

Raman Study of Anharmonic Effects in Vibrational Spectra of Acetylenic Compounds

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The π -conjugated compounds consisting of an acetylenic chain $[-(C\equiv C)_n-]$ are calculated to be one-dimensional conductors and could be utilized as molecular electronic devices. The variation of the functional groups attached to the terminal carbon atoms and the length of the acetylenic chain can be the test for the molecular ability to serve as a molecular wire [1].

During spectroscopic investigations of acetylenic compounds with phenyl and trimethylsilyl terminal group(s) (Fig. 1), an unusual and hitherto unexplained phenomenon has been observed in their Raman spectra. The band that originates from the acetylenic stretching has pronounced asymmetry on the low-frequency side (Fig. 2). The asymmetry is most probably a consequence of the unresolved hot band sequence that occurs due to the coupling between the acetylenic stretching at $(2130 \pm 100) \text{ cm}^{-1}$ and the linear bending at around $(200 \pm 100) \text{ cm}^{-1}$. The hypothesis is based on the existence of such a sequence in gas and liquid phase spectra of halogeno substituted acetylenes [2] and also on the experimental results that have already been obtained for **DPA** and **PA** under different conditions [3].

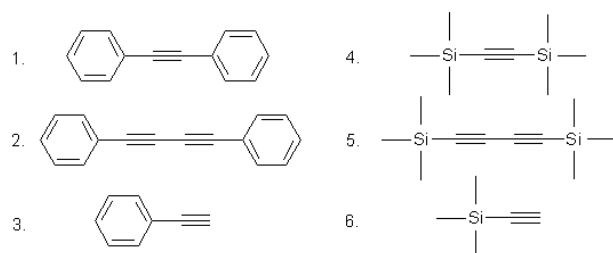


Figure 1:

1. Diphenylacetylene (**DPA**),
2. Diphenyldiacetylene (**DPDA**),
3. Phenylacetylene (**PA**),
4. Di(trimethylsilyl)acetylene (**DTMSA**),
5. Di(trimethylsilyl)diacetylene (**DTMSDA**),
6. Trimethylsilylacetylene (**TMSA**)

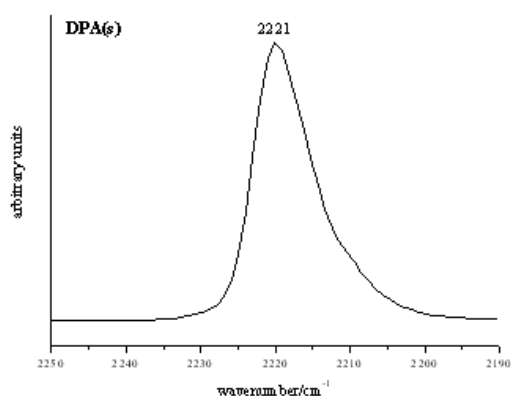


Figure 2: FT Raman spectrum of **DPA(s)**

The asymmetry of this feature is present in Raman spectra of all the studied molecules regardless of the phase. However, the splitting of the bands seems to be at the resolution limit and therefore, it had to be quantified as the skewness with an error defined as the skewness of the perfectly symmetric Raman band of $\text{KMnO}_4(\text{s})$ at 350 cm^{-1} . The asymmetry is more pronounced for compounds with phenyl terminal groups than for those with trimethylsilyl terminal groups, and, additionally, it is the most pronounced in Raman spectra of **DPDA** and **DTMSDA** that have the longest acetylenic chain.

[1] R.L. Carrol, C.B. Gorman, *Ang. Chem. Int. Ed.* 41 (2002) 4378.

[2] J.K. Brown, N. Sheppard, *Spectrochim. Acta* 23A (1967) 129.

[3] (a) H. Abramczyk, M. Kolodziejski, G. Waliszewska, *Chem. Phys.* 228 (1998) 313; (b) H. Abramczyk, G. Waliszewska, M. Kolodziejski, *J. Phys. Chem. A* 102 (1998) 7765.