

Computational investigation of dissociative electron attachment to ammonia

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In this paper we have studied the dissociative electron attachment (DEA) to ammonia (NH_3) molecule using electronic structure theory. We have optimized neutral and anionic ammonia molecules using different electronic structure methods like Hartree-Fock (HF), second order Møller-Plesset perturbation (MP2) theory and Coupled Cluster with Singles and Doubles excitations (CCSD) with different choice of basis sets. We have found that aug-cc-pVQZ basis set provided the better results among those chosen in our investigation. Using the optimized geometries of neutral and anionic NH_3 molecules, we have further computed the potential curves of neutral and anionic NH_3 molecules varying N-H bond. Results from the potential energy curves show that anionic NH_3 molecule is metastable than that of neutral NH_3 . This provides a possibility of shape resonance which further results into dissociative electron attachment process in NH_3 molecule. We have also computed transition state followed by an intrinsic reaction coordinate calculations to see the mechanism of the DEA process. Finally, we have analysed our results from the plots of singly occupied molecular orbitals (SOMOs) of reactant, transition state and product.

Keywords: Electron attachment, Hartree-Fock, second order Møller-Plesset perturbation theory, Coupled Cluster with Singles and Doubles Excitations, shape resonance, dissociative electron attachment, singly occupied molecular orbitals.

Introduction

Electron atom/molecule interaction or electron induced reactions have wide range of applications in the areas such as environmental science, material science, biology and astrochemistry etc.¹. For example, various electron-molecule scattering processes in a diatomic target molecule (AB) can be picturized in Fig. 1.

As we can see, from Fig. 1, on electron interaction with a target molecule (AB) give rise to three main pathways. These are

1. Electron impact ionization

In this process, electron interaction with AB molecule at first generates a radical cation which further dissociates to a radical and a cation as can be seen from following¹



The energy of the incident electron in this process is nearly 10 eV.

2. Electron impact excitation

In this process, electron collision with a neutral target

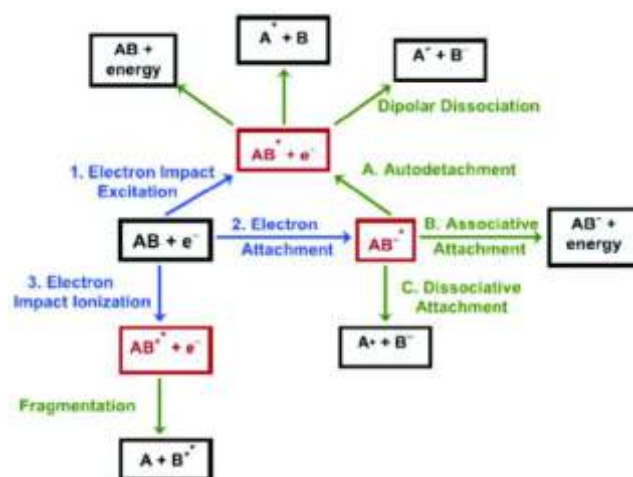


Fig. 1. Electron-induced pathways [Reprinted from Surface Science Reports, 65, C. R. Arumainayagam, L. H. Lee, B. R. Nelson and D. R. Haines, Low-Energy Electron-Induced Reactions in Condensed Matter, 1-44, Copyright (2019), with permission from Elsevier].

molecule like AB fragmented to an excited species (A^*) and a free radical (B^*) as given below¹





This process is not a resonant process as in case of photon excitation. Energy required for excitation is transferred by electron and excess is removed by scattered electrons. The third type of interaction on which we are mainly focusing in this paper is the electron attachment.

3. Electron attachment (EA)

In this process, electron attachment to a neutral target (XY) forms a transient negative anion (TNA). Actually, electron will go in a previously unfilled lowest unoccupied energy orbital. It is a resonant process as the energy of upcoming electron should be in the range of that molecular orbitals defined by Frank-Condon principle. The negative ion formed has a very short life time ranging from 10^{-15} – 10^{-12} s^{1,2}. The extra negative charge destabilizes the system and cause nuclei to move away from neutral bond distance.

