



Mono and di-substituted ammonia borane: A computational study



Mahadevappa Naganathappa^a, Tahemina Qureshi^b, Ajay Chaudhari^{c,*}

^a Department of Physics, GITAM University, Hyderabad Campus, Hyderabad, 502329 TS, India

^b School of Physical Sciences, S. R. T. M. University, Nanded 431606 India

^c Department of Physics, The Institute of Science, Fort, Mumbai 400032, India

ARTICLE INFO

Article history:

Received 5 March 2015

Received in revised form 17 June 2015

Accepted 20 July 2015

Available online 15 August 2015

Keywords:

Ammonia borane

Vibrational spectrum

Electronic absorption spectrum

Hyperpolarizability

ABSTRACT

This work reports vibrational spectra and electronic absorption spectra along with the first and second hyperpolarizabilities for ammonia borane, mono and disubstituted ammonia boranes using quantum chemical methods. The substituents used here are Cl, Br and F. A large difference in the vibrational and electronic absorption spectra is observed upon mono and disubstitution. All the electronic transitions for the mono as well as disubstituted ammonia borane molecules are found to be $\sigma \rightarrow \sigma^*$ transitions. Direction of applied field and method dependent hyperpolarizabilities are obtained. The hyperpolarizabilities are found to be higher when the field applied is along Y direction than that applied in X or Z direction. The first hyperpolarizability is found to be enhanced upon mono as well as disubstitution in ammonia borane. Mono as well as disubstituted ammonia boranes are not good materials for second order nonlinear optics.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In recent years there has been a growing interest in spectroscopic, electrical, optical and magnetic properties of molecules due to possible setting up of electronics at molecular scale. Many molecules show unconventional properties in the presence of an applied field and on substitution of different donor–acceptor groups [1]. Because of their applications in designing electro-optic devices also, substituted compounds with large molecular second-order nonlinear optical (NLO) responses are receiving enhanced interest [2]. The macroscopic nonlinearity of a molecular material is mainly decided by its NLO properties [3]. A knowledge of NLO properties helps in designing new optical devices. Molecular materials with NLO applications contain molecules with substituent groups and show high values of hyperpolarizabilities [4–8]. The NLO properties can be found in various substituted organic and inorganic molecules, semiconductors and polymeric materials with donor–acceptor groups [9–12].

The ammonia borane (NH_3BH_3) has received enhanced interest due to its high hydrogen content [13]. Several investigations are made on ammonia borane. Most of them are focused on its application as a hydrogen storage material and use with proton exchange membrane fuel cells. The potential energy surface for H_2 release from ammonia borane with a novel bifunctional cationic ruthenium catalyst based on sterically bulky β -diketiminato ligand has been constructed using density functional theory by Bandaru et al. [14] They investigated the interaction of ammonia borane and related substituted ammonia borane with a bifunctional η^6 -arene ruthenium catalyst and associated variants

for dehydrogenation. Bandaru et al. have used classical and AIMD simulations to study and compare implicit and explicit solvent representations of tetrahydrofuran effects on the structural, energetic and dynamical behavior of Ru catalyst used for dehydrogenation of ammonia borane [15]. The differences between ammonia- and phosphine boranes have been explained by Balazs et al. theoretically and experimentally [16]. The reaction pathways for catalyzed chemical hydrogen uptake and release in ammonia boranes, hydrazine and ammonia alane derivatives have been carried out using density functional theory modeling by Swinnen et al. [17,18] The mechanism involved in the dehydrogenation of ammonia borane by a novel bifunctional η^6 -arene β -diketiminato ruthenium catalyst has been studied by Schreiber et al. [19] It is observed that the additions of mono, di-F and phenyl-N-substituted amine borane systems to the Ru-catalyst results in lowering the activation energy barrier via *in-situ* amino borane [14]. The dehydrogenate intermediate is rapidly formed in the gas phase. It has been found that the ammonia borane complexes containing alkali or other metals improve the hydrogen release properties significantly [20,21].

In addition to hydrogen storage application, the molecular and electronic structure of ammonia borane is also of fundamental interest. The ammonia borane contains the highly polarized dative N–B bond which is formed by the electron donor–acceptor pair. The dissociation energy for the N–B bond is of the order of 130 kJ^{-1} and much stronger than the typical van-der Waals interaction [22]. The properties of NH_3BH_3 at high pressure have been studied earlier [23,24]. The X ray diffraction technique has been used to study the crystal structure of ammonia borane [25–27]. The ammonia borane has also been studied using spectroscopy under different conditions. Raman spectroscopy has been used by Hess et al. to study the single crystal ammonia borane complexes [28]. The

* Corresponding author.

