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# DFT study of ground state proton transfer in 2-pyridone/2-hydroxypyridine–ammonia clusters

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Received 23 July 2004; accepted 10 November 2004

Available online 8 December 2004

## Abstract

DFT calculations in the ground state have been performed for 2-hydroxypyridine–ammonia clusters  $2\text{HP} \cdot (\text{NH}_3)_n$  ( $n = 1$  to 5) and their tautomers. Structures, relative energies and vibrational frequencies of these species were obtained at the B3LYP/6-31++G\*\* level of theory. It was found that some structural parameters such as intra- and intermolecular distances and vibrational frequencies of O–H and N–H stretching, serve as probes and indicators of proton transfer in these clusters. The study of neutral forms shows that intermolecular proton transfer to the  $(\text{NH}_3)_n$  occurs for  $n = 4$  and 5 in enol and keto clusters, respectively. For enol form, ion-pair cluster calculated for  $n = 4$  is less stable than the neutral form by 7.1 kJ/mol. While, for keto form, it is calculated to be 25.4 kJ/mol less stable than the neutral form.

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## 1. Introduction

Proton transfer (PT) reactions play an important role in many biologically and chemically relevant processes [1–3]. They are generally highly sensitive to the solvent, which makes a variety of intermolecular hydrogen bonding complexes  $\text{A-H} \cdot \text{B}_n$  ( $n = \text{integer}$ ). This interaction between acid molecules and polar solvents can shift the equilibrium (1) to the polar form



Intermolecular proton transfer to the  $\text{B}_n$  occurs, once a critical cluster size  $n_c$  is reached.  $n_c$  depends on both the acidity of A–H and the proton affinity of the solvent B. Previous studies were interested in the ground state proton transfer (GSPT) reactions in  $\text{A-H} \cdot (\text{NH}_3)_n$  clusters, where acid A–H was one of the following molecules; *p*-CN-phenol and *p*-CHO-phenol [4], 1-naphthol [5,6] and

phenol [7–9]. For these clusters, the  $n_c$  reached are, respectively,  $n_c = 5$ ,  $n_c = 6$  and  $n_c = 5$ .

Tautomeric systems such as 2-hydroxypyridine (2HP)/2-pyridone (2PY) and 7-hydroxyquinoline (7HQ)/7-ketoquinoline (7KQ) are bifunctional hydrogen bonding molecules, which acts as an H donor at the O–H group and as an H acceptor at the N atom in the enol form (Fig. 1(a)), and acts as an H donor in the N–H group and as an H acceptor at the O atom in the keto form (Fig. 1(b)).

Proton transfer reactions in the 7-hydroxyquinoline–ammonia clusters have been previously studied by Leutwyler and co-workers [10–12]. SCF and experimental studies confirm the existence of proton transfer reaction in both the excited state  $S_1$  and the ground state  $S_0$  via the formation of locally stable ion-pair structures. The proton transfer to the  $\text{NH}_3$  neighbor of ammonium clusters is found to be an energetically possible process from the O–H group of the enol form and N–H group of the keto tautomer. The ion-pair formation reactions are calculated to be endoergic by 6 kcal/mol relative to the enol form. Recently, chromophore to solvent, excited state

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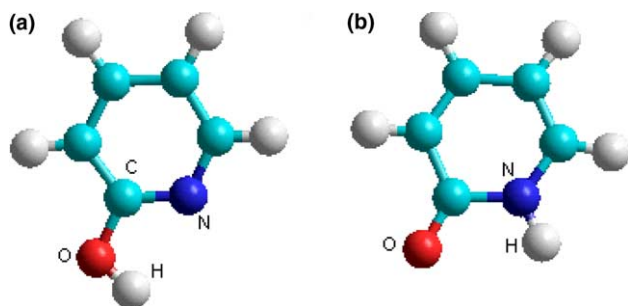


Fig. 1. Schematic view of the 2-hydroxypyridine enol (a) and keto (b) tautomers.

proton transfer reaction is more appropriately classified as a hydrogen or coupled electron–proton transfer, therefore the formation of a radical pair is the primary step in these types of reactions [13–16].

Because of its importance in the mutation of DNA [17], the tautomerization process in the 2HP/2PY molecular system, assisted by proton transfer reaction (PT) has been subject of many studies [18–22]. Some of these studies show a large energy barrier for the proton transfer (PT) reaction in the ground state ( $\approx 2$  eV) [19,20] and the tautomeric equilibrium depends on the environment surrounding the molecule [18]. Interaction of 2PY/2HP with one or two ammonia molecules were investigated focusing on DFT and ab initio structure calculations and harmonic frequencies [23,24]. These calculations confirm some experimental results concerning gas-phase structure of  $2PY \cdot NH_3$  and  $2PY \cdot (NH_3)_2$  in their  $S_0$  and  $S_1$  electronic states [25]. These structures of  $2HP \cdot NH_3$  and  $2PY \cdot NH_3$  complexes show a nonlinearity of  $O-H \cdots NH_3$  and  $N-H \cdots NH_3$  hydrogen bonding and for each complex the ammonia molecule is a strong proton acceptor and a much weaker proton donor. For  $n = 2$  clusters, structures are stabilized by three nonlinear hydrogen bonds and the cooperative effects are very large. These studies lead to the conclusion that in the gas phase, 2PY interacts more strongly than 2-HP with a single as well as with a dimer ammonia. On the other hand, a red shift of frequencies  $\nu(N-H)$  and  $\nu(O-H)$  have been noticed. In contrast, they have not shown neither ground state proton transfer nor tautomerization reaction for these clusters.