After forming the TNA, there are two possibilities can be seen: (a) electron separates from temporary negative ion a process which is known as autodetachment where the neutral species formed is in a vibrationally excited (VE) state. In the second case, the nuclei may apart sufficiently and this process is known as dissociative electron attachment (DEA) or simply dissociative attachment (DA). Both these processes can be schematically represented as

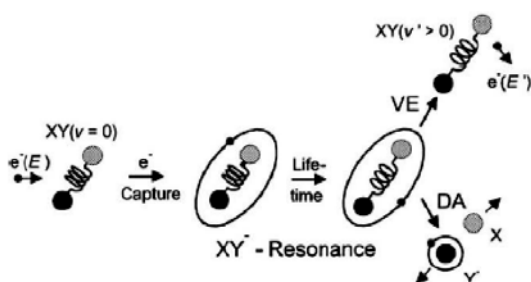


Fig. 2. Resonant electron-molecule scattering leading to dissociative attachment (DA) and vibrational excitation (VE). [Reprinted from Surface Science Reports, 65, C. R. Arumainayagam, L. H. Lee, B. R. Nelson and D. R. Haines, Low-Energy Electron-Induced Reactions in Condensed Matter, 1-44, Copyright (2019), with permission from Elsevier].

Study of electron interaction with ammonia is of great importance^{3–20}. In interstellar space, ammonia was observed as the first polyatomic molecule³. It was also discovered on

the atmosphere of outer planets and comets¹². Thus, electron interaction study can find application in space physics and in manipulating the atmosphere of outer planets. Importance was given to study about its dynamical and spectroscopical data when it was discovered in space¹². Further, it is useful in plasma chemistry for fabricating nitride films it acts as nitrogen atom source¹⁹. It has applications in pharmaceuticals and fertilizer field¹. Due to its polarity ($\mu = 1.47D$) and long-range order, it shows some interesting behavior on electron interaction which is the main aim of this paper. It is isoelectronic with 10 electron species such as H₂O, CH₄, HF etc. which are frequent choice of organized study.

Our group has been involved in this area of electron-molecule scattering from a long time where we have shown using both time independent and time dependent quantum mechanics from small molecules like H₂, N₂, F₂, HCl etc. to large molecules like DNA fragments^{21–35}.

In areas like nanotechnology industry, new materials could be synthesized using such reactions. As electron beam can be focused into spots that are smaller than 1 nm in size. Therefore, patterning of materials like semiconductor is feasible using electron induced process¹.

For better understanding of mutagenic role and ionizing radiation, the little perception of electron induced reaction is quite useful. Electron generated during high energy radiation therapy are capable of breaking strands of DNA^{1,25,27,29–35} and cleavage of DNA base at specific site³⁶.

In many other fields like astrochemistry, environmental science etc., there have been wide range of applications of electron induced chemistry. We have come to know that these electrons induced reaction are quite useful but current understanding about these reactions are limited and data is there for only dozens of molecules¹.

It is therefore purpose here in this paper to investigate electron interaction with ammonia from the time independent quantum mechanical methods. We, however, delinked the time dependent part of electron – NH₃ interaction in this investigation.

Method

In this investigation, our main focus was to investigate the dissociative electron attachment process on ammonia using electronic structure theory methods. To begin with, we have used Hartree-Fock (HF) method^{37,38} with smaller to

reasonably large basis set. Once we got a large sampling of basis sets, then we have extended our investigation using other correlated methods like second order Møller-Plesset perturbation (MP2) method^{37,38} and coupled cluster with singles and doubles excitations^{38,39} (CCSD) to get a better understanding of the resonant process.

Results and discussion

Geometry optimization

To begin with, we have optimized neutral NH₃ molecule using different basis sets at the RHF theoretical accuracy using Gaussian 09 program suite⁴⁰. We have summarized our results from the optimization calculations along with experimentally available data in Table 1.

Table 1. Results from optimization calculations using RHF method for neutral NH₃ molecule

Basis set	R _{N-H} (Å)	Dipole moment (Debye)	∠H-N-H (°)
3-21G	1.003	1.75	112.36
6-31G	0.991	1.38	116.12
DGDZVP	1.002	1.91	107.48
cc-pVDZ	1.008	1.72	105.97
cc-pVTZ	0.999	1.60	107.66
cc-pVQZ	0.998	1.57	107.97
aug-cc-pVDZ	1.004	1.58	107.56
aug-cc-pVTZ	0.998	1.54	108.14
aug-cc-pVQZ	0.998	1.54	108.21
Experiment ¹⁰	1.012	1.46	106.70

On comparison with the experimental data¹⁰, we have found that the aug-cc-pV(D/T/Q)Z basis sets appropriate for the optimization of neutral NH₃ molecule. Therefore, we have chosen aug-cc-pV(D/T/Q)Z as the basis sets for further computations. We have further used correlated methods like MP2 and CCSD to see the method dependencies in the results. Table 2 provides the results from the MP2 calculations using aug-cc-pV(D/T/Q)Z basis sets and Table 3 provides that of from CCSD calculations. It is to be noted that we have performed MP2 and CCSD calculations using (a) frozen core (FC) approximation and (b) including all electrons of the molecule.

