**Ab initio** study of the dissociative recombination of HCNH$^+$

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**Abstract.** Dissociative recombination of protonated hydrogen cyanide HCNH$^+$ is a very important process in dark interstellar molecular clouds. The dominant mechanism that drives this process, either ‘direct’ through a resonance, or ‘indirect’ through Rydbergs is currently an issue of controversy. Only qualitative conclusions for the branching ratio between the HCN and HNC fragments is available. We will report *ab initio* electron scattering calculations using the complex Kohn variational method for low energy electron scattering from HCNH$^+$ using a correlated wave function for the target. Resonance energies and widths were abstracted and their behavior as a function of the internuclear geometry is studied.

1. Introduction

Dissociative recombination of protonated hydrogen cyanide HCNH$^+$ is a very important process in dark interstellar molecular clouds. It has often been postulated as the cause of the thermochemically unrealistic abundance of hydrogen isocyanide HNC relative to hydrogen cyanide HCN in interstellar medium [1]. Indeed HNC being less stable by almost 0.6 eV than HCN, its abundance should be negligible relative to the abundance of HCN in thermodynamically equilibrated systems. However, the HNC/HCN abundance ratio has been observed to be sometimes higher than unity in dark interstellar molecular clouds such as OMC, LMC... [2], and HCNH$^+$ + e$^-$ is considered to be the main reaction which forms these species in the above mentioned media. On the other hand, dissociative recombination of polyatomic molecular ions such as HCNH$^+$ is of fundamental theoretical importance, with many vibrational degrees of freedom and opportunities for interaction between excited electronic surfaces in several dimensions. Unlike diatomic molecular ions, polyatomic systems have many degrees of freedom which can interact leading to the possibility of far richer and more complex dynamics.

The theoretical study of such processes involves two equally important aspects, which may be treated in a single step or in sequence, depending on the approach. One first needs a good knowledge of the electronic structure of the system, both of the ion HCNH$^+$ and of the neutral molecule HCNH formed by electron recombination: potential energy surfaces, electronic or non-adiabatic interactions, Rydberg states and their quantum defects. The second aspect is the treatment of the dynamics, which involves both electronic and nuclear dynamics, and their mutual interactions. Indeed, we have to deal with a "reactive" collision event with electron scattering in the entrance channel, and heavy particles as products. The process can be solved by global approaches like the $R$-matrix, mostly used for calculating vibrational [3] and rotational [4] transitions, or by two-step methods such as multichannel quantum defect theory (MQDT) [5] or wave packets [6].

Recent experimental studies of the DR reaction of HCNH$^+$ have been carried out by Semaniak *et al.* [7] at the heavy ion storage ring CRYRING. The high thermal DR rates obtained (2.8 $\times$ 10$^{-7}$ cm$^{-3}$/s
at 300 K) seem to indicate the presence of a neutral state of HCNH which crosses the HCNH$^+$ lowest state near the equilibrium geometry and could drive the process. However, the measured cross section decreases faster with energy than the $E^{-1}$ scaling law expected when the DR process is evidently driven by the direct mechanism [8]. This could indicate that the indirect mechanism involving Rydberg-type excited states plays a non-negligible role in the DR of the HCNH$^+$ ion. In the same set of experiments, the branching ratio for the HCNH$^+$ + e$^-$ DR products near zero electron energy was also measured, with a global production of 67.5% for both HCN and HNC. Unfortunately the experiments cannot distinguish between the HCN and HNC channels since the two species have the same molecular mass. The remaining 32.5% of the flux goes into 3 body fragmentation (CN + H + H).

The first detailed theoretical investigation of the branching ratio for HCNH$^+$ dissociative recombination was made by Herbst [9] using a quantum formulation of the statistical phase-space theory of chemical reactions. He predicted that HNC and HCN are produced in almost equal amount. Two computations of potential energy surfaces (PES) involved in the DR reaction of HCNH$^+$ carried out more recently [10, 11] support the hypothesis of equal formation of HNC and HCN. These studies draw only a qualitative conclusion for the branching ratio, and give controversial results about the efficient mechanism which drives the process.

These controversial results and the lack of molecular parameters needed for the quantitative study of the formation of HCN and HNC by electronic dissociative recombination of HCNH$^+$ were the primary reasons for this work. We have carried out ab initio [12] calculations of electron scattering from HCNH$^+$ at fixed-nuclei geometries, using accurate correlated target wave functions. These calculations allowed the determination of the resonance energies and autoionization widths of HCNH. The complex Kohn variational method was used. Although the fixed nuclei problem is only a part of the full electron-ion scattering picture, it provides the input necessary to solve the full problem including nuclear dynamics in processes such as dissociative recombination.

