OVERTONE ABSORPTIONS OF METHANE: ANOMALOUS TRANSITION FROM NORMAL MODE TO LOCAL MODE

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The C-H vibrational overtone transitions between 500 and 16600 cm^{-1} of methane were obtained in diluted argon solutions at temperatures between 88 and 121 K and compared with gas phase spectra obtained at room temperature. The simplification of the spectra allows the observation and assignment of hidden transitions in the room temperature absorptions. Although vibrational assignments in the gas phase have been made in several regions, the vibrational and rotational congestion in each region, as well as strong interactions between levels, have made the interpretation very difficult. The interpretation of the overtone spectra at rotational resolution has been limited to the overtones $2\upsilon_3$, $3\upsilon_3$, and $3\upsilon_1 + \upsilon_3$. The interpretation has not been possible for levels such as $4\upsilon_1 + \upsilon_3$. and $5\upsilon_1 + \upsilon_3$. The positions of the $n\upsilon_1 + \upsilon_3$ series of bands are known from n = 3 to 8 [1] but there is uncertainty with respect to the position of the $\upsilon_1 + \upsilon_3$ and the $2\upsilon_1 + \upsilon_3$ bands. Several experimental [2] and theoretical [3] reports assign them differently. It is shown that in very dilute solutions at low temperatures, the absorption bands are easier to interpret than the room temperature gas phase bands, due to the reduction in the contribution of the rotational envelope and the hot bands.

[1] GIVER, L. P., 1978, J. Quant. Spec. Radiat. Transfer, **19**, 311.
[2] MCKELLAR, A. R. W., 1989, Can. J. Phys. **67**, 1027.
[3] HALONEN, L., and CHILD, M. S., 1982, Molec. Phys., **46**, 239.