As we can see from Table 2 and Table 3, it is the aug-cc-pVQZ basis set which predict better comparison with the experimental data. Therefore, we will use this basis set for

further computations. It is to be noted that, there is negligible difference between FC approximation results and Full electrons results.

Table 2. Results from optimization calculations using RMP2 method for neutral NH₃ molecule

Basis set	R _{N-H} (Å)	Dipole moment (Debye)	∠H-N-H (°)
aug-cc-pVDZ (FC)	1.020	1.64	106.28
aug-cc-pVDZ (Full)	1.019	1.64	106.33
aug-cc-pVTZ (FC)	1.012	1.61	106.76
aug-cc-pVTZ (Full)	1.001	1.60	107.03
aug-cc-pVQZ (FC)	1.010	1.61	106.77
aug-cc-pVQZ (Full)	1.008	1.60	106.98
Experiment ¹⁰	1.012	1.46	106.70

Table 3. Results from optimization calculations using RCCSD method for neutral NH₃ molecule

Basis set	R _{N-H} (Å)	Dipole moment (Debye)	∠H-N-H (°)
aug-cc-pVDZ (FC)	1.021	1.64	106.25
aug-cc-pVDZ (Full)	1.020	1.64	106.28
aug-cc-pVTZ (FC)	1.012	1.62	106.65
aug-cc-pVTZ (Full)	1.001	1.61	106.78
aug-cc-pVQZ (FC)	1.010	1.62	106.67
aug-cc-pVQZ (Full)	1.008	1.60	106.95
Experiment ¹⁰	1.012	1.46	106.70

Using the optimized geometries of neutral NH₃ molecule, we have further optimized anionic NH₃ molecule using three different methods viz. UHF, UMP2 and UCCSD and aug-cc-pVQZ basis set. In Table 4, we have summarized the results those obtained from the optimization of the anionic NH₃ molecule.

Table 4. Results from optimization calculations using aug-cc-pVQZ basis set for anionic NH₃ molecule

Method used	R _{N-H} (Å)	Dipole moment (Debye)	∠H-N-H (°)
UHF	1.000	1.79	107.04
UMP2 (FC)	1.016	1.87	105.43
UMP2 (Full)	1.013	1.86	105.58
UCCSD (FC)	1.016	1.87	105.43
UCCSD (Full)	1.013	1.86	105.60
Experiment	NA	NA	NA

As there is no experimental data available for anionic

NH₃ molecule, hence we could not make a comparison with the same. However, we have compared the energies of both neutral and anionic NH₃ molecules from the optimization calculations at the HF, MP2 and CCSD methods using aug-cc-pVQZ basis and are provided in Table 5.

Table 5. Comparison of energies from optimization calculations for both neutral and anionic NH₃ molecules using aug-cc-pVQZ basis set. We have used restricted method for the neutral moiety and unrestricted method for the anionic moiety

Method used	E_{Neutral} (Hartree)	E_{Anion} (Hartree)	$\Delta E = E_{\text{Anion}} - E_{\text{Neutral}}$ (Hartree)
HF	-56.2244	-56.1980	0.0264 (0.72 eV)
MP2 (FC)	-56.4778	-56.4565	0.0213 (0.58 eV)
MP2 (Full)	-56.5082	-56.4869	0.0213 (0.58 eV)
CCSD (FC)	-56.4868	-56.4659	0.0209 (0.57 eV)
CCSD (Full)	-56.5181	-56.4971	0.021 (0.57 eV)

Vertical attachment energy

From the Table 5, we have seen that in all methods anionic NH₃ molecule has higher energy than that of neutral NH₃ molecule. That is, anion is less stable than the neutral moiety. In order to make an affirmative answer, we have calculated the vertical attachment energy (VAE) which is the energy difference between anionic and neutral NH₃ moiety at neutral's equilibrium geometry. Table 6 summarizes the VAEs of NH₃ molecule in three methods, viz. HF, MP2 and CCSD. VAE values in eV are also provided in the parenthesis of Table 6.