In the present paper, we have used theoretical investigation of proton transfer in  $2HP/2PY \cdot (NH_3)_n$  ( $n = 1$  to 5) clusters focusing on structures, energetic and harmonic frequencies aspects. Optimized geometries of some isomers of  $2HP \cdot (NH_3)_n$  and  $2PY \cdot (NH_3)_n$  are performed. Structural parameters and vibrational frequencies are computed in an attempt to help resolve the problem of the threshold size for proton transfer from  $O-H$  and  $N-H$  of enol and keto forms, respectively, to the solvent in the ground state. For each geometry, ion-pair structure is computed to confirm these results.

## 2. Theoretical methods

Calculations of  $2HP \cdot (NH_3)_n$  and  $2PY \cdot (NH_3)_n$  ( $n \leq 5$ ) clusters were performed, these calculations have been done for different isomers for each cluster, and ion-pair structures for each isomer. The methodology of the theoretical investigations involves the following sequences: The initially optimized structure used for the DFT calculations is performed with the semi-empirical AM1 method. DFT calculations were performed using Gaussian 03 program package [26]. Geometry optimization for all structures were carried out in final form with the 6-31++G\*\* standard basis set at the combined Becke's three-parameters exchange functional and the gradient functional of Lee, Yang and Parr (B3LYP) level [27,28]. The integration grid employed for the DFT calculation is pruned (75,302), having 75 radials shells and 302 angular points per shell, resulting in about 7000 points per atom. Throughout the optimization process, both inter and intramolecular degrees of freedom were optimized without symmetry restriction and converged until the largest component of the force on the nuclei was  $10^{-6}$  hartree/Bohr (hartree/rad) and the change in total energy was less than  $10^{-7}$  hartree. The calculated vibrational frequencies for all clusters gave real values, it turns out that the corresponding geometries represent equilibrium ones. The directly calculated zero-point vibrational energies (ZPE) were scaled by 0.97 [24]. After that, the Boys–Bernardi [29] counterpoise correction was applied to give the basis set superposition errors (BSSE) corrected energies. Additional optimization of different clusters and total energy calculation were performed at B3LYP/6-31G, B3LYP/6-31G\* and B3LYP/6-31G\*\* levels to investigate the effect of basis set on structures as well as on energies.

## 3. Results and discussion

### 3.1. Geometries

In all clusters, we note a- $NH_3$ , ammonia molecule which makes a nonlinear hydrogen bonding with  $H_0-O$  and  $N_0-H_0$  of enol and keto forms, respectively, in 2HP/2PY tautomeric system (Fig. 2(a) and (a')). The second ammonia molecule noted b- $NH_3$ , forms two hydrogen bonds,  $N_0 \cdots H-N$  or  $O \cdots H-N$  with, respectively, enol and keto forms, and an  $N \cdots H-N$  with a- $NH_3$  (Fig. 2(b) and (b')). On Fig. 2(c) and (c'), for both  $2HP \cdot (NH_3)_3$  and  $2PY \cdot (NH_3)_3$  clusters, the third ammonia molecule, c- $NH_3$ , inserts itself between a- and b- $NH_3$ , forming two  $N \cdots H-N$  intermolecular bonds.

For  $2HP \cdot (NH_3)_4$ , we present two isomers. In the first one, which is the most stable and shown in Fig. 3(4-I-a), a- and b- $NH_3$  keep the same positions as in the cases

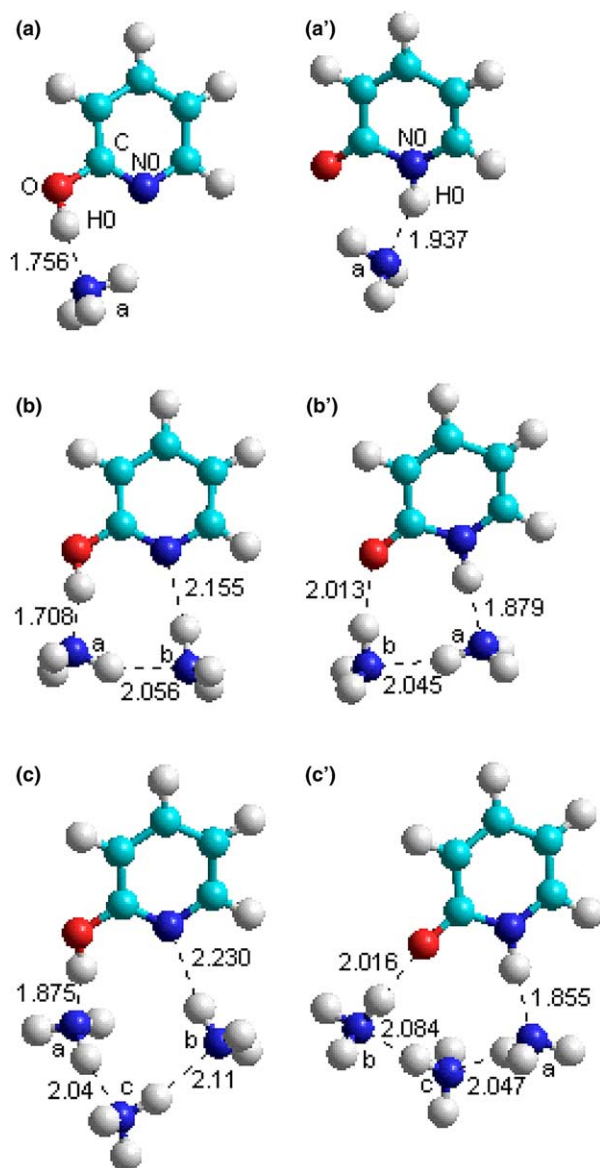


Fig. 2. Minimum-energy structures for  $2\text{HP} \cdot (\text{NH}_3)_n$  (a,b,c) and  $2\text{PY} \cdot (\text{NH}_3)_n$  (a',b',c') ( $n = 1$  to 3). Intermolecular  $\text{H} \cdots \text{N}$  bond lengths are in Å.

