645 *vw*			$\nu_1 + \nu_{10}$	*A″*
1391 *s,P*	1388 *s,P*	1389 *s,P*	1388 *s,P*	1392 *s,P*	ν_5	*a′*
		1008 *w,P*			imp.?	
982 *vw*		986 *w,D*	989 *w,D*	988 *w,D*	ν_{10}	*a″*
947 *m*	951 *m,P*	952 *m,P*	952 *m,P*	947 *vw,P*	ν_6	*a′*
694 *vw*	700 *w,D*	698 *w,D*	681 *w,D*	710 *vw,D*	ν_{11}	*a″*
659 *vw*		665 *vw,P*		710 *vw,D*	ν_7	*a′*
619 *s,P*	620 *m,P*	622 *s,P*	620 *s,P*	620 *s,P*	ν_8	*a′*
259 *w,D*	262 *w,D*	258 *w,D*	259 *w,D*	261 *m,P*	ν_{12}	*a″*
208 *s,P*	218 *s,P*		218 *s,P*	226 *s,P*	ν_9	*a′*

* Data from ref. [4].

† Abbreviations: *s*, strong; *m*, medium; *w*, weak; *v*, very; *P*, polarized and *D*, depolarized.

be polarized and depolarized, respectively. Again this agrees perfectly with the results of BRAND *et al.* [5] but disagrees with the previous Raman work [4].

Very strong, polarized Raman bands were observed at 1701 cm^{-1} in the vapour phase and shifted to *ca.* 1675 cm^{-1} in solution, definitely connected with the *a′* mode ν_4 (C=O stretch). A band at 1658 cm^{-1} without intensity description was reported for this Raman mode [4]. Finally, we did not observe any Raman band at 3381 cm^{-1}, as previously reported [4], but detected bands at 3324 cm^{-1} (vapour) and around 3280 cm^{-1} in solution. These values agree well with the vapour frequency at 3326 cm^{-1} [3, 5] from i.r. and u.v. spectra.

Because of the restricted laser power imposed by the instability of propynal, the vapour spectrum was recorded at slits sometimes as high as 10 cm^{-1}. Therefore, the rotational fine structure which is particularly well resolved for the *a′* bands ν_2 and ν_4 in i.r. with rotational lines *ca.* 2 cm^{-1} apart, were not resolved in our Raman spectra. However, the intense Raman band around 2115 cm^{-1}, connected with the

Table 2. Fundamental vibrational frequencies for propynal and the halopropynals (X—C≡C—CHO, X=H, D, Cl, Br, I)

		H*	D*	Cl†	Br†	I†	Description
a′	ν_1	3326	2605	473	395	360	C—X str.
	ν_2	2858	2859	2860	2858	2850	C—H str.
	ν_3	2110	1978	2220	2196	2159	C≡C str.
	ν_4	1698	1697	1694	1692	1676	C=O str.
	ν_5	1383	1386	1387	1386	1385	C—H rock
	ν_6	935	924	1077	1030	1005	C—C str.
	ν_7	663	500	114	105	107	CCX bend
	ν_8	615	609	738	691	670	C—C=O bend
	ν_9	203	193	312	290	276	CCC bend
a″	ν_{10}	981	981	945		960	CHO wag
	ν_{11}	693	548	152	143	131	CCX bend
	ν_{12}	261	249	352	340	330	CCC bend

* Values from ref. [7].

† Values from ref. [14].

C≡C stretching mode ν_4 could be recorded with *ca.* 3 cm^{-1} spectral resolution. A progression of peaks with *ca.* 6 cm^{-1} separation were detected for ν_4 undoubtedly due to a hot band progression, involving the lowest bending mode as commonly observed in acetylenes [12]. For diiodo acetylene [13] dissolved in C_6H_6 a corresponding hot band progression was also seen in the Raman solution spectrum. A slight shoulder on the low frequency side could be observed for the ν_4 Raman band of propynal in solution (C_6H_6, CCl_4 and CS_2).

In Table 2 the fundamentals for propynal are compared with those of the halopropynals [14]. As a first approximation the vibrational modes are listed in terms of localized vibrations. It appears that many of the vibrations are group frequencies, relatively unchanged by deuterium or halogen substitution. The stretching and deformation modes involving the ≡C—X bond (ν_1, ν_7 and ν_{11}) are obviously greatly perturbed upon substitution.

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