2. Scattering

The complex Kohn variational method rests on a stationary principle for the $T$-matrix:

$$T_{\text{stat}}^{T_{\text{tr}}}=T_{\text{trial}}^{T_{\text{tr}}}-2\int\Psi_{\Gamma}(H-E)\Psi_{\Gamma}^{\text{stat}}.$$  
(1)

The trial wave function for the $(N+1)$-electron system is expanded as

$$\Psi_{\Gamma}^{\text{stat}} = \sum_{\Gamma} A[\Phi_{\Gamma}(\vec{r}_1..\vec{r}_N)F_{\Gamma}(\vec{r}_{N+1})] + \sum_{\mu} d_{\mu}^{\Gamma} \Theta_{\mu}(\vec{r}_1..\vec{r}_{N+1})$$  
(2)

where the first sum is over electronic target states, $\Phi_{\Gamma}$, $A$ antisymmetrizes the coordinates of the incident electron with those of the target electrons and the second sum contains square-integrable, $(N+1)$-electron terms that describe correlation and polarization effects.

In the Kohn method, the scattering functions are further expanded in a combined basis of Gaussian ($\phi_i$) and continuum (regular Coulomb wave $F_i$ and outgoing Coulomb wave $G_i$) basis functions:

$$F_{\Gamma}(\vec{r}) = \sum_i c_i^{\Gamma} \phi_i(\vec{r}) + \sum_{lm} \left[ F_i(k_r \vec{r}) \delta_{il} \delta_{mm} + T_{\Gamma}^{T_{\Gamma}} G_i(k_r) \right] Y_{lm}(\hat{r})/r.$$  
(3)

The $T$-matrix elements $T_{\Gamma}^{T_{\Gamma}}$ are the fundamental dynamical quantities from which all fixed-nuclei cross sections are derived.

To relax any orthogonality constraints on the trial wave function imposed by orthogonalizing the continuum function $F_i$ and $G_i$ to the orbitals used to expand the target states, we included in Q-space all possible $(N+1)$-electron configurations, consistent with the total space/spin symmetry, in which only natural orbitals are occupied. The optical potential also included Configuration Interaction (CI) relaxation terms [12], which are the complement (1-P) of the $P$-space portion of the wave function. We have computed partial cross sections for $^2\Sigma^+$ and $^2\Pi$ total symmetry.
3. Description of calculations

The ground state of HCNH$^+$ is:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4$$  (4)

The low-lying excited states of this system can be formed by exciting one electron into the unoccupied low-lying orbitals.

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^3(2\pi)$$  (5)

The C$_{2v}$ point group was adopted in the present calculations for HCNH$^+$ and HCNH since both are most stable in their linear form [10]. The calculations were carried out in a contracted basis set of triple zeta plus polarization Gaussian functions. We first performed a Self Consistent Field (SCF) calculation on the ion. We then froze the lowest three orbitals, and performed an all single and double excitations calculation from a reference space generated by a full CI (Configuration Interaction) to obtain the natural orbitals (NO) of the one-particle density matrices.

We used two procedures to obtain the natural orbitals. In one case we used the NOs from the ground state only. In the second, to obtain a balanced treatment between the singlet and triplet states, we took natural orbitals from averaging the density matrices for the lowest two states of the ion. Although we deal only with the low energy region (below the first excitation threshold of the HCNH$^+$ ion), we have checked the first excited states of the ion in order to predict the shape of the resonant states which may be viewed as Rydberg states converging to one of these excited states. In order to test the convergence we performed calculations including four natural orbitals ($\pi, \sigma_{CH}$ and $\sigma_{NH}$) besides the occupied orbitals. The basis set was expanded to include additional diffuse orbitals. The target states were determined from a full CI in the natural orbital space of eleven orbitals with the largest occupation number.

The complex Kohn trial function included all CSFs (Configuration Space Functions) generated by placing 10 electrons in the five frozen core orbitals, 4 electrons in the 6 orbitals of the active space and one electron in the augmented virtual space (71 orbitals). This set plus the remaining “penetration terms” gave trial functions of $\sim 5000$ configurations for each total symmetry considered. For the resonant $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ symmetries, calculations were performed over a range of internuclear distances and the resonance parameters extracted by fitting the eigenphase sums to a Breit-Wigner form. No resonances were found in $^2\Delta$ symmetry, so we will report results only for $^2\Sigma$ and $^2\Pi$.

4. Results and discussion

The presence of resonance states is detected by the jump of $\pi$ they produce in the eigenphase sum. An example is shown in figure 1, where the eigenphase sum (a) as well as the corresponding elastic scattering cross section (b) as a function of the collision energy are shown for one of the resonances. All following results were obtained with natural orbitals averaged over the lowest two states of the HCNH$^+$ ion.

We will first concentrate on scattering in $\Pi$ symmetry. The resonances are plotted in figure 2(a) as functions of the C–H bond distance (for fixed N–H bond distance) and in figure 2(b) as functions of the N–H bond distance (for fixed C–H bond distance), and compared to the potential energy surfaces for the two lowest ion states. The corresponding autoionization widths as a function of the C–H bond distance (for fixed N–H) are also shown in figure 2(c).

