A quantum chemical study of the $\text{N}_2\text{H}^+ + e^- \rightarrow \text{NH} + \text{N}$ reaction

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Abstract. A theoretical investigation of the DR of N$_2$H$^+$ to give N + NH has been undertaken because it is of interest for astrochemistry but also because the DR of N$_2$H$^+$ has been determined experimentally leading to controversial results. Using the same level of theory used to investigate the DR of N$_2$H$^+$ along the N$_2$ + H reaction path, the present study shows that the lowest repulsive state of N$_2$H leading to the NH and N fragments in their ground electronic states is likely going to cross the N$_2$H$^+$ ionic curve far above its v=0 vibrational energy level. This study suggests that the DR of N$_2$H$^+$ to give N + NH should not be efficient in the low temperature of the interstellar clouds.

1. Introduction
N$_2$H$^+$ is detected in a large number of astronomical objects [1-6]. In astrochemical models, it is considered that N$_2$ is almost completely recycled through the electronic dissociative recombination (hereafter DR) of N$_2$H$^+$

$\text{N}_2\text{H}^+ + e^- \rightarrow \text{N}_2 + \text{H}$

In 2001, Geppert et al. [7] measured the DR of N$_2$H$^+$ using the CRYRING ion storage apparatus throwing doubt on the validity of the astrophysical hypothesis. The unexpected experimental results posing the problem of the mechanism involved by the DR of N$_2$H$^+$ as well as of the abundance of N$_2$ in space has motivated an extensive theoretical study [8] of the DR of N$_2$H$.^+$. The DR of N$_2$H$^+$ along the N$_2$ + H channel has been first undertaken and is published elsewhere [8]. In this study and using state of the art methods of quantum chemistry it is shown that the lowest repulsive $\Sigma$ state of N$_2$H is very low in energy. Its curve passes below the $^1\Sigma$ state of N$_2$H$^+$ and below the lowest bound $^5\Sigma$ state of linear N$_2$H (a Rydberg state). However it is also shown that there exist a higher repulsive $^3\Sigma$ state of N$_2$H (the second repulsive state) crossing the ion curve for its v=0 vibrational energy level. Moreover, even if this crossing is shown to occur at the turning point of the vibrational v=0 wave function of the ion and of the nuclear wave function of the second $^3\Sigma$ repulsive state it is also shown that for slightly bend geometries of the ion (5-10°) this second repulsive $^3\Sigma$ state of N$_2$H is lowered toward the minimum of the potential energy curve of the ion (see Figure 1) leading to a very efficient curve crossing because of a good overlap between the vibrational wave functions of N$_2$H$^+$ (v=0) and of the second $^3\Sigma$ repulsive state of N$_2$H. It is therefore expected that the DR of N$_2$H$^+$ will be efficient for slightly bent geometries of the ion, geometries that can be expected at the low temperature of the cold interstellar clouds for this loose ion.

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Figure 1: Quasi-diabatic potential energy surfaces for the $\text{N}_2\text{H}^+ + e^- \rightarrow \text{N}_2 + \text{H}$ reaction. Energies (in a.u.) are reported as a function of the $\text{N}_2$-$\text{H}$ distances (Å). The top bound curve is the ion. The lower bound curves are the Rydberg states. While bending the NNH angle by 10° does not affect the shape of the potential energy surfaces of the ion nor of the Rydberg states, it does lower the energy of the repulsive states. This lowering is reported only for the second repulsive state, the one of interest for us in the present case.

The same theoretical study has been extended to the $\text{N} + \text{NH}$ channel. It is presented below.