$n = 2$  and 3. In contrast, c- $\text{NH}_3$  makes a hydrogen bond  $\text{O} \cdots \text{H}-\text{N}$  with 2-hydroxypyridine, while the fourth ammonia molecule d- $\text{NH}_3$ , forms two hydrogen bonding with a- and c- $\text{NH}_3$ . The second isomer denoted (4-II-a) in Fig. 3 is 5.1 kJ/mol less stable than the first one, four ammonia molecules are combined with 2-HP via  $\text{O}-\text{H}_0 \cdots \text{N}$  and  $\text{O} \cdots \text{H}-\text{N}$  to form a cyclic structure. Only the first isomer (4-I-a) allows proton transfer to form the corresponding metastable ion-pair cluster  $2\text{HP}^- \cdot \text{NH}_4^+(\text{NH}_3)_3$ . In  $2\text{PY} \cdot (\text{NH}_3)_4$  cluster, the first isomer denoted (4-I-a') in Fig. 3, hydrogen bond form a bicyclic structure as in enol form. In the second isomer (Fig. 3(4-II-a')), 4.1 kJ/mol less stable than the first one (4-I-a'), c- $\text{NH}_3$  takes place between a- and b- $\text{NH}_3$ , while d- $\text{NH}_3$  makes a hydrogen bond with oxygen of 2PY. In

$2\text{PY} \cdot (\text{NH}_3)_4$  isomers, no proton transfer to the solvent is noticed.

$2\text{HP} \cdot (\text{NH}_3)_5$  can be arranged in various ways in neutral forms as well as in ion-pair forms as shown in Fig. 4. For neutral forms, the most stable isomer found is a combination of two cycles, three ammonia connecting O and a- $\text{NH}_3$ , and a- $\text{NH}_3$  with b- $\text{NH}_3$  (5-I-a). The second isomer (5-II-a) is very close in energy compared with the first one (0.2 kJ/mol less stable). This second isomer is also formed by two cycles, the first connecting oxygen to a- $\text{NH}_3$  via two ammonia molecules and three ammonia molecules connecting O-H and the N atom of 2-HP. The third isomer (5-III-a) is 5.0 kJ/mol less stable than the first one, this isomer is a combination of three cycles. In the fourth isomer denoted (5-IV-a) a- and b- $\text{NH}_3$  are not connected by hydrogen bonding. All these isomers allow proton transfer reaction to form the corresponding quasi-stable ion-pair clusters, denoted 5-I-b, 5-II-b, 5-III-b and 5-IV-b.

For  $2\text{PY} \cdot (\text{NH}_3)_5$  (Fig. 5), the most stable isomer (5-I-a') corresponds to the same distribution of solvent as in the enol third isomer ((5-III-a) Fig. 4). The second isomer, (5-II-a'), presents nearly a  $C_s$  symmetry: Three ammonia are in the same plane with 2PY molecule. This isomer is 1.5 kJ/mol less stable than the first one. The third isomer (5-III-a') have the same solvent distribution as (5-I-a) in Fig. 4, the most stable one in the other tautomer. The fourth isomer (5-IV-a') may be viewed as the most stable structure for  $n = 4$ , in which the added  $\text{NH}_3$  makes hydrogen bonding with a- and b- $\text{NH}_3$ , and its energy is less stable by 4.8 kJ/mol. For keto form, we note that only for the first and the second isomers as shown in 5-I-b' and 5-II-b', ion-pair clusters are metastable.

For both enol and keto forms, ion-pair clusters present a solvent shell orientation similar to that of neutral species.

For the related systems like  $\text{phenol} \cdot (\text{H}_2\text{O})_n$  with  $n \leq 7$ , A. Lüchow et al. [30] performed quantum Monte Carlo calculations and double resonance experiments. The most stable for  $n = 1$  consider the phenol molecule acts as a proton donor and the water molecule as proton acceptor. This is analogous to  $2\text{HP} \cdot \text{NH}_3$ . The most stable phenol water trimer, tetramer and pentamer are cyclic with the phenyl ring and the free O-H pointing alternating down and up. These structures are analogous to the most stable water trimer, tetramer and pentamer [31]. The  $\text{phenol} \cdot (\text{H}_2\text{O})_5$  cluster is the smallest cluster, where the  $\pi$  hydrogen bond is sterically possible. In contrast, for the most stable  $2\text{HP}/2\text{PY} \cdot (\text{NH}_3)_n$  ( $n = 1$  to 5) clusters we do not note any  $\pi$  hydrogen bond.

