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H-BOND VIBRATIONS IN AMMONIA-AMMONIA AND AMMONIA-WATER DIMERS*

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Abstract

The influence of intermolecular interaction on monomer vibrations of the ammonia-ammonia and ammonia-water dimers have been studied at the level of second order Møller-Plesset perturbation theory using 6-31G and 6-311++G(2d,2p) basis sets. The basis set superposition error (BSSE) in harmonic and anharmonic vibrational frequencies of monomer type normal modes was considered taking into account the widely used *a posteriori* "counterpoise" correction scheme. The results show an important frequency shift of harmonic vibrational frequency and strong anharmonic effects depending on the molecular system, especial for ν_6 umbrella type vibrational motion of ammonia. In the case of 6-31G basis set we found very important BSSE effects in the harmonic and anharmonic frequencies, while in the case of 6-311++G(2d,2p) basis set these effects were small. In order to ascertain the real geometry and molecular symmetry of ammonia-ammonia system, a detailed analysis of normal mode vibrations including anharmonic corrections is required.

*Dedicated to Prof. J. Csikai on the occasion of his 75^{th} birthday

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Introduction

Theoretically determined harmonic vibrational frequencies of molecular monomers usually overestimate the experimental fundamental frequencies due to the basis set incompleteness, electron correlation effects and anharmonicity. In addition, considering molecular clusters (dimer, trimer, tetramer ...), these theoretical values present an important frequency shift owing to the intermolecular interactions. We mention that from a total of 3N-6 vibrational frequencies, these dimers have six intermolecular modes, the remaining ones being the original normal mode vibrations of the isolated monomers, hereafter called monomer type vibrations. In our previous studies [1, 2] we have analyzed the far infrared (IR) frequencies of the intermolecular normal modes of ammonia-ammonia (NH_3-NH_3) and ammonia-water (NH_3-H_2O) dimers (See Fig.1 and Fig.2), taking into account the basis set superposition error (BSSE). The results showed large discrepancies between theoretical (BSSE uncorrected) and experimental values in the case of ammonia-water dimers [2]. Although, considering the "counterpoise" (CP) [3, 4] and the chemical Hamiltonian approach (CHA) [5, 6] correction schemes for BSSE, and suitably large basis set, the theoretical values were found closer to the experimental ones. However, the difference was still relevant, which requires an additional study. The intermolecular interactions influence not only the intermolecular vibrational frequencies, but they can also influence the monomer type vibrations.

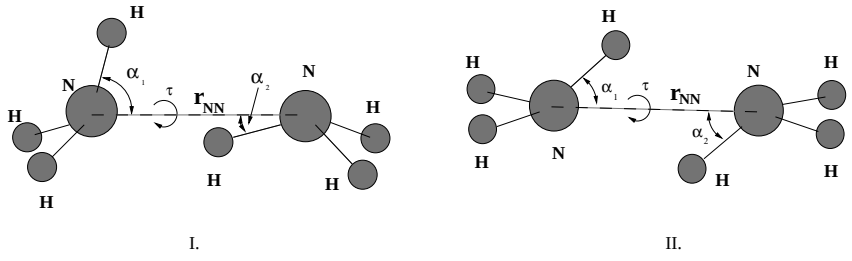

Figure 1. The antisymmetric (I) and centrosymmetric (II) structures of ammonia-ammonia dimer.

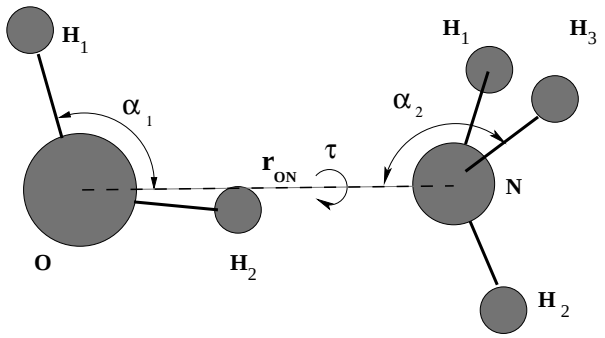

Figure 2. The geometrical structure of ammonia-water system.

