Bending Energy Minimisation Criterion for Molecular Geometry in XY_3 Pyramidal Systems

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A study of the variation of the vibrational potential energy contribution with interbond angles in XY_3 pyramidal molecules confirms the observation previously made for XY_2 bend symmetric systems that the actual equilibrium configuration lies in the premises of minimum V_{bend} and zero $V_{stretch\text{-}bend}$.

An analysis of the variation of the vibrational potential energy with geometry in simple molecules can be of fundamental interest and a mathematical formalism for this purpose has been developed recently [1]. The plots of various contributions to the potential energy V with semi interbond angle θ in XY_2 bend symmetric systems seem to suggest that the actual equilibrium configuration lies in the premises of minimum for V_{bend} and zero for $V_{bend\text{-}stretch}$. Extension of the analysis to XY_3 pyramidal systems is discussed below.

XY_3 pyramidal molecules belong to the C_{3v} point group, have the vibrational representation $T = 2A_1 + 2E$, and contributions to the potential energy come from stretching, bending, and different mutual interactions between the two. The recipe for plotting the potential energy contributions as a function of the semi interbond angle θ is almost the same as given in the earlier work [1] except that here one has to deal with two vibrational species viz., A_1 and E, both of order two (as against one vibrational species of order two and one vibrational species of order one viz., A_1 and B_1 in XY_2 bend symmetric systems).

Fortunately, there are a few XY_3 pyramidal molecules in the literature for which the interbond angles are uniquely fixed and the normal and isotopic frequencies have been exactly determined [2]. Moreover, these happen to be hydrides where the isotopic fre-

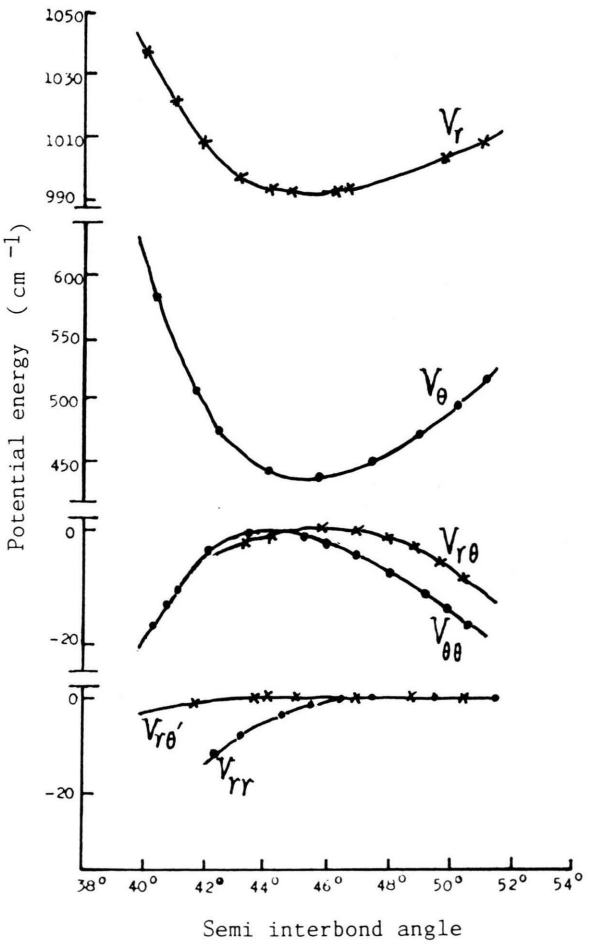

Fig. 1. Variation of the vibrational potential energy with the semi interbond angle in SbH_3 molecule.

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Table 1. Semi interbond angle determined from energy considerations.

Molecule	Semi interbond angle based on		Experimental value [2]
	$V_\theta = \min$	$V_{r\theta} = 0$	
SbH_3, SbD_3	45.75°	46°	45.75°
AsH_3, AsD_3	45.25°	44°	46°
PH_3, PD_3	45.75°	44.75°	46.75°
NH_3, ND_3	53.6°	53.6°	53.5°

quency shifts are comparatively large. This has enabled us to draw the $V-\theta$ plots for such molecules which verify the criterion of V_{bend} minimum for the equilibrium configuration.

The results are given in Table 1 along with a typical plot in Figure 1. The values of interbond angles corresponding to the V_{bend} minimum show even better agreement than in the case of XY_2 bend symmetric systems [1].

[1] K. Indira, M. K. Rudra Warier, T. R. Ananthakrishnan, and C. M. Paul, Z. Naturforsch. **47a,** 765 (1992).
[2] W. Lewin and O. W. Adams, J. Mol. Spectrosc. **39,** 380 (1971).