LEAST SQUARES FITTING OF PERTURBED VIBRATIONAL POLYADS NEAR THE ISOMERIZATION BARRIER IN THE S_1 STATE OF C_2H_2

A. J. MERER, *Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Z1 AND Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.*; J. H. BARABAN, P. B. CHANGALA, and R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*.

The S_1 electronic state of acetylene has recently been shown to have two potential minima, corresponding to cis- and trans-bent structures. The trans-bent isomer is the more stable, with the cis-bent isomer lying about 2670 cm^{-1} higher; the barrier to isomerization lies roughly 5000 cm^{-1} above the trans zero-point level. The "isomerization coordinate" (along which the molecule moves to get from the trans minimum to the barrier) is a combination of the ν_3 (trans bending) and ν_6 (cis bending) vibrational normal coordinates, but the spectrum is very confused because the ν_6 vibration interacts strongly with the ν_4 (torsion) vibration through Coriolis and Darling-Dennison resonances. Since the ν_4 and ν_6 fundamental frequencies are almost equal,[a] the bending vibrational structure consists of polyads. At low vibrational energies the polyads where these three vibrations are excited can be fitted by least squares almost to experimental accuracy with a simple model of Coriolis and Darling-Dennison interactions, but at higher energies the huge x_{36} cross-anharmonicity, which is a symptom that the levels are approaching the isomerization barrier, progressively destroys the polyad structure; in addition the levels show an increasing even-odd staggering of their K-rotational structures, as predicted by group theory. It is not possible to fit the levels near the barrier with a simple model, though some success has been achieved with extended models. Progress with the fitting of the polyads near the barrier will be reviewed.

[a] A. L. Utz, J. D. Tobiason, E. Carrasquillo M., L. J. Sanders and F. F. Crim, *J. Chem. Phys.* **98**, 2742, 1993.