Table 6. Vertical attachment energies (VAEs) of NH₃ molecule using aug-cc-pVQZ basis set. We have used restricted method for the neutral moiety and unrestricted method for the anionic moiety

Method used	E_{Neutral} (Hartree)	E_{Anion} (Hartree)	$\text{VAE} = E_{\text{Anion}} - E_{\text{Neutral}}$ (Hartree)
HF	-56.2245	-56.1979	0.0266 (0.72 eV)
MP2 (Full)	-56.5079	-56.4862	0.0217 (0.59 eV)
CCSD (Full)	-56.5177	-56.4961	0.0216 (0.59 eV)

Potential energy curves

The VAE values provide an indication that at what electron's energy, the formation of temporary negative anion (anionic NH₃) occurs. In order to justify our assumption, we have calculated the potential energy (PE) curves of neutral and anionic NH₃ molecules along the N-H bond from the

respective optimized geometries at the HF, MP2 and CCSD theoretical accuracies with aug-cc-pVQZ basis set. We have considered 128 steps with initial value of $R_{\text{N-H}} = 0.5 \text{ \AA}$ and a step size of 0.05 \AA . The computed PE curves are provided in Figs. 3-5 for all three methods mentioned above.

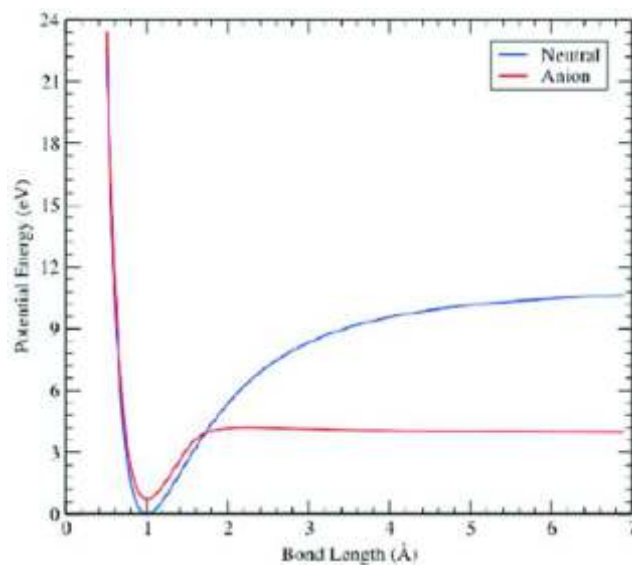


Fig. 3. Potential energy (PE) curves of neutral and anionic NH₃ moiety calculated at the HF/aug-cc-pVQZ theoretical accuracy. We have used restricted method for the neutral moiety and unrestricted method for the anionic moiety.

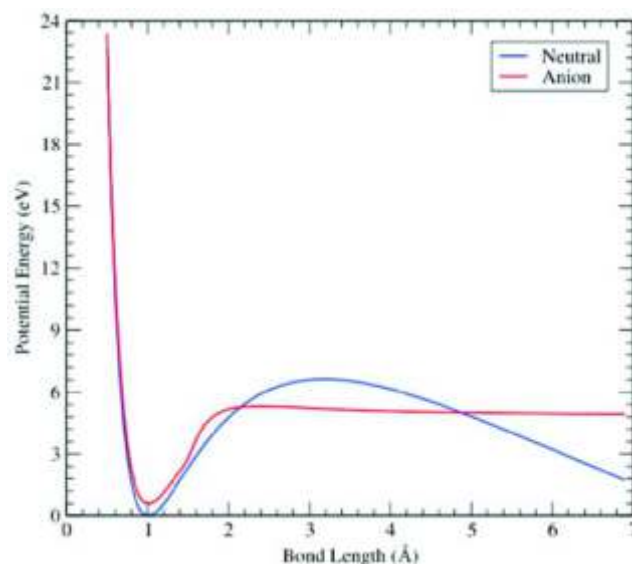


Fig. 4. Same as in Fig. 3 except method used here is MP2/aug-cc-pVQZ.