### 3.2. Structural parameters

In this part, we are interested in the study of the behavior of structural parameters of  $2\text{PY}/2\text{HP} \cdot (\text{NH}_3)_n$

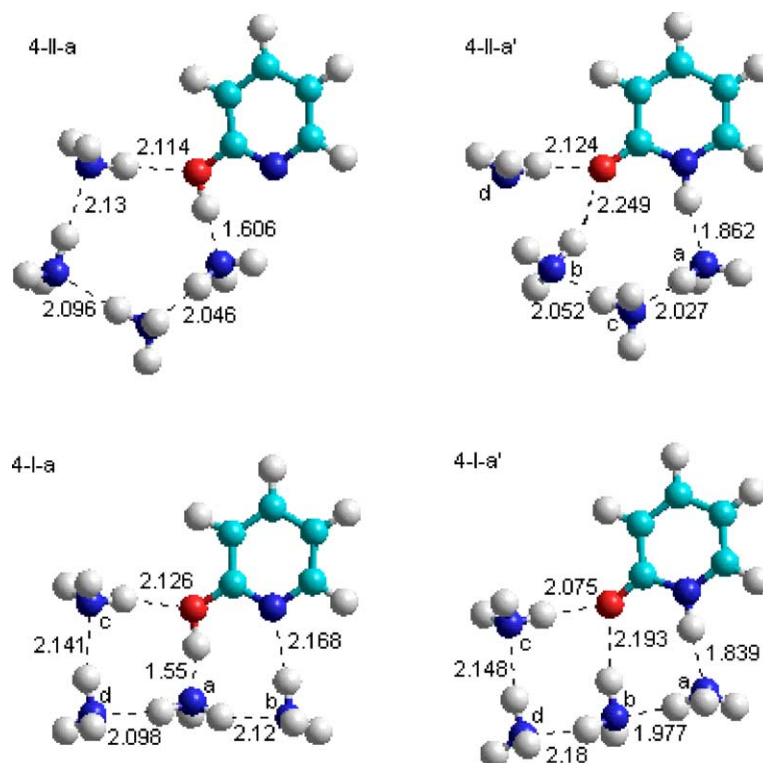


Fig. 3. Minimum energy structures for  $2\text{HP} \cdot (\text{NH}_3)_4$  (4-I-a and 4-II-b) and  $2\text{PY} \cdot (\text{NH}_3)_4$  (4-I-a' and 4-II-a'). The isomers are arranged in ascending energetic order from above.

as a function of cluster size  $n$ . The aim of these studies is to check if these parameters could be seen as indicators or probe of proton transfer in clusters. The study concerns the intramolecular  $\text{O}-\text{H}_0$ ,  $\text{N}_0-\text{H}_0$  bond lengths, the intermolecular hydrogen bond  $\text{H}_0 \cdots \text{N}$  in each cluster and the  $\nu(\text{O}-\text{H}_0)$  and  $\nu(\text{N}_0-\text{H}_0)$  frequencies in both clusters.

Tables 1 and 2 give important information on the differences in some bonding interactions in these tautomeric complexes. From these tables, it is clear that these structural parameters change with cluster size. Interestingly, we note a notable decrease of  $\text{H}_0 \cdots \text{aN}$  and  $\text{O} \cdots \text{aN}$  and increase  $\text{OH}_0$  for the most stable one of enol form at  $n = 4$  (Table 1). Similar results are observed for intramolecular  $\text{N}_0-\text{H}_0$  bond and intermolecular  $\text{H}_0 \cdots \text{aN}$  in  $2\text{PY} \cdot (\text{NH}_3)_n$  clusters as shown in Table 2. From these behaviors are shown Tables 1 and 2, we may conclude that  $2\text{HP} \cdot (\text{NH}_3)_4$  and  $2\text{PY} \cdot (\text{NH}_3)_5$  constitute a critical size for proton transfer for 2-hydroxypyridine–ammonia and 2-pyridone–ammonia clusters, respectively.

Fig. 6 depicts the intramolecular harmonic frequencies  $\nu(\text{O}-\text{H}_0)$  (a) and  $\nu(\text{N}_0-\text{H}_0)$  (a') for  $2\text{HP}/2\text{PY} \cdot (\text{NH}_3)_n$  clusters. These modes are studied because they are strongly perturbed upon formation of a hydrogen bond. The calculated  $\text{O}-\text{H}$  stretching vibration of bare 2HP is  $3771 \text{ cm}^{-1}$ , while the  $\text{N}-\text{H}$  stretching vibration of bare 2PY is  $3605 \text{ cm}^{-1}$ . The values scaled with a

scaling factor of 0.97 are very close to the experimental one observed in a supersonic jet [32,33]. These modes are also strongly red-shifted upon solvation with regard to the bare molecule. The red shift increases with  $n$  with a notable one at  $n = 4$  and  $n = 5$  for enol and keto forms, respectively. This is due to the important stretching of  $\text{O}-\text{H}$  and  $\text{N}-\text{H}$  bonds at these sizes for the most stable one.

### 3.3. Energetics

The calculated electronic energies  $E_e$  of each cluster and relative energy,  $\Delta E(\text{keto/enol})$  ( $\Delta E(\text{keto/enol}) = E_e(\text{keto}) - E_e(\text{enol})$ ) between  $2\text{PY} \cdot (\text{NH}_3)_n$  and  $2\text{HP} \cdot (\text{NH}_3)_n$  ( $n = 1$  to 5) are illustrated in Table 3. For every cluster size,  $2\text{PY} \cdot (\text{NH}_3)_n$  is more stable than  $2\text{HP} \cdot (\text{NH}_3)_n$ . The bare keto tautomer is calculated to be more stable than the enol form  $\Delta E = -1.5 \text{ kJ/mol}$ .  $\Delta E$  decreases from  $-2.1 \text{ kJ/mol}$  for  $n = 1$  to  $-7.8 \text{ kJ/mol}$  for  $n = 3$ . For  $n = 4$ ,  $\Delta E$  increases to become  $-2.5 \text{ kJ/mol}$ , and decreases again for  $n = 5$ , to become  $-6.2 \text{ kJ/mol}$  for the most stable isomer in each tautomer.