The structure and dynamics of the weakly-bound ammonia-ammonia [7, 8, 9, 10, 11, 12, 13, 14] and ammonia-water [15, 16, 17, 18, 19] have been the subject of many experimental and theoretical investigations. Theoretical studies have shown that one can find stationary points for NH_3-NH_3 with two C_s and C_{2h} symmetries, and for NH_3-H_2O with two different C_s symmetries. *Ab initio* and density functional studies of ammonia-ammonia dimers confirmed that the equilibrium geometry of the molecular system may have a linear hydrogen-bond structure with C_s symmetry. At the same time it has been also accepted that the molecular conformation belonging to C_{2h} symmetry is a saddle point structure. However, a detailed theoretical [1, 7, 8, 10] and experimental [11] investigation revealed a different hydrogen-bond configuration, which is an intermediate conformation between the centrosymmetric cyclic and linear hydrogen-bonded structure. These differences in theoretical results are due to the intermolecular BSSE effect which can substantially influence the equilibrium geometry structure of ammonia dimers. The intermolecular BSSE effects in ammonia-water systems have less important influence on the molecular geometry, as only the r_{ON} intermolecular distance is affected.

The BSSE is a pure "mathematical effect", which occurs in the course of the computation of the interaction energy of the weakly-bounded molecular complex and it represents an unbalanced effect between the complex and its components energies. This effect only appears due to the use of finite basis sets, because applying the same basis set, the description of the monomer is actually better within the supermolecule than in the free monomer. All

these facts lead to an incomplete description of individual monomers. Due to the BSSE, the calculated interaction energies show too deep minima, and the computed potential energy surfaces (PES) are distorted. These errors affect not only the intermolecular interaction energies, but also the second and third derivatives of energy, namely the harmonic vibrational frequencies and the anharmonic frequency corrections [20].

It is well-known that in the dimer system, the monomer vibrational frequencies are usually (blue- or red-) shifted. The magnitude of these frequency shifts could give us important informations about the dynamics of these weakly-bounded systems. As mentioned before, the BSSE effects can influence the different harmonic and anharmonic frequency values and thus their frequency shifts.

The main goal of our work is to give an accurate description of the harmonic frequencies and anharmonic frequency corrections of the monomer vibrations, and of their frequency shifts in ammonia-ammonia and ammonia-water dimers.

Results and Discussions

The calculations were carried out in Heidelberg on a Hewlett-Packard cluster. The standard MP2, and the CP-corrected MP2 calculations were performed by the Gaussian 03 computer code [21], using two different, 6-31G and 6-311++G(2d,2p) standard Pople basis sets. The conventional supermolecule geometries were optimized with MP2 method applying the analytical gradient, while CP-corrected harmonic and anharmonic frequencies were obtained using the standard full-CP method included in Gaussian 03. Tables 1 and 2 show the uncorrected and CP-corrected harmonic frequencies as well as the diagonal anharmonic frequencies of the ammonia-ammonia dimer and the ammonia monomer. Tables 3 and 4 show the uncorrected and CP-corrected harmonic frequencies as well as the diagonal anharmonic frequencies of ammonia-water dimer, and ammonia and water monomers. The results were computed at MP2 level of theory using 6-31G and 6-311++G(2d,2p) basis sets.

Table 1.

The uncorrected and CP-corrected harmonic and diagonal anharmonic frequency of ammonia-ammonia dimer computed at MP2 level of theory, using 6-31G basis set.

No.	ν^{dim}	ν^{CP}	ν^{mon}	x_{ii}^{dim}	x_{ii}^{CP}	x_{ii}^{mon}
			Ammonia			
1	3735.4	3735.8	3767.1	−46.7	−53.0	−53.8
	3734.8	3729.0		−46.7	−50.0	
2	3720.1	3727.0	3766.3	−25.6	−49.4	−53.7
	3718.4	3692.4		−25.1	−40.9	
3	3534.1	3538.7	3569.1	−15.8	−29.3	−32.2
	3525.8	3501.9		−16.3	−38.9	
4	1783.2	1794.2	1748.9	4.8	1.1	−16.1
	1762.8	1755.7		−23.2	−27.6	
5	1756.6	1756.5	1748.5	−3.4	2.0	−15.9
	1742.2	1752.2		−9.2	−7.3	
6	914.9	880.8	701.6	−42.4	−48.6	−160.5
	823.3	871.5		−52.3	−48.2	

