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Density functional study of structures and interaction hyperpolarizabilities of NH_3 -HCl- $(H_2O)_n$ (n = 0-4) clusters

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Abstract

The optimized structures of NH_3 -HCl-(H_2O)_n (n = 0-4) clusters have been obtained by B3LYP/d-aug-cc-pVDZ method. In the structure of n = 1, proton transfer occurs. It is different from the results of some references. The first hyperpolarizabilities (β_0) and some other properties of the clusters were calculated and the basis set effects were also studied. On the properties of the clusters, the β_0 value reduces with the increasing number of water molecules. For the subunits NH₃-HCl, the β_0 value increases with the extent of proton transfer that result from an important solvent effects of water molecules.

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1. Introduction

Hydrogen-bonded complexes and the gas-phase reaction between ammonia and hydrogen chloride have been widely studied from experimental and theoretical. Mulliken [1] alluded to inner complexes $H_3N-H^+Cl^-$ and outer complexes H_3N-HCl in his classic paper. Clementi [2–4] has carried out early *ab initio* calculations on this system. Aull and Pimentel [5] provided the first experimental characterization of the ammonia–hydrogen chlo-

ride complex, using infrared spectroscopy in a low temperature nitrogen matrix. The structure of the ammonia-hydrogen chloride complex in the gas phase was finally established in 1986 by Legon and co-workers [6,7]. Latajka and co-workers [8,9] have studied the hydrogen-bond between NH3 and HCl. Janda and co-workers [10], Del Bene [11] and Bevitt et al. [12] have studied the spectroscopy and the potential surface about the NH₃-HCl. Fu-Ming Tao [13] have investigated the direct formation of solid ammonium chloride particles from HCl and NH₃ vapors. Legon's group [14] have researched the extent of proton transfer in aminehydrogen chloride complex with the gas phase. Fu-Ming Tao's group [15,16], Latajka and co-worker [17] proved that there is proton transfer process in

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NH₃–HCl system with the presence of several water molecules.

Recently, the research on intermolecular hyperpolarizability was gain widely attention. The studies of the interaction hyperpolarizability of some small van der Waals clusters have already been carried out. The clusters involve in He₂, He₃ and Ne₂ [18]; Ar₂ and He₂ [19–21]; H₂–H₂, Ne– HF, Ne-FH, He₂, Ar₂ and Kr₂ [22]; (H₂O)₂ [23]. For the complex clusters NH_3 -HCl-(H₂O)_n (n = 0-4), the calculation on interaction hyperpolarizabilities is a challenge to quantum chemistry, which includes the effects of the intermolecular proton transfer on the dipole moment μ_0 , polarizability α_0 and first hyperpolarizability β_0 of the NH₃-HCl subunits. This Letter mainly aims at revealing these properties of the clusters NH₃- $HCl-(H_2O)_n$ (n = 0-4) and exposing the solvent effects of water molecules on μ_0 , α_0 and β_0 of the clusters and the influence of proton transfer on these properties of their NH₃-HCl subunits.

2. Computational details

The structures of the NH₃–HCl– $(H_2O)_n$ (n = 0–4) clusters have been optimized by the B3LYP/d-aug-cc-pVDZ method, and μ_0 , α_0 , β_0 were calculated according to the optimized geometries at B3LYP level. The basis sets effects on properties of the clusters were studied with aug-ccpVDZ, aug-cc-pVDZ+BF, aug-cc-pVTZ, d-augcc-pVDZ and t-aug-cc-pVDZ basis sets. The finite field method was applied in the calculation of the physical properties of the clusters and their NH₃– HCl subunits.

In even weak electric field, the energy of the molecule can be defined as [24]

$$E(F) = E_0 - \mu_i F_i - (1/2!) \alpha_{ij} F_i F_j - (1/3!) \beta_{ijk} F_i F_j F_k + \cdots,$$

where μ_i , α_{ij} , β_{ijk} are the components of static dipole moment, polarizability and the first hyperpolarizability, respectively.