The solvation energies ( $\Delta E_n$ ) for the clustering reaction (2) were calculated according to the following equation:  $\Delta E_n = E_X(\text{NH}_3)_n - (E_X + nE_{\text{NH}_3})$ , where ( $X = 2\text{HP}$  or  $2\text{PY}$ ).





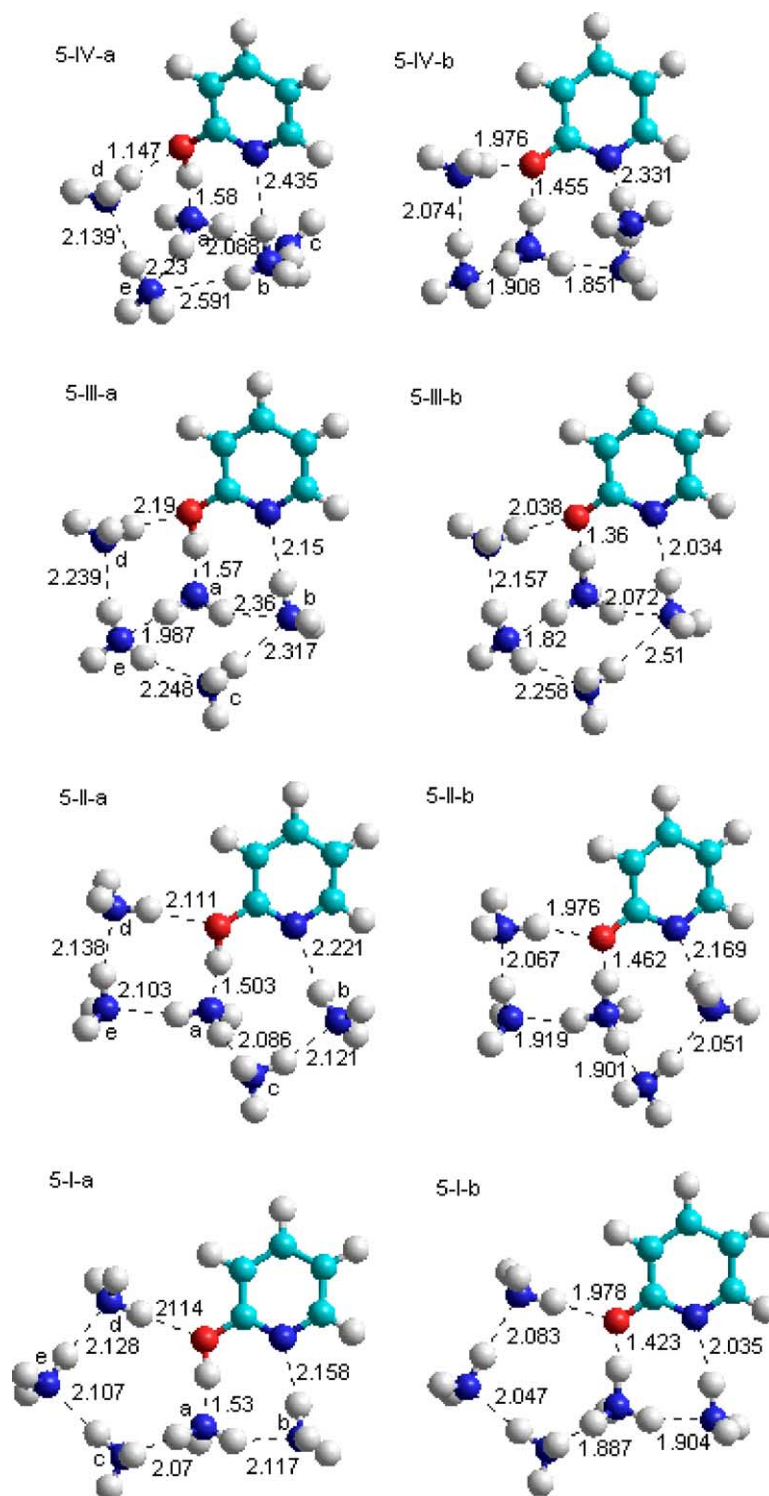


Fig. 4. Minimum energy structures for 2HP · (NH<sub>3</sub>)<sub>5</sub> isomers in the ground state from the most stable 5-I-a to the less stable 5-IV-a. The corresponding stable structures with the proton transferred to the solvent shell (5-I-b, 5-II-b, 5-III-b and 5-IV-b).

All these values of energies with ZPE and BSSE corrections are given in Table 3.

Fig. 7 explains the behavior of stabilization energies  $\Delta E_n^{\text{stab}}$  as function of cluster size  $n$ , for both enol and keto forms.  $\Delta E_n^{\text{stab}}$  decreases with cluster size. We also notice that  $\Delta E_n^{\text{stab}}$  for the keto form decreases more rap-

idly than the enol form. This is principally due to the large dipole moment of the first tautomer (see Table 3). We also note that 2PY interacts more strongly with ammonia clusters than does 2HP (see also Table 3).