A. Monomers. The ammonia monomer has six normal mode vibrations (Tables 1 and 2) among which three are *N-H* bond stretching vibrations (ν_1, ν_2, and ν_3) and the other three are *H-N-H* angle bending vibrations (ν_4, ν_5, and ν_6). The most important vibration is the so-called "umbrella" motion of whole *H-N-H* angles with ν_6 vibrational frequency. Applying the 6-31G and 6-311++G(2d,2p) basis sets, we found a significant frequency increase, but only for the ν_6 normal mode when the large and well-balanced 6-311++G(2d,2p) basis set is applied. Also, the anharmonic frequency corrections show very large basis set dependency, again for the ν_6 normal mode.

The water monomer has three vibrational normal modes (Tables 3 and 4), two of them being *O-H* bond stretching vibrations, while the third normal mode presents an *H-O-H* angle bending vibration. In contrast to the ammonia monomer, in this case we observed an important basis size effect in the stretching vibrations, which manifests in increasing the frequency values. The basis size effects on the anharmonic frequency corrections do not show such large shifts as for the ammonia monomer.

Table 2.

The uncorrected and CP-corrected harmonic and diagonal anharmonic frequency of ammonia-ammonia dimer computed at MP2 level of theory, using 6-311++G(2d,2p) basis set.

No.	ν^{dim}	ν^{CP}	ν^{mon}	x_{ii}^{dim}	x_{ii}^{CP}	x_{ii}^{mon}
Ammonia						
1	3667.9	3669.1	3673.7	−43.4	−42.4	−43.4
	3665.2	3669.0		−42.9	−42.0	
2	3661.7	3663.1	3673.0	−41.6	−41.0	−43.4
	3632.7	3639.6		−33.4	−35.0	
3	3523.1	3524.9	3531.1	−26.0	−26.0	−26.8
	3495.2	3503.9		−35.2	−32.3	
4	1717.5	1712.3	1691.4	−24.0	−18.6	−11.4
	1688.6	1693.6		−10.9	−11.7	
5	1693.7	1697.4	1691.9	−5.8	−6.0	−11.4
	1682.2	1683.9		−5.6	−5.6	
6	1100.3	1101.5	1065.1	−24.2	−24.6	−51.3
	1089.1	1086.6		−24.5	−24.8	

B. Ammonia-ammonia dimer. Considering the ammonia-ammonia dimer it is very important to know, how much the monomer type vibrations will be influenced by the adjoining monomer. As we shall see in the following, these effects help us to explain the structure and dynamics of the ammonia dimer. Applying the 6-31G basis set, the energetically preferred structure is the centrosymmetric conformation, while in the case of 6-311++G(2d,2p) basis set, the "intermediate" type linear bond structure is obtained as the equilibrium geometry. Both theoretical and experimental results prove that the "intermediate" structure must be the real equilibrium geometry of ammonia dimer, but it is not exactly clear whether this structure is closer to the centrosymmetric conformation or to the linear asymmetric conformation.

Both ammonia monomers have six normal modes, which means that in the case of ammonia dimer we can find twelve different frequency lines in the *IR* spectra. Their vibrations appear duplicate for molecular similarity reasons. A detailed normal mode analysis show that different synchronization of monomer type vibrations can be observed due to the high or low symmetry of the dimer (C_{2h} symmetry for the centrosymmetric and C_s symmetry