The total static dipole moment is defined as

$$\mu_0 = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}.$$

The average polarizability is written as

$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

The first hyperpolarizability is given as

$$\beta_0 = (3/5)(\beta_x \mu_x + \beta_y \mu_y + \beta_z \mu_z)/\mu_0,$$

where
$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$
, $\beta_y = \beta_{xxy} + \beta_{yyy} + \beta_{yzz}$,
 $\beta_z = \beta_{xxz} + \beta_{yyz} + \beta_{zzz}$.

All the calculations were performed with GAUSSIAN 98 [25] program.

3. Results and discussion

3.1. Geometries

The optimized structures of the NH₃-HCl- $(H_2O)_n$ (n = 0-4) clusters have been obtained by the B3LYP/d-aug-cc-pVDZ method. The structures and related geometrical parameters are shown in Fig. 1 and Table 1. It is noted that the NH₃-HCl unit becomes an ionic pair, $NH_4^+ \dots Cl^-$, resulting from a proton transfer from HCl to NH₃ in the NH₃-HCl-H₂O cluster. The $N \dots H$ distance (1.1502 A) is 0.5220 A shorter than that in the NH₃-HCl-(H₂O)_n (n = 0), and the H-Cl distance (1.7399 Å) is 0.3716 Å longer correspondingly, which reflects a proton transfer in the NH₃-HCl-H₂O cluster. Our calculated result for n = 1 is different from the result (no proton transfer) of the previous works (using 6-311+ +G(d, p), 116 basis functions) [15–17]. According to [16], we performed the optimization of the NH_3 -HCl-H₂O by the MP2/6-311++G(d, p) method and the result with no proton transfer as [16] (the NH₃-HCl unit exists as a usually hydrogen-bonded structure) is reproduced. In order to make sure if the proton transfer happened in the NH₃-HCl-H₂O cluster, the larger basis sets and method were employed. Using larger scale basis sets d-aug-cc-pVDZ (178 basis functions) and 6-311++G(2df,2p) (170 basis functions), the MP2 results $(R_{\text{N...H}} = 1.1452 \text{ Å}, R_{\text{H-Cl}} = 1.7256 \text{ Å} \text{ and}$ $R_{\text{N...H}} = 1.1406 \text{ A}, R_{\text{H-Cl}} = 1.7184 \text{ A}, \text{ respectively}$ is similar to the B3LYP/d-aug-cc-pVDZ result. And a frequency calculation (all real, see Table 2) shows that the NH₃-HCl-H₂O structure is stable (see Fig. 1). Then it is believed that a proton



Fig. 1. Geometry structures of NH_3 -HCl- $(H_2O)_n$ (n = 1-4) cluster.

transfer from HCl to NH₃ occurs in the cluster series NH₃-HCl-(H₂O)_n (n = 1-4) and for theoretical research on proton transfer of the small system (NH₃-HCl-H₂O), the basis set needed should be larger than 6-311++G(d, p).

The relationship between the extent of proton transfer and the number of solvent water molecules is shown in Fig. 1 and Table 1. The $R_{\text{H-Cl}}$ is lengthened and the $R_{\text{N...H}}$ distance is shortened with the increasing *n* value, which reflects the increasing extent of the proton transfer with the in-

Table 1 Interatomic distances (in Å) in NH_3 -HCl- $(H_2O)_n$ (n = 0-4) clusters

	$R_{\rm NH}$		$R_{ m H-Cl}$	
n = 0 n = 1 n = 2 (I) (II) n = 3 (I) (II) n = 4	1.6722 1.1502 1.0780 1.1177 1.0699 1.0694 1.0646	$1.733^{a} \\ 1.613^{b} \\ 1.069^{a} \\ 1.102^{a}$	1.3683 1.7399 1.9515 1.8031 1.9802 1.9476 1.9964	$\begin{array}{c} 1.346^{a} \\ 1.361^{b} \\ 1.957^{a} \\ 1.827^{a} \end{array}$

^a Ref. [17].

^b Ref. [16].

creasing number of solvent water molecules. Here the $R_{\text{H-Cl}}$ value maybe stands for the extent of proton transfer. The $R_{\text{H-Cl}}$ values are 1.7399 Å for n = 1, 1.9515 Å (1.8031 Å for structure II) for n = 2, 1.9802 Å (1.9476 Å for structure II) for n = 3, and 1.9964 Å for n = 4. The $R_{\text{N}_{n},\text{H}}$ values in turn are 1.1502 Å for n = 1, 1.0780 Å (1.1177 Å for structure II) for n = 2, 1.0699 Å (1.0694 Å for structure II) for n = 3, and 1.0646 Å for n = 4.