For  $n = 4$ , the proton transfer is calculated to be endoergic by 7.1 kJ/mol relative to the enol and highly

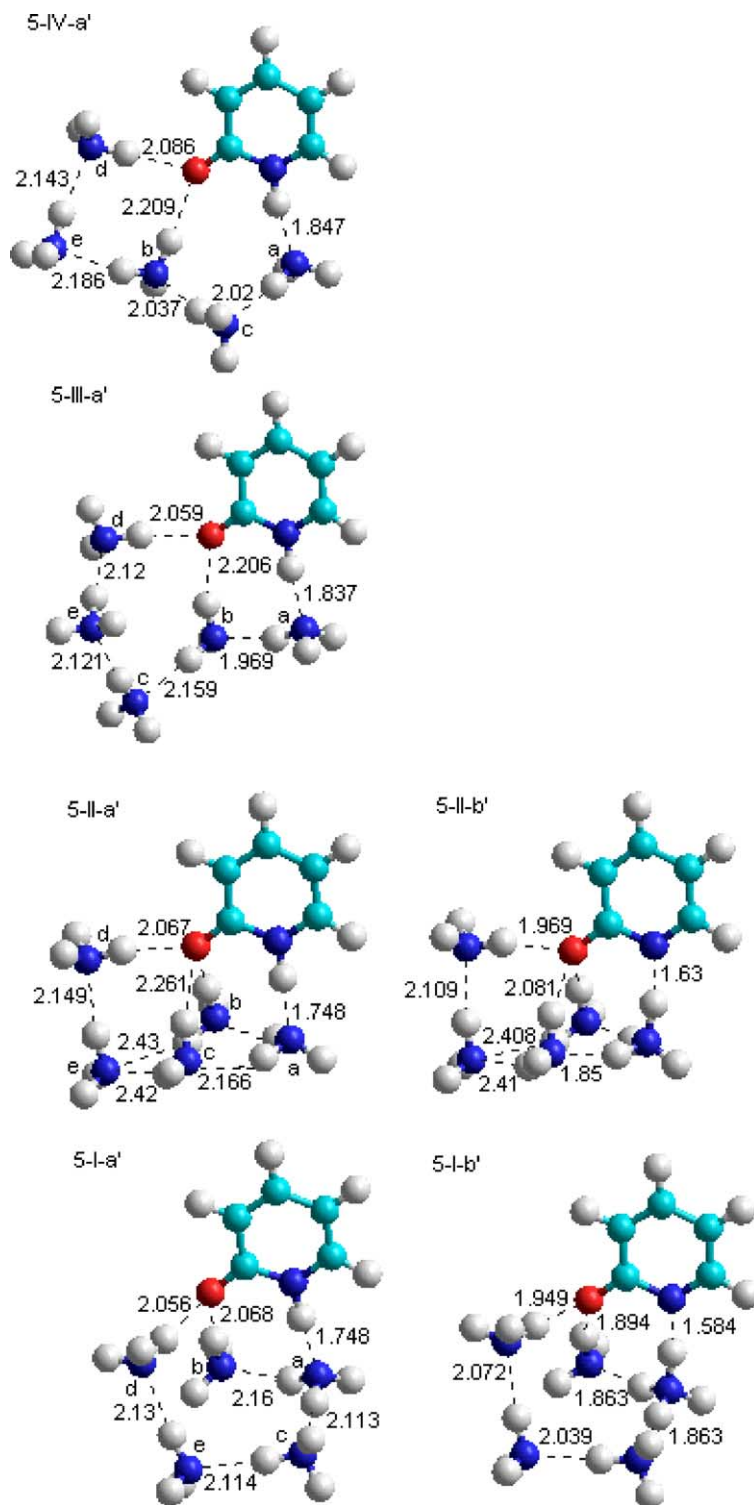


Fig. 5. Minimum energy structures for  $2\text{PY} \cdot (\text{NH}_3)_5$  isomers in the ground state from the most stable 5-I-a' to the less stable 5-IV-a' (left). The corresponding stable structures with the proton transferred to the solvent shell (5-I-b' and 5-II-b'). For 5-III-a' and 5-IV-a' isomers the corresponding ion-pair structures are not stable.

endoergic by 9.6 kJ/mol relative to the keto form. For  $n = 5$ , the endoergicity of the proton transfer reaction decreases slightly relative to the enol form, being 6.8 kJ/mol and increases to be 13.0 kJ/mol relative to the

keto form. Conversely, the directly transferred proton from the keto tautomer is exoergic by 19.2 kJ/mol relative to the enol form and endoergic by 25.4 kJ/mol relative to the keto form. In the case of the other isomers,

Table 1  
Equilibrium bond lengths (Å) of structural isomers of  $2\text{HP} \cdot (\text{NH}_3)_n$  ( $n = 1$  to 5)

Cluster	$d(\text{O}-\text{aN})$	$d(\text{H}_0 \cdots \text{aN})$	$d(\text{O}-\text{H}_0)$
1	2.751	1.756	1.003
2	2.711	1.708	1.014
3	2.684	1.674	1.021
4-I	2.6	1.55	1.06
	<i>2.536</i>	<i>1.151</i>	<i>1.387</i>
4-II	2.644	1.606	1.038
5-I	2.59	1.53	1.068
	<i>2.555</i>	<i>1.134</i>	<i>1.423</i>
5-II	2.57	1.503	1.078
	<i>2.577</i>	<i>1.118</i>	<i>1.462</i>
5-III	2.613	1.57	1.052
	<i>2.524</i>	<i>1.166</i>	<i>1.361</i>
5-IV	2.617	1.58	1.05
	<i>2.569</i>	<i>1.119</i>	<i>1.453</i>

The values in italic correspond to the ion-pair clusters.