E-mail address: ajaychau5@yahoo.com (A. Chaudhari).

nature and behavior of B–N bond in ammonia borane and its isotopologues have been studied using IR and Raman spectroscopies [24,29,30]. Ziparo et al. have measured the Raman spectrum of ammonia borane at temperature $T=15$ K and across the orthorhombic-to-tetragonal phase transition at $T=225$ K [31]. The vibrational frequencies of ammonia borane and its isotopologues have been investigated using an argon matrix by Taylor and Cluff [29] and computationally on free molecules by Dillene et al. and Allis et al. [32,33]. The Raman spectroscopy has been used to study the ammonia borane under pressure as high as 4 GPa [24,30,32–34]. Xie et al. have investigated the pressure induced structural transformations of the ammonia borane complex in diamond anvil cells by Raman spectroscopy and synchrotron IR spectroscopy up to 14 GPa at room temperature [35]. The structural and vibrational properties of ammonia borane have been studied by using the density functional theory at ambient as well as high pressures up to 10 GPa by Lingam et al. [36].

The aim of this article is to study the effect of mono and di-substitution on properties of ammonia borane using quantum chemical methods. In mono substituted ammonia borane one of the hydrogens either in NH_3 group or BH_3 group is substituted either with Cl, Br or F. For di-substituted ammonia borane, one of the hydrogens in NH_3 as well as BH_3 group is substituted either with Cl, Br or F. We have studied vibrational spectra, electronic absorption spectra and components of the first and second hyperpolarizabilities of several mono and di-substituted ammonia boranes.

2. Computational details

The geometries of ammonia borane, mono and disubstituted ammonia boranes are optimized at MP2/aug-cc-pvdz level. We compared the geometrical parameters of ammonian borane from this work with the available experimental values and found that the geometries of ammonia borane at MP2 level with aug-cc-pvdz basis set are in excellent agreement with the experimental values [37,38]. We then optimized the geometries of mono and di-substituted ammonia boranes at the same level viz. MP2/aug-cc-pvdz level. The vibrational frequencies for ammonia borane and substituted ammonia boranes are also obtained at the same level of theory. The vibrational modes of amino borane and substituted amino boranes are calculated by normal mode analysis without considering temperature and anharmonic effects. The components of the first and second hyperpolarizabilities are obtained using the finite field method [39–43]. Since the finite-field approach is essentially a derivative method, one cannot avoid the numerical problem. Finding out the suitable value of the field strength for the calculation of hyperpolarizabilities is essential for the numerical stability.

The β and γ are calculated by the numerical differentiation of total energy E with respect to the applied field by following equations:

$$\beta = \{-E(2Fi) + E(-2Fi) + 2[E(Fi) - E(-Fi)]\} / 4(Fi)^3 \quad (1)$$

$$\gamma = \{E(3Fi) - 12E(2Fi) + 39E(Fi) - 56E(0) + 39E(-Fi) - 12E(-2Fi) + E(-3Fi)\} / 36(Fi)^4 \quad (2)$$

Here, $E(Fi)$ indicates the total energy of a molecule in presence of a field strength F applied in the i^{th} direction ($i = x, y$ or z). All the calculations are carried out with the program package Gaussian 03 [44].

3. Results and discussions

The optimized structures of mono and di substituted ammonia boranes at MP2/aug-cc-pvdz level are shown in Figs. 1 and 2 respectively. Six mono-substituted ammonia borane studied here are NH_2BrBH_3 , NH_2ClBH_3 , NH_2FBH_3 , $\text{NH}_3\text{BH}_2\text{Br}$, $\text{NH}_3\text{BH}_2\text{Cl}$ and $\text{NH}_3\text{BH}_2\text{F}$. The di-substituted ammonia boranes considered here are $\text{NH}_2\text{BrBH}_2\text{Br}$, $\text{NH}_2\text{BrBH}_2\text{Cl}$, $\text{NH}_2\text{BrBH}_2\text{F}$, $\text{NH}_2\text{ClBH}_2\text{Br}$, $\text{NH}_2\text{ClBH}_2\text{Cl}$, $\text{NH}_2\text{ClBH}_2\text{F}$, $\text{NH}_2\text{FBH}_2\text{Br}$, $\text{NH}_2\text{FBH}_2\text{Cl}$ and $\text{NH}_2\text{FBH}_2\text{F}$. Their geometrical parameters

viz. the bond lengths, angles, dihedral angles and dipole moments are summarized in Tables 1 and 2. Tables 1 and 2 show that there is no large change in the B–H, N–H and B–N bond lengths upon mono and disubstitution in ammonia borane. However a significant change in angles and dipole moment can be seen. Two angles $\angle\text{H–B–H}$ and $\angle\text{H–B–N}$ are increased in mono as well as di-substituted ammonia boranes than the respective angles in ammonia borane. In monosubstituted ammonia boranes a maximum change of 2.2° and 1.9° is observed for the angles $\angle\text{H–B–H}$ and $\angle\text{H–B–N}$ respectively than the corresponding angle in ammonia borane. When the substituent is for the amino group, the dipole moment is lower and when it is for BH_3 group it is higher than the dipole moment of unsubstituted ammonia borane.