3.2. The μ_0 , α_0 and β_0 of the clusters

Basis set is an important factor in accurate quantum chemistry calculations. Five basis sets aug-cc-pVDZ, aug-cc-pVDZ+BF, aug-cc-pVTZ, d-aug-cc-pVDZ, t-aug-cc-pVDZ are used to calculate the properties at the B3LYP level and the results are shown in Table 3. The calculated results show that the basis set d-aug-cc-pVDZ is satisfying basis set as the results from this basis set are similar to that from the larger basis set t-aug-ccpVDZ (see the last two columns in Table 3). Comparing the results from the two different basis sets, the relative errors are less that 0.025% for μ_0 , 0.04% for α_0 and 1% for β_0 . The μ_0 value of the NH_3 -HCl-(H_2O), slightly reduces with the increasing number of the water molecules. The μ_0 values from d-aug-cc-pVDZ are 2.6772 a.u. for n = 1, 2.3689 a.u. (2.5953 a.u. for structure II) for n = 2, 2.1633 a.u. (1.5698 a.u. for structure II) for n = 3, 1.8826 a.u. for n = 4, as listed in Table 3. An obviously increasing of α_0 with the n value is 48.655 a.u. for n = 1, 58.106 a.u. (58.907 a.u. for structure II) for n = 2, 68.225 a.u. (67.461 a.u. for

The frequencies i	n (cm ^{-1}) of the NI	H ₃ -HCl-H ₂ O clust	er				
157.3379	164.3112	205.6532	224.8738	340.6717	388.3913	444.9523	
511.1198	670.1983	1178.8797	1418.9611	1462.7327	1584.4953	1636.3758	
1650.0247	1752.9225	3237.3775	3438.6426	3510.9749	3587.8927	3865.5195	

Table 2 The frequencies in (cm^{-1}) of the NH_3 -HCl-H₂O cluster

Table 3 Static dipole moments (μ_0), polarizabilities (α_0) and the first hyperpolarizabilities (β_0) (in a.u.) for NH₃–HCl–(H₂O)_n (n = 0-4) clusters

		aug-cc-pVDZ	aug-cc-pVDZ+BF	aug-cc-pVTZ	d-aug-cc-pVDZ	t-aug-cc-pVDZ
μ_0	n = 0	1.9666	1.9677	1.9534	1.9638	1.9640
	n = 1	2.6802	2.6807	2.6750	2.6772	2.6769
	n = 2 (I)	2.3693	2.3701	2.3669	2.3689	2.3685
	(II)	2.5976	2.5974	2.5938	2.5953	2.5950
	n = 3 (I)	2.1621	2.1631	2.1616	2.1633	2.1632
	(II)	1.5684	1.5715	1.5655	1.5698	1.5694
	n = 4	1.8802	1.8808	1.8813	1.8826	1.8826
α ₀	n = 0	33.776	34.028	35.132	35.694	35.697
	n = 1	46.753	47.126	48.096	48.655	48.652
	n = 2 (I)	56.550	56.885	57.671	58.106	58.112
	(II)	57.262	57.548	58.436	58.907	58.908
	n = 3 (I)	66.876	67.135	67.863	68.225	68.230
	(II)	65.880	67.461	67.033	67.461	67.468
	n = 4	77.203	77.427	78.115	78.427	78.458
β_0	n = 0	27.68	22.08	12.32	-3.35	-0.63
	n = 1	267.40	253.71	239.57	209.74	210.49
	n = 2 (I)	208.23	197.62	180.14	158.80	159.80
	(II)	226.11	212.72	204.80	180.80	181.64
	n = 3 (I)	154.91	144.90	132.68	116.88	118.00
	(II)	128.47	124.63	103.71	95.83	95.95
	n = 4	116.46	108.29	95.34	90.01	90.49