Table 2  
Equilibrium bond lengths (Å) of structural isomers of  $2\text{PY} \cdot (\text{NH}_3)_n$  ( $n = 1$  to 5)

Cluster	$d(\text{H}_0 \cdots \text{aN})$	$d(\text{N}_0-\text{H}_0)$
1	1.937	1.034
2	1.879	1.043
3	1.901	1.042
4-I	1.839	1.049
4-II	1.862	1.047
5-I	1.748	1.065
	<i>1.114</i>	<i>1.584</i>
5-II	1.748	1.064
	<i>1.099</i>	<i>1.63</i>
5-III	1.837	1.049
5-IV	1.846	1.048

The values in italic correspond to the ion-pair clusters.

(5-II-b), (5-III-b) and (5-IV-b) are calculated to be endoergic by 6.9, 5.8 and 5.1 kJ/mol, respectively, relative to the enol form. While, the (5-II-b') ion-pair is relatively highly endoergic by 22.0 kJ/mol relative to the keto form.

### 3.4. Discussion

B3LYP/6-31++G\*\* calculation show that for different clusters sizes, keto form is computed to be more stable than the enol form. For  $n = 2$  and 3 clusters, their energetically most stable structure for each tautomer, correspond to a unidirectional hydrogen bond topology, extending from O–H (or N–H) group, acting as a hydrogen donor to the N (or O) of 2HP (or 2PY). This structure has been verified experimentally for other tautomeric system such as 7-hydroxyquinoline (7HQ), this verification is through the analysis of the  $S_1 \leftarrow S_0$  R2PI and fluorescence spectra for the supersonically cooled  $7\text{HQ} \cdot (\text{NH}_3)_n$  clusters [10]. For  $n = 4$ , the most stable cluster for each tautomer, corresponds to the for-

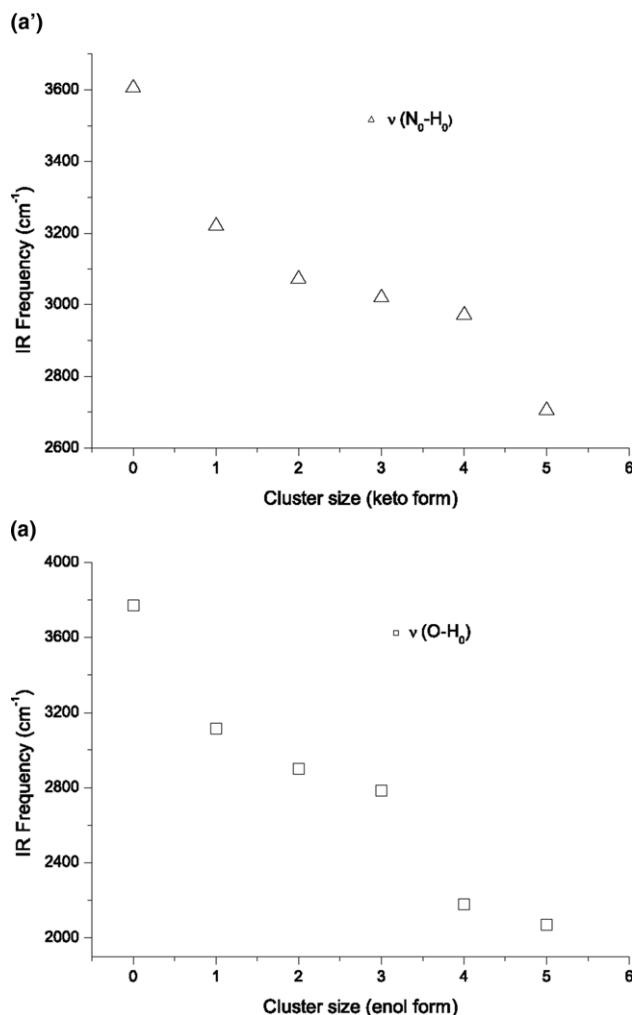


Fig. 6. Vibrational frequency as a function of ammonia cluster size for enol and keto forms in the most stable structures. Square symbols are for  $\nu(\text{O}-\text{H}_0)$  and triangles for  $\nu(\text{N}_0-\text{H}_0)$ .

mation of two cycles, this result is also found in 7HQ by SCF calculation [11]. For  $n = 5$ , the most stable structure for enol and keto forms obtained have not the same solvent distribution around the bare molecule (Fig. 4(5-I-a) and Fig. 5(5-III-a')). These structures have not also the same order of stability compared to those obtained in 7HQ ammonia clusters [11].