for the asymmetric conformation). But in both cases we obtained significant frequency shifts in comparison with the isolated monomer, because of the strong intermolecular interaction effects. These frequency shifts have not the same magnitude, but mostly depends on the H-N bond position in the dimer and on the nature of the vibrations (stretching or bending). For example, in the case of ν_1 stretching vibration, the frequency shift is quite smaller than for ν_2 and ν_3 vibrations, because in ν_1 case only the external H-N bonds are implicated in the vibrational motion. Similar large frequency shifts can be found in the case of ν_4, ν_5, and ν_6 angle bending vibrations. Usually those vibrations of which oscillating molecular fragments take part in the formation of the weakly-bounded van der Waals complex have larger shift. At the same time the frequency splittings are not same for the same monomer type vibrations. Following these frequency splittings for each normal mode and comparing them to the experimental results, we can conclude different findings about the symmetry of the molecular dimer. Applying the CP type BSSE correction, the centrosymmetric structure (6-31G) is lost and the linear bonded structure (6-311++G(2d,2p)) appears. It can be observed (Table 1) that the harmonic frequencies and their splitting will suffer major changes during this geometry transformation.

Regarding the anharmonic frequency corrections their study could give useful complementary information about monomer vibrations. As for the harmonic frequencies, similar conclusions can be drawn for anharmonic frequency corrections. In particular, apart from the x_{11} correction where this shift is $\approx 6\, cm^{-1}$, in the rest of normal modes we found more than $10\, cm^{-1}$ shifts (the largest shift can be observed in the case of x_{66}: $> 100\, cm^{-1}$). This fact can be explained by the intermolecular interaction effects, which influence different normal modes in different ways. At the same time it is obvious that these correction splittings have not the same magnitude for the similar normal modes of the different monomers. The most conspicuous case is the ν_4 normal mode, using a 6-31G basis set, where the anharmonicity of the individual monomer $x_{44} = -16.1 cm^{-1}$ can split into two very different correction values ($x_{44} = 4.8 cm^{-1}$ and $x_{44} = -23.2\, cm^{-1}$) in the dimer system. The BSSE effects are also very important. The change in the geometry structure and symmetry induce significant alteration in the anharmonic frequency corrections.

Scrutinizing jointly the harmonic frequencies and their anharmonic corrections we can draw conclusions about the molecular symmetry. In the case of 6-31G basis set and without BSSE corrections, the ν_2 and ν_3 frequency values, having similar monomer vibrations, split with two different (synchronous and asynchronous) motions within the dimer and the frequency values are shifted with different magnitude from the isolated monomer frequency. At the same time, their anharmonic corrections are very close. This fact is characteristic only for centrosymmetric structure. Using 6-31G with the BSSE correction or 6-311++G(2d,2p) basis sets, we found splittings and shifts for both harmonic frequency and their anharmonic corrections, which is typical for the linear bonded structure. Furthermore, totally different behaviour can be observed in the case of ν_6 normal mode: using 6-31G basis set without BSSE correction we obtained different anharmonicity in the centrosymmetric structure for both synchronous and asynchronous motion within the dimer.

Table 3.

The uncorrected and CP-corrected harmonic and diagonal anharmonic frequency of ammonia-water dimer computed at MP2 level of theory, using 6-31G basis set.

No.	ν^{dim}	ν^{CP-dim}	ν^{mon}	x_{ii}^{dim}	x_{ii}^{CP-dim}	x_{ii}^{mon}
Ammonia						
1	3704.8	3708.2	3767.1	−47.6	−47.9	−53.8
2	3700.7	3703.7	3766.3	−46.0	−46.9	−53.7
3	3521.7	3524.6	3569.1	−27.2	−27.5	−32.2
4	1758.0	1759.1	1748.9	−6.3	−6.3	−16.1
5	1754.7	1756.2	1748.5	−47.9	−48.3	−15.9
6	988.1	1003.8	701.6	−49.6	−49.4	−160.5
Water						
1	3781.0	3779.9	3832.0	−83.1	−82.6	−55.8
2	3449.7	3454.8	3655.9	−102.5	−97.1	−48.0
3	1723.9	1725.8	1663.2	−16.5	−16.8	−22.8

Table 4.

The uncorrected and CP-corrected harmonic and diagonal anharmonic frequency of ammonia-water dimer computed at MP2 level of theory, using 6-311++G(2d,2p) basis set.