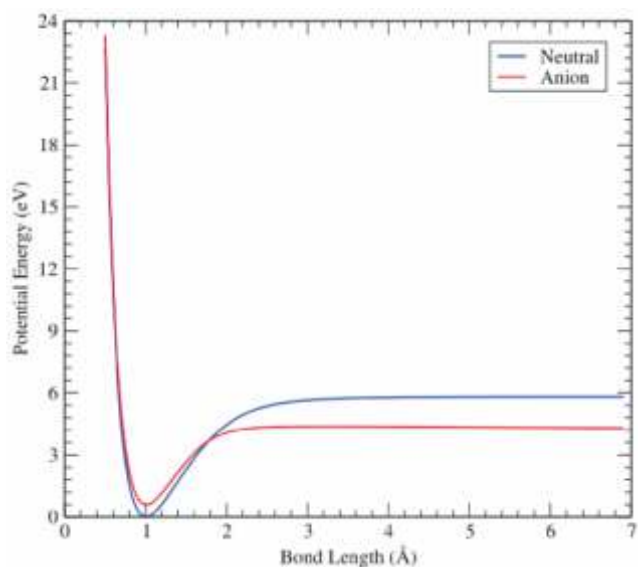
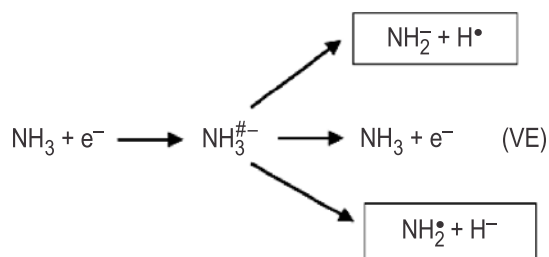


Fig. 5. Same as in Fig. 3 except method used here is CCSD/aug-cc-pVQZ.

It is evident from our PE curves that anionic NH_3 moiety is metastable than the neutral NH_3 moiety. Hence, PE curves corroborate the VAE results as discussed. In order to verify the metastable behavior, calculations of resonance width and nuclear dynamics of the anionic NH_3 are required and is underway in our group.

It is expected that with electron attachment to the neutral NH_3 molecule, the probable reactions would be



As we can see from above, there are three possible reactions that may occur from the metastable $\text{NH}_3^{\#-}$. In this investigation, we have delinked the vibrational excitation pathway and DEA pathway for $\text{NH}_2 + \text{H}^\bullet$ products. We have concentrated on DEA pathway which yields $\text{NH}_2^\bullet + \text{H}^-$ as products.

In order get these products, we have performed the transition state search calculations using quadratic synchronous transit (QST2) approach⁴¹. In this approach, we have used

the reactant geometry (which is the optimized anionic geometry) and probable product geometry (an asymptotic value of the N-H bond, taken from the anionic PE) and performed a transition state search. Our QST2 calculations provided a transition state with a single negative imaginary frequency. Finally, using this transition state, we have done intrinsic reaction coordinate (IRC) calculation^{42,43} to get the reaction pathway. The IRC path along with reactant, transition state and product geometries are provided in Fig. 6 and summarized in Table 7.

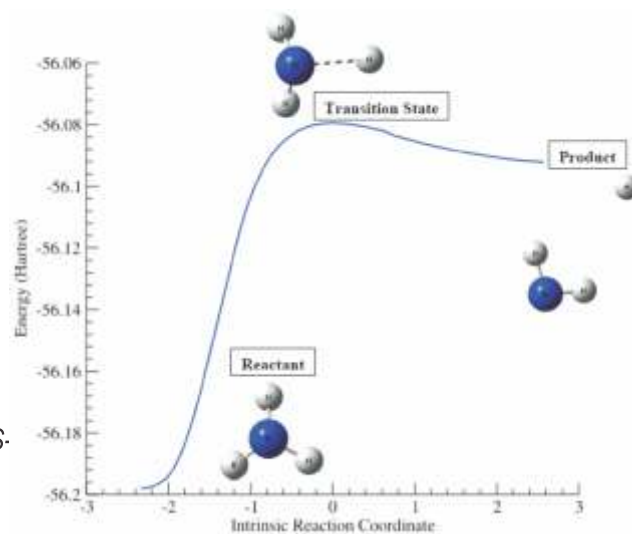


Fig. 6. Intrinsic reaction coordinate (IRC) pathway calculated at the UHF/aug-cc-pVQZ theoretical accuracy.