Locally stable ion-pair structure is obtained in the enol and keto forms for a critical size of solvent to be  $n = 4$  and  $n = 5$ , respectively. In these ion-pair clusters, intermolecular H bonding are reduced comparing them to the neutral form because in this latter intermolecular interactions are governed by van der Waals once ( $-r^{-6}$ ), while in ion-pair clusters, interactions diminish with  $r$  as  $-r^{-4}$ . In  $2\text{HP} \cdot (\text{NH}_3)_4$  cluster, proton transfer reaction is calculated to be endoergic by 7.1 kJ/mol, this decreases in  $2\text{HP} \cdot (\text{NH}_3)_5$  cluster, being 6.8 kJ/mol. Therefore, it seems possible that the addition of more ammonia molecules may alter the structure of the



Table 3

Calculated electronic energies ( $E_e$ ), dipole moment ( $\mu$ ), solvation energies  $\Delta E_n$  and tautomerization energy  $\Delta E(\text{keto/enol})$ 

Cluster	$E_e(\text{keto})$	$\mu(\text{keto})$	$\Delta E_n(\text{keto})$	$E_e(\text{enol})$	$\mu(\text{enol})$	$\Delta E_n(\text{enol})$	$\Delta E(\text{keto/enol})$
0	−323.453765	4.591		−323.453213	1.456		−1.5
1	−379.999465	3.212	−31.3	−379.9986766	1.932	−30.7	−2.1
2	−436.542035	2.915	−54.4	−436.539459	1.804	−49.1	−6.8
3	−493.080108	2.418	−65.7	−493.077126	2.293	−59.4	−7.8
4-I	−549.619378	2.609	−80.2	−549.618422	0.942	−79.1	−2.5
				−549.615708	3.694		
4-II	−549.617824	3.1	−76.1	−549.616452	1.531	−74.0	−3.6
5-I	−606.158761	1.283	−94.8	−606.156408	0.872	−90.2	−6.2
	−606.149094	4.405		−606.153823	3.942		12.4
5-II	−606.158145	2.116	−93.3	−606.156322	0.243	−90.0	−4.8
	−606.149759	2.892		−606.153676	3.705		10.3
5-III	−606.157285	2.336	−91.1	−606.154491	2.456	−85.2	−7.3
				−606.152261	3.836		
5-IV	−606.156889	2.789	−90.0	−606.154268	1.946	−84.6	−6.9
				−606.152326	3.280		

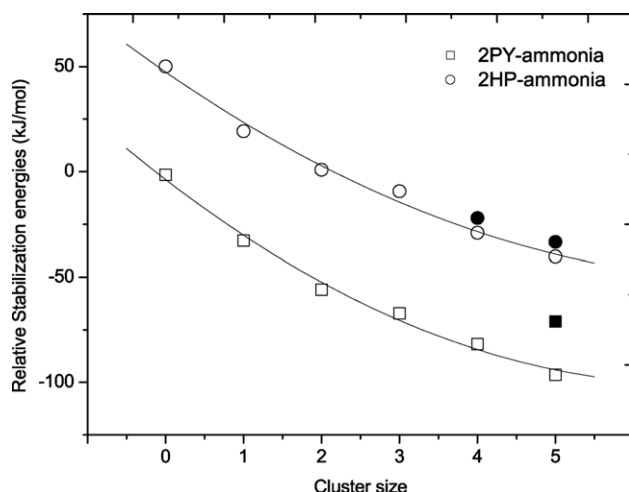
Electronic energies are in hartree, dipole moment in debye,  $\Delta E_n$  and  $\Delta E$  are in kJ/mol. All these values of energies are corrected from ZPE and BSSE.

Fig. 7. Relative stabilization energies for the most stable clusters of 2PY ( $\square$ ) and 2HP ( $\circ$ ). The solid circle and square indicate the locally stable energy proton transferred structures of enol and keto tautomer respectively. Relative stabilization energy of 2HP are translated by +50 kJ/mol.

solvent shell and give rise to a significant further stabilization of the ion-pair cluster relative to its neutral parent [8]. It is also found that the most stable ion-pair isomer has not the same order of stability as its corresponding neutral isomer. For  $2\text{PY} \cdot (\text{NH}_3)_5$  cluster, proton transfer reaction is calculated to be endoergic by 25.4 kJ/mol, that is highly larger compared with its tautomer. SCF calculation of  $7\text{HQ} \cdot (\text{NH}_3)_n$  clusters in the electronic ground state for these tautomers indicate that the smallest species for which proton transfer may occur is  $n = 6$  [11]. Proton transfer can be predicted by characterization of several parameters as a function of cluster size. We have focused our attention on the study of distances and vibrational frequencies. Interestingly, this

study shows a significative decrease or increase at a critical cluster size, this critical size being the lowest for the transfer of proton to the solvent. We can conclude that these parameters are indicators and probe for the formation of quasi-stable ion-pair clusters in each tautomer.

#### 4. Conclusion

In this work, B3LYP/6-31++G\*\* has been applied to investigate the most stable isomers structures of 2-HP ammonia clusters and their tautomers. These calculations represent the first attempt to investigate the structure and energy of these complexes near the proton transfer threshold in ground state. It is found by the study of some structural parameters (inter and intramolecular distances) and vibrational frequencies, that endoergic proton transfer with formation of a locally stable ion-pair can occur for  $n = 4$  and  $n = 5$  in  $2\text{HP} \cdot (\text{NH}_3)_n$  and  $2\text{PY} \cdot (\text{NH}_3)_n$  complexes, respectively. These parameters have a significative change when critical size  $n = n_c$  is reached. Metastable ion-pair clusters for this  $n_c$  confirm this result. On the other hand, DFT calculations show that for the enol form, the addition of a fifth molecule reduces the overall endoergicity of proton transfer from 7.1 to 6.8 kJ/mol. This indicates that the charge-separated ion-pair states will be increasingly stabilized with increasing number of solvent molecules and may become most stable than neutral form.

#### Acknowledgments

One of the authors, M.E., is grateful to Drs. C. Jouvet and C. Dedonder-Lardeux (L.P.P.M, Université Paris IX) for valuable suggestions and comments.

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