No.	ν^{dim}	ν^{CP-dim}	ν^{mon}	x_{ii}^{dim}	x_{ii}^{CP-dim}	x_{ii}^{mon}
Ammonia						
1	3664.9	3668.4	3673.7	−42.4	−42.3	−43.4
2	3661.7	3664.5	3673.0	−41.9	−41.2	−43.4
3	3524.0	3527.1	3531.1	−25.8	−25.8	−26.8
4	1684.9	1692.6	1691.4	−10.0	−11.5	−11.4
5	1680.2	1682.8	1691.9	−16.0	−18.1	−11.4
6	1119.2	1120.8	1065.1	−39.2	−40.7	−51.3
Water						
1	3944.2	3946.2	3981.6	−80.2	−79.1	−48.5
2	3646.1	3672.8	3860.1	−110.7	−104.1	−43.9
3	1703.1	1702.1	1660.2	−22.9	−16.9	−19.4

C. Ammonia-water dimer. The ammonia-water system has nine different monomer type normal modes (Tables 3 and 4.) of which six belong to the ammonia monomer and the other tree normal modes are characteristic to the water molecule. Due to the geometry position of the ammonia molecule the frequency shifts are not so spectacular than in the previous system, but similar effects can be found for the water monomer. The most important shift of the ammonia monomer frequency can be observed in the case of ν_6^a "umbrella" normal mode. Owing to the intermolecular interaction effects, both harmonic frequency and their anharmonic correction undergo important changes. The harmonic frequency value presents a shift of $286.5\,cm^{-1}$ for 6-31G and $54.1\,cm^{-1}$ for 6-311++G(2d,2p), while the anharmonic frequency correction shows a shift corresponding to $-110.9\,cm^{-1}$ for 6-31G and $-12.1\,cm^{-1}$ for 6-311++G(2d,2p) values. Furthermore, the BSSE corrections are not so important. No considerable change have been found in the equilibrium geometry.

But, in contrast to the ammonia monomer, in the case of water molecule we found considerable basis size, BSSE and intermolecular interaction effects, which change the harmonic frequencies very much. Those normal modes, where the internal *O-H* bond takes part into the formation of weakly-bounded van der Waals complex suffer a much larger shift in frequency and in their correction values, than that with the external *O-H* bond. These vibrations are ν_2^w and ν_3^w normal modes, where ν_2^w is an *O-H* stretching mode, while ν_3^w is *H-O-H* bending vibration. The ν_1^w normal mode is characteristic to the external *O-H* stretching vibration. Again, important differences for the calculated values are obtained, using the two basis sets. The 6-31G is a relatively small basis set, where the intermolecular interaction effects are not entirely taken into account. The larger and well-balanced 6-311++G(2d,2p) basis set, poses high polarization and diffuse functions, by means of which these intermolecular interactions can be characterized much more efficiently. We found more than $100\,cm^{-1}$ frequency corrections for ν_1^w and ν_2^w stretching modes, and $\approx 20\,cm^{-1}$, for the ν_3^w bending vibration. Regarding the anharmonic frequency corrections, the influence of the adjoining ammonia molecule is very important ($> 50\,cm^{-1}$), but the basis size effects and the BSSE influence in these values are not so significant.

Conclusion

From the theoretical study of harmonic frequencies and anharmonic frequency corrections for ammonia-ammonia and ammonia-water systems we can tentatively draw the following conclusions: *i)* The most important shifts in monomer type harmonic frequencies and their anharmonic corrections are generated by the presence of intermolecular interaction effects of the adjoining molecule. The sign and amplitude of the shifts depend on the specific normal mode and on the monomer position within the dimer. *ii)* Harmonic frequency shifts are much larger than the magnitude of anharmonic corrections. *iii)* The basis completeness also plays an important role when we describe these systems: the frequency values depend very much on the quality of the applied basis set. *iv)* In the case of small basis set

(6-31G) the BSSE effects can significantly influence the harmonic frequency and anharmonic correction values. *v)* In order to ascertain the real geometry and molecular symmetry, in case of ammonia-ammonia system, a detailed analysis of normal mode vibrations including anharmonic corrections is required.

Acknowledgements

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