Table 7. Energies of the reactant (E_R), transition state (E_{TS}) and product (E_P) calculated at UHF/aug-cc-pVQZ theoretical accuracy

Method used	E_R (Hartree)	E_{TS} (Hartree)	E_P (Hartree)	$E_A = E_{TS} - E_R$ (Hartree)
UHF	-56.1980	-56.0795	-56.0924	0.1185 (3.22 eV)

We have also analyzed our results from the molecular orbitals (HOMO-LUMO) plots of neutral NH_3 and singly occupied molecular orbitals (SOMOs) plots of anionic NH_3 . These are provided in Fig. 7 and Fig. 8 respectively.

As we can see from Fig. 8, initial localization of the electron density in the anionic NH_3 molecule (Reactant) has been transferred to the H^- (Product) with extra electron is seen located in the Product. Therefore, our prediction for the DEA reaction is turn out to be correct. However, for a definitive

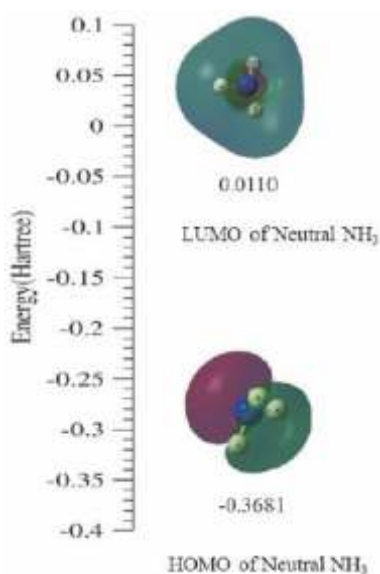


Fig. 7. Molecular orbitals (HOMO and LUMO) with orbital energies of neutral NH_3 calculated at RHF/aug-cc-pVQZ theoretical accuracy.

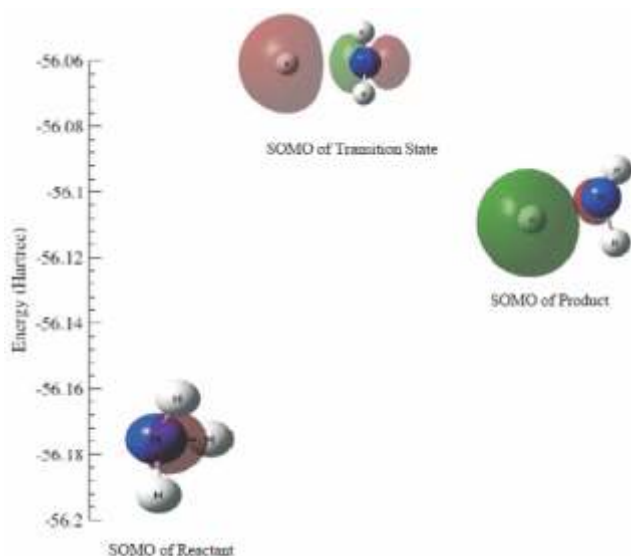


Fig. 8. Singly occupied molecular orbitals (SOMOs) with energies of anionic NH_3 calculated at UHF/aug-cc-pVQZ theoretical accuracy.

conclusion use of correlated methods are highly desirable and is underway in our group.

Concluding remarks

In this computational investigation of electron attachment to the neutral ammonia molecule, we have performed cal-

culations at three theoretical accuracies such as HF, MP2 and CCSD using aug-cc-pVQZ basis set. The choice of basis set is done after performing the series of calculations using other basis sets. Results obtain from CCSD/aug-cc-pVQZ method offer better agreement with the experimental results. We have also calculated VAEs of NH_3 molecule which gives an indication of electron attachment energy in all three methods mentioned above. We have computed the PE curves of neutral and anionic NH_3 molecules. PE curves show the metastable nature of the NH_3 anion.

To investigate the reaction mechanism in the DEA process of NH_3 , we have performed transition state search calculation and found a transition state using the HF/aug-cc-pVQZ method. Finally, using the transition state we have done IRC calculations and got the minimum energy path with an activation energy of 0.1185 Hartree (3.22 eV). This much energy is required to break the NH bond in anionic NH_3 molecule.

In future, we would like to investigate other DEA pathway and vibrational excitation process as mentioned earlier with a detail mappings of electronic structure theory methods. Later, we would like to study the nuclear dynamics of the metastable anion followed by calculating the life time of the same. An effort along these lines are underway in our group.

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