structure II) for n = 3 and 78.427 a.u. for n = 4. A mean contribution to α_0 per water molecule is about 9.924 a.u. The first hyperpolarizability β_0 in the cluster series NH_3 -HCl- $(H_2O)_n$ (n = 1-4) evidently decreases with increasing n value. The β_0 values are 209.74 a.u. for n = 1, 158.80 a.u. (180.80) a.u. for structure II) for n = 2, 116.88 a.u. (95.83) a.u. for structure II) for n = 3 and 90.01 a.u. for n = 4. The each water molecule reduces about 39.58 a.u. β_0 value. Then the NH₃-HCl-H₂O cluster has the largest β_0 value (in Table 3). For a molecule with a large μ_0 value it often has a large β_0 value. The decreasing of β_0 value maybe owns to the decreasing of μ_0 value. Fig. 2 shows the solvent effects of water molecules on the μ_0 , α_0 and β_0 of the cluster series.



Fig. 2. Static dipole moment μ_0 polarizability α_0 and the first hyperpolarizability β_0 (in a.u.) for NH₃-HCl-(H₂O)_n (n = 1-4) clusters.

	$R_{\rm H-Cl}$ (in Å)	Waters	aug-cc-PVDZ	aug-cc-PVTZ	d-aug-cc-PVDZ
μ_0	3.4615	n = 1	3.4708	3.4616	3.4615
	3.9178	n = 2	3.9314	3.9201	3.9178
	3.7055		3.7157	3.7064	3.7055
	4.0568	n = 3	4.0756	4.0597	4.0568
	4.0209		4.0342	4.0239	4.0209
	4.1759	n = 4	4.1898	4.1792	4.1759
α0	3.4615	n = 1	37.656	39.403	40.499
	3.9178	n = 2	39.625	41.508	42.861
	3.7055		38.478	40.300	41.536
	4.0568	n = 3	40.228	42.147	43.580
	4.0209		39.559	41.491	42.934
	4.1759	n = 4	40.655	42.611	44.120
β_0	3.4615	n = 1	492.42	459.25	413.52
, ,	3.9178	n = 2	820.89	772.97	703.32
	3.7055		623.77	586.39	538.66
	4.0568	n = 3	920.29	869.11	800.48
	4.0209		828.69	780.21	718.57
	4.1759	n = 4	1003.94	950.66	886.41

The influence of proton transfer effects on static dipole moments μ_0 , polarizabilities α_0 and the first hyperpolarizabilities β_0 (in a.u.) for the subunits NH₃-HCl

The influence of the solvent effects on the structures of the NH₃-HCl subunit in the clusters NH₃-HCl-(H₂O)_n (n = 0-4) has been stated, as shown in Table 1 and Fig. 1. The proton transfer occurs in the NH₃-HCl-(H₂O)_n from n = 1 to 4.

Table 4

The influence of the proton transfer on μ_0 , α_0 and β_0 for the NH₃–HCl subunits in the cluster series is valuable information. The structures of the NH₃-HCl subunits come from the optimized NH3-HCl-(H₂O)_n (n = 0-4). The calculated values of μ_0 , α_0 and β_0 for the subunits are shown in Table 4. The values of μ_0 , α_0 and β_0 are larger than that of the pure NH₃-HCl (without H₂O) and are all increasing with the extent of proton transfer (the $R_{\text{H-Cl}}$). The μ_0 values of the NH₃-HCl (n = 0, no proton transfer) is only 1.9638 a.u. The μ_0 values of the NH₃-HCl subunits for n = 1-4 are 3.4615 a.u. for n = 1, 3.9178 a.u. (3.7055 a.u. for structure II) for n = 2, 4.0568 a.u. (4.0209 a.u. for structure II) for n = 3 and 4.1759 a.u. for n = 4. The α_0 values are only 35.694 a.u. for n = 0, but 40.499 a.u. for n = 1, 42.861 a.u. (41.536 a.u. for structure II) for n = 2, 43.580 a.u. (42.934 a.u. for structure II) for n = 3 and 44.120 a.u. for n = 4. The first hyperpolarizability β_0 for the NH₃-HCl subunits dramatically increases with the enhanced

extent of proton transfer from solvent effects of water molecules.

