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Microsolvation of NO_2^+ in Helium: An *Ab Initio* Study on NO_2^+ - He_n Clusters ($n \leq 7$)

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In this study, the interaction between NO_2^+ cation and He_n ($n = 1-7$) clusters is investigated by means of *ab initio* calculations at MP2/aug-cc-pVTZ and QCISD/aug-cc-pVTZ computational levels. The first and second solvation shells were obtained while N atom of NO_2^+ interacts with five and two He atoms, respectively. Stabilization energies of the studied complexes including basis set superposition errors (BSSE) and zero-point energy (ZPE) corrections at MP2/aug-cc-pVTZ level are in the range of 1.5-7.6 kJ mol⁻¹. Energy decomposition analysis (EDA) shows that polarization effects are the main source of the attraction energy in these complexes. The second most important attraction term is dispersion energy.

Keywords: Microsolvation, NO_2^+ , He, *Ab initio*, EDA, Blue shift

INTRODUCTION

Intermolecular forces play an important role in chemistry, physics and biology. Accurate intermolecular potential energy surfaces are mainly derived in the gas phase in combination with quantum chemical calculations. In contrast to neutral species, intermolecular forces in ionic complexes are spectroscopically less studied, mostly due to the difficulties encountered in the creation of large number densities. Therefore, it is clear that the combination of non-covalent interaction and microsolvation process can be an interesting field in contemporary physical chemistry which can be described further future of ion-ligand interactions. Recently microsolvation of cations in non-polar solvents such as He, Ne, Ar and N_2 has been reported in literature [1-8].

NO_2^+ is one of the simplest polyatomic cations. Its structure and spectroscopy are therefore of fundamental interest. It is also a species playing a significant role in a number of practical contexts. For example, the dissociation

of protonated nitric acid produces NO_2^+ in the stratosphere [9-11].

An experimental and trajectory study was carried out on $[\text{NO}_2^+\text{-rare gas}]$ complexes with a ratio of 1:1 cation and rare gas (Ne, Ar, Kr and Xe) by Liu *et al.* [12]. They have studied the excitation and dissociation of NO_2^+ in collisions with Ne, Ar, Kr and Xe. Hence, in the current study, we present a detailed characterization of microsolvation of NO_2^+ cation in helium clusters $[\text{NO}_2^+\text{-He}_n]$ ($n = 1-7$) by means of *ab initio* calculations. To the best of our knowledge, there is no systematic study for this proposed model in literature. The results of this study can be helpful for the design and application of this model, especially, in experimental investigations.

Such research work is of great significance as its results may benefit other fields of knowledge currently seeking molecular-level understanding on ion solvation to develop their own models. The interest in cluster systems is mainly due to a marked variation of their properties with size. Indeed, clusters may be regarded as intermediate entities exhibiting size-dependent chemical and physical properties connecting the single atom or molecule with the corresponding bulk phase. Thus, by adding step-wise

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solvent molecules to the solute, it is possible to acquire a molecular-level perception of the solvation phenomena. From the theoretical point of view, the study of microsolvation of ionic species takes advantage of using state of the art optimization methods for discovering low-energy structures of the clusters formed by both the solute and the solvent molecules.

COMPUTATIONAL DETAILS

Molecular orbital calculations were carried out using GAMESS suite of programs [13]. The geometry optimization of monomer and complexes were performed with subsequent frequency calculations using second-order Møller-Plesset perturbation theory (MP2) and quadratic configuration interaction with single and double excitations (QCISD) methods in combination with aug-cc-pVTZ basis set. Validity of this basis set has been verified from comparison of theoretical and experimental results in complexes pairing formamide and methyl cations with rare gases [2,8]. The stabilization energy was calculated as the difference of the total energy of the complexes and the sum of the isolated monomers using the following equation.

$$\Delta E = E(\text{NO}_2^+ \text{He}_n) - E(\text{NO}_2^+) - nE