

Chapter 67

Dipole Moment as a Possible Diagnostic Descriptor of the Conformational Isomerism of the Ammonia Molecule¹

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ABSTRACT

In this chapter, Ghosh and Rajak have made a detailed quantum mechanical study of the variation of the dipole moment of ammonia as a function of its conformations evolving during the process of its umbrella inversion by invoking their method of dipole correlation of electronic structure as basis. Ghosh et al discover a surprising result that the variation of dipole moment mimics the total energy curve as a function of reaction coordinates revealing the fact that the dipole moment is one possible diagnostic descriptor of the conformational isomerism of molecules containing lone pair electrons. The dipole is calculated and partitioned into bond and lone pair components for a large number of conformations between the equilibrium shape and the transition state of inversion and the results are interpreted and correlated in terms of the localized molecular orbitals, LMOs generated from the canonical molecular orbitals, CMO's of each conformation. Anderson, from the concept of space time symmetry, postulated that ammonia has zero dipole moment. Present study reveals that Anderson's correlation relied upon the bond moment only while the major component of dipole of ammonia originates from the lone pair of nitrogen.

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INTRODUCTION

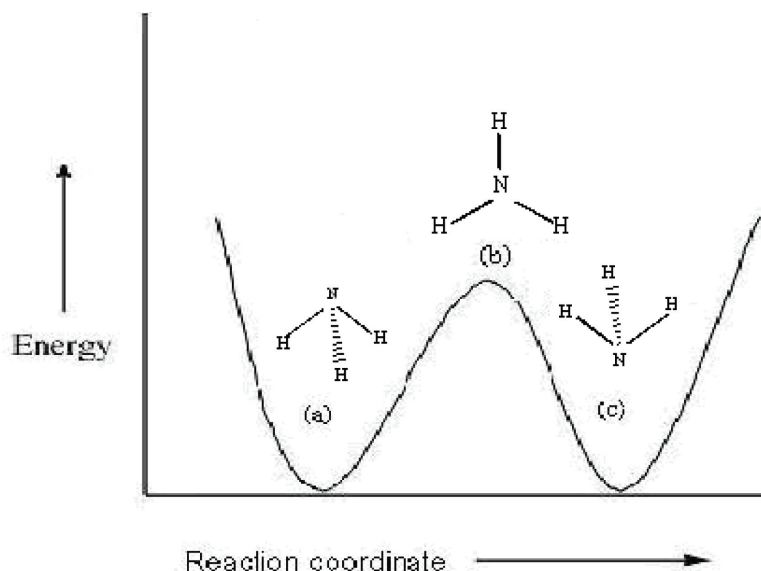
The variation of lone pair component of the dipole with structural evolution is correlated in terms of the asymmetry or hybridization of orbitals accommodating the lone pairs. All the aspects of vanishing dipole of ammonia at the transition state of inversion and in the bulk are brought into consideration. The dipole moment of the transition state is zero due to cancellation of bond moment and vanishing of lone pair moment. Because of very fast rate of inversion, a structure and its mirror image are present in equal proportion to make the dipole of ammonia zero in a bulk. The Anderson's maxim that ammonia has zero dipole is justified in a deeper way. Ammonia, NH_3 , is an important and interesting chemical system having some unique chemico-physical properties. The molecule, with a lone pair of electrons on N atom, is a strong Lewis base (Shriver & Atkins, 1990). It combines with the transition metal ions, hydrogen ion and forms adducts with all Lewis acids. Because of its structural asymmetry, the ammonia molecule is a seat of dipole moment. The important structural aspect of the molecules

is that it undergoes a physical process of umbrella inversion entailing a phenomenon of conformational isomerism. Because of its versatile use and interesting chemico-physical behavior, a plethora of information have appeared relating to the study of ammonia molecule and the molecule has been one of the most frequently studied species in the whole history of quantum chemistry.

The shape of the molecule is pyramidal (C_{3v}) in its equilibrium conformation. But the molecule does not remain stationary at its equilibrium conformation rather; it prefers to execute a physical process of continuous structural inversion called the umbrella inversion of ammonia. The mechanism of inversion of ammonia may be visualized as follows. The molecule, following the normal modes of vibration, reorganizes very fast from its equilibrium conformation (C_{3v}) to a planar (D_{3h}) transition state which quickly collapses to its original shape and inverted shape. This phenomenon may be grossly depicted in Figure 1.

The phenomenon of the umbrella inversion of ammonia is widely studied both experimentally and theoretically (Cherry & Epiotis, 1976; Ghosh, Jana & Biswas, 2000; Good, 1946; Laerdahl,

Figure 1. Ammonia inversion potential energy surface



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