The β_0 value is only -3.35 a.u. for the pure NH₃-HCl (n = 0 and no proton transfer), while the β_0 values of NH₃-HCl subunits in the NH3-HCl-(H₂O)_n from n = 1 to 4 are 413.52 a.u. for n = 1, 703.32 a.u. (538.66 a.u. for structure II) for n = 2, 800.48 a.u. (718.57 a.u. for structure II) for n = 3, and 886.41 a.u. for n = 4.

4. Summary

According to the optimized structures of the NH₃-HCl-(H₂O)_n (n = 0-4) clusters from B3LYP/d-aug-cc-pVDZ method, we suggest that in the structure of the NH₃-HCl-H₂O (n = 1), the proton transfer occurs. The calculated values of μ_0 , α_0 and β_0 for the NH₃-HCl-(H₂O)_n (n = 0-4) clusters were given. For the solvent effects of water molecules on the properties of the clusters, the β_0 value reduces with the increasing number of the water molecules. The effect of the proton transfer in the properties of the NH₃-HCl subunit is a new and great factor (see Fig. 3) and the β_0 value of the subunit NH₃-HCl dramatically increases with the



Fig. 3. The influence of proton transfer effects on static dipole moment μ_0 , polarizability α_0 and the first hyperpolarizability β_0 (in a.u.) for the NH₃–HCl.

enhanced extent of proton transfer that comes from the solvent effects of the water molecules.

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References

- [1] R.S. Mulliken, J. Phys. Chem. 56 (1952) 801.
- [2] E. Clementi, J. Chem. Phys. 46 (1967) 3851.

- [3] E. Clementi, J. Chem. Phys. 47 (1967) 2323.
- [4] E. Clementi, J.N. Gayles, J. Chem. Phys. 47 (1967) 3837.
- [5] B.S. Aull, G.C. Pimentel, J. Phys. Chem. 77 (1973) 1649.
- [6] E.J. Goodwin, N.W. Howard, A.C. Legon, Chem. Phys. Lett. 131 (1986) 319.
- [7] N.W. Howard, A.C. Legon, J. Chem. Phys. 88 (1988) 4694.
- [8] Z. Latajka, S. Sakai, K. Morokuma, Chem. Phys. Lett. 110 (1984) 464.
- [9] Z. Latajka, S. Scheiner, J. Chem. Phys. 81 (1984) 4014.
- [10] G.M. Chabana, R.B. Gerber, K.C Janda, J. Phys. Chem. A 105 (2001) 8323.
- [11] J.E. Del Bene, J. Chem. Phys. 108 (1998) 3205.
- [12] J. Bevitt, K. Chapman, D. Crittenden, M.J.T. Jordan, J.E. Del Bene, J. Phys. Chem. A 105 (2001) 3371.
- [13] F.M. Tao, J. Chem. Phys. 110 (1999) 11121.
- [14] A.J. Barnes, A.C. Legon, J. Mol. Struct. 448 (1998) 101.
- [15] R. Cazar, A. Jamka, F.M. Tao, Chem. Phys. Lett. 287 (1998) 549.
- [16] R.A. Cazar, A.J. Jamka, F.M. Tao, J. Phys. Chem. A 102 (1998) 5117.
- [17] M. Biczysko, Z. Latajka, Chem. Phys. Lett. 313 (1999) 366.
- [18] M.G. Papadopoulos, J. Waite, Chem. Phys. Lett. 135 (1987) 361.
- [19] B. Femàndez, C. Hättig, H. Koch, A. Rizzo, J. Chem. Phys. 110 (1999) 2872.
- [20] C. Hättig, H. Larsen, J. Olsen, P. Jørgensen, H. Koch, B. Femández, A. Rizzo, J. Chem. Phys. 111 (1999) 10099.
- [21] H. Koch, C. Hättig, B. Femández, A. Rizzo, J. Chem. Phys. 111 (1999) 10108.
- [22] G. Maroulis, J. Phys. Chem. A 104 (2000) 4772.
- [23] G. Maroulis, J. Chem. Phys. 113 (2000) 1813.
- [24] A.D. Buckingham, Adv. J. Chem. Phys. 12 (1967) 107.
- [25] M.J. Frisch et al., GAUSSIAN 98, Revision X, Gaussian, Pittsburgh, PA, 1998.