2. The theoretical approach

The theoretical method used to study the DR of $\text{N}_2\text{H}^+$ for the $\text{N}_2 + \text{H}$ channel has been applied here. Therefore only the philosophy of this approach is recalled and the reader is sent to the paper of D. Talbi [8] for more details. For a quantitative study of the DR of $\text{N}_2\text{H}^+$ along the $\text{N} + \text{NH}$ channel, the even handed treatment of both the ionic, the excited (mainly Rydberg) and the dissociative states of $\text{N}_2\text{H}$ has to be insured which implies that the correlation energy for all these states has to be treated through the same CI procedure (so as not to favour one state over another). To fulfil this requirement, molecular orbitals with a strong localized character are used to build the CI wave functions. The advantage of such a method is that the CI n-particle space is defined in terms of orbitals whose chemical significance is clearly identified. Configurations can be selected according to chemical evidence and the type of arbitrariness associated with the energy related selection processes can be avoided. Moreover the CI expansion is directly obtained in a configuration space that contains the approximate diabatic representation of the problem (hereafter quasi-diabatic). Indeed, thanks to the use of orbitals with a strong localized character to construct the configuration space, it is possible to identify most configuration state functions with a quasi-diabatic state (repulsive, excited valence, Rydberg) according to the weights of the relevant configurations in the CI wave functions. The orbitals of localized character have been obtained with the MCSCF n-particle space of table 1 given in Reference [8] but with a different number of electrons in set1 and set2. In the present case where we are interested by the dissociation along the NN reaction coordinate, two electrons have been distributed in set1 (NH and NH*) and three in set2 (NN and NN*). In the same way the CI n-particle space designed to evaluate the correlation energy and to calculate the potential energy surfaces is the one reported in table 2, in Reference [8]. The 6-311G(d,p) and 4s3p1d atomic basis extended by diffuse functions, used respectively for nitrogen and hydrogen, are also the ones used in Reference [8].
Let us mention here that thanks to the design of the same CI n-particle space to built the potential energy surfaces along the two dissociation channels i.e \( \text{N}_2 + \text{H} \) and \( \text{N} + \text{NH} \), the DR of \( \text{N}_2\text{H}^+ \) along these two channels is treated at the same correlation level and the relative position of respective potential energy surfaces can be compared.

All the calculations have been performed in C\(_{2v}\) symmetry using ALCHEMY-CI II program \[9\].

### 3. The adiabatic and quasi-diabatic potential energy surfaces

The NH bond being almost identical in \( \text{N}_2\text{H}^+ \) and \( \text{NH} \), the study of the \([\text{N}_2\text{H}^+ + \text{e}^-]\) complex along the NN dissociative reaction coordinate, has been carried for fixed NH bond optimized in the ion at the present MRCI level i.e. \( \text{NH}=1.033\text{Å} \). The expected reliability of the present CI calculations has already been assessed in the previous paper \[8\] from the energetics deduced from the \( \text{N}_2\text{H} \) (\( ^2\Sigma \)) and \( \text{N}_2\text{H}^+ \) (\( ^1\Sigma \)) energies calculated at the dissociation limits within the super molecule approach. It will not be discussed here.

![Figure 2: \( ^2\Lambda_1 \) adiabatic potential energy surfaces for the \( \text{N}_2\text{H}^+ + \text{e}^- \rightarrow \text{N} + \text{NH} \) reaction. Energies (a.u.) are reported as a function of the N-NH distances (Å). The top bound curve is the ion.](image)

The adiabatic potential energy surfaces for the three lowest \( ^2\Lambda_1 \) state of \( \text{N}_2\text{H} \) (states of \( \Sigma \) and \( \Delta \) symmetry in \( C\_\infty v \) notation) as well as that of the ion \( \text{N}_2\text{H}^+ \) (\( ^1\Sigma \_g^+ \)) are presented in Figure 2. They are calculated along the NN reaction coordinate keeping the NH bond frozen at 1.033Å. This figure shows curves with strong avoided crossings indicating a change in their character. The shape of these adiabatic surfaces as well as the analysis of the corresponding MRCI wave functions argue for the existence of curve crossing in a quasi-diabatic representation, between \( \text{N}_2\text{H} \) bound excited states and repulsive ones.

The quasi-diabatic potential energy surfaces (extracted from the analysis of the MRCI wave functions) for the lowest Rydberg state and for the two lowest repulsive states of linear \( \text{N}_2\text{H} \) are reported in
Figure 3 together with the potential energy curve of the ion. Even if only the lowest Rydberg state of N₂H is shown in the figure, the reader has to keep in mind that above it exists a series of parallel Rydberg curves converging towards the ionic state. Figure 3 shows that the two lowest repulsive states of linear N₂H correlating to N (²D) + NH (X ³Σ⁻) are high in energy and are not expected to cross the curve of the ion close to its minimum of energy i.e. below v=0.

Figure 3: Quasi-diabatic potential energy surfaces for the N₂H⁺ + e⁻ → N + NH reaction. Energies (a.u.) are reported as a function of the N-NH distances (Å). The top bound curve is the ion. The one below is the lowest Rydberg state.

4. Conclusion
The present study of the DR of N₂H⁺ to give N + NH, completes the study undertaken on the DR of N₂H⁺ to give N₂ + H. It appears from this study that the lowest repulsive state of N₂H along the N + NH dissociation path is much too high in energy to lead to an efficient curve crossing with the corresponding ion. Bent geometries has not yet been considered along this dissociation channel, but regarding the position of the lowest repulsive state of N₂H, we do not expect to improve the position of the crossing to a point which will lead to an efficient DR of N₂H⁺ to N + NH. At the low temperature of the interstellar medium the DR of N₂H⁺ should lead essentially to N₂. This conclusion is in total agreement with the experimental results of N. Adams [10].

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