The potential energy surface for the first excited state of the ion shows evidence of an ‘avoided crossing’ with a higher state of the ion not shown in the figure. The resonance energies and the strength of their interactions with the continuum show that they will have similar effect on C–H and N–H bond breaking and they appear to be parallel to the first excited state of the ion. They are members of a Rydberg series converging to this ionic state. The lowest resonance in this symmetry lies about 2.5 eV above the ion ground state and cannot efficiently drive low-energy dissociative recombination. Moreover it does not have a repulsive character as the high lying resonances of the same symmetry. Therefore, no favorable crossing with the ion ground state will occur as needed for a strong “direct” dissociative recombination.
Figure 1. Eigenphase sum (a) and elastic scattering cross section in Å² (b) as a function of the collision energy.

Figure 2. Resonance energies (*) and autoionization widths (●) for the 2Π states of HCNH as a function of the C–H distance for fixed N–H (a) and as a function of the N–H distance for fixed C–H (b). The full and dashed lines represent the ion ground state and first excited state, respectively.

Note that as these resonances lie above the ground state of the ion, they appear as scattering resonances, the so-called ‘core-excited’ resonances seen in OH⁺ [13] and CH⁺ [14] DR.

Figure 3(a) presents the Σ resonance energies as functions of the C–H bond distance (for fixed N–H), the corresponding autoionization widths are shown in figure 3(c). The same resonance energies as functions of the N–H bond distance (for fixed C–H) are plotted in figure 3(b). The scattering in Σ symmetry yields a resonance that lies around 1eV above the ground state of the ion at the equilibrium geometry. We can identify the nature of the resonant states by doing a CI on the neutral and studying the configurations of the states. Examination of these resonances indicates that the lowest three states should cross the ion at equilibrium geometry and become bound states of the neutral (represented by the diamonds in figure 3). Further calculations are necessary to confirm this prediction and generate the complete resonance potential energy surfaces required for the calculation of the full dissociative recombination dynamics.
5. Conclusion

The preliminary results presented here indicate the presence of a low lying Σ resonant state while no Δ resonance is found and the lowest Π one is high in energy. More extensive scattering calculations must be carried out to determine the shape of the resonance curves, particularly near the crossing with the ionic curve. In addition, we need to carry out additional structure calculations to determine the behavior of the curves after crossing the ion, and the coupling to the Rydberg states as dissociation occurs. These structure calculations are also important for the determination of Rydberg-type excited states of HCNH which are very important for the description of the indirect mechanism of dissociative recombination. If such a Rydberg-type state has a repulsive character and is close enough to be coupled to the ion ground state via non-adiabatic interactions [15], it could efficiently drive the dissociation of the molecular complex.

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References

[1] Watson W G 1974 Ap. J. 188 35
[2] Schilke P, Walmsley M C, Pineau Des Forêts G, Roueff E, Flower D R and Guilloteau S 1992 Astron. Astrophys. 256 595
[3] Sarpal B K and Tennyson J 1993 Mon. Not. R. Astron. Soc. 263 909
[4] Faure A and Tennyson J 2001 Mon. Not. R. Astron. Soc. 325 443
[5] Giusti A 1980 J. Phys. B: At. Mol. Phys. 13, 3867
[6] Orel A E 2000 Phys. Rev. A 62 020701
[7] Semaniak J et al. 1974 Ap. J. Suppl. Ser. 135 275
[8] Mitchell J B A 1990 Phys. Rep. 186 215
[9] Herbst E 1978 Ap. J. 222 508
[10] Shiba Y, Hirano T, Nagashima U and Ishii K 1998 J. Chem. Phys. 108 698
[11] Talbi D and Ellinger Y 1998 Chem. Phys. Lett. 288 155
[12] Rescigno T N, Lengsfield B H and McCurdy C W 1995 Modern Electronic Structure Theory vol 1 ed Yarkony D R (Singapore: World Scientific) p 501
[13] Guberman S L 1995 J. Chem. Phys. 102 1699
[14] Carata L, Orel A E and Suzor-Weiner A 1999 Phys. Rev. A 59 2804
[15] Florescu A, Ngassam Y, Schneider I F and Suzor-Weiner A 2003 J. Phys. B: At. Mol. Opt. Phys. 36 1205

Figure 3. Resonance energies (*) and autoionization widths (●) for the $^2\Sigma$ states of HCNH as a function of the C−H distance for fixed N−H (a) and as a function of the N−H distance for fixed C−H (b). The full and dashed lines represent the ion ground state and first excited state, respectively. A bound neutral state which the resonant states may turn into when they cross the ionic ground state is also represented (diamonds), starting from R=2.5 Bohr.