In disubstituted ammonia borane when H is substituted by F in amino group, a large change in angle $\angle\text{H–N–H}$ is observed. Two angles $\angle\text{H–B–H}$ and $\angle\text{H–B–N}$ are also increased significantly upon disubstitution in ammonia borane. A maximum change in $\angle\text{H–B–H}$ and $\angle\text{H–B–N}$ is found to be 4.1° and 3.7° respectively upon disubstitution in ammonia borane. The dipole moment for all the disubstituted ammonia borane molecules studied here is lower than that for the unsubstituted ammonia borane.

3.1. Infrared spectra

3.1.1. Monosubstitution

A comparison of vibrational spectra for the ammonia borane, and monosubstituted ammonia borane is shown in Fig. 3. The most intense peak in the vibrational spectrum of ammonia borane is observed at 2455 cm^{-1} which corresponds to the BH asymmetric stretching mode. The second intense peak representing the BH symmetric stretching deformation mode is observed at 1163 cm^{-1} . The third and fourth intense peaks representing the NH_3 symmetric deformation and BH_3 symmetric stretching mode appeared at 1278 and 2394 cm^{-1} respectively. The NH_2 wagging mode is the fifth intense mode which appeared at 1144 cm^{-1} . The NH_3 as well as NH_2 symmetric stretching mode at 3496 cm^{-1} is the sixth intense mode. The seventh intense mode is the NH_2 scissoring mode which appeared at 1490 cm^{-1} .

The most intense mode for the NH_2BrBH_3 is the same as the one observed for the ammonia borane viz. the BH asymmetric stretching mode and appeared at 2499 cm^{-1} . It is blue shifted by 44 cm^{-1} than the ammonia borane. The second and third intense modes for the NH_2BrBH_3 are the BH_3 asymmetric stretching and BH_3 symmetric deformation mode which appeared at 2460 cm^{-1} and 1155 cm^{-1} respectively. The former is blue shifted by 5 cm^{-1} and the latter red shifted by 8 cm^{-1} than the corresponding mode in ammonia borane. The modes BH_3 torsion, B–N–Br stretching, NH_2 twisting and N–B stretching are of very low intensity. The modes BH_2 asymmetric stretching, BH_3 asymmetric stretching, BH_3 symmetric stretching, NH_2 asymmetric stretching and BH_3 symmetric deformation are also quite intense. The Br substitution in place of H in amino group of ammonia borane results in the appearance of the N–Br stretching mode at 706 cm^{-1} .

The first intense mode is the BH_2 asymmetric stretching mode for the NH_2ClBH_3 which appeared at 2504 cm^{-1} . It is blue shifted by 50 cm^{-1} than the ammonia borane. Other intense modes which appeared in the vibrational spectrum of NH_2ClBH_3 are at 2465 , 2382 and 1149 cm^{-1} which represent the BH_3 asymmetric stretching, BH_3 symmetric stretching and BH_3 symmetric deformation mode respectively. The weak modes in the vibrational spectrum of NH_2ClBH_3 are the BH_3 asymmetric deformation at 1135 cm^{-1} , N–B stretching at 590 cm^{-1} , NH_2 rocking at 576 cm^{-1} and BH_3 torsion at 226 cm^{-1} . The highest blue shifted mode for the NH_2ClBH_3 molecule as compared to the ammonia borane is the BH_3 rocking mode. It is blue shifted by 134 cm^{-1} in the former than the latter and is equal intense.

The most intense mode in the vibrational spectrum of NH_2FBH_3 is the BH_2 asymmetric stretching mode observed at 2522 cm^{-1} and blue shifted by 67 cm^{-1} than the ammonia borane. The BH_3 rocking mode is the highest blue shifted mode in the vibrational spectrum of NH_2FBH_3 than the corresponding mode in ammonia borane. This

Download English Version:

<https://daneshyari.com/en/article/5410692>

Download Persian Version:

<https://daneshyari.com/article/5410692>

[Daneshyari.com](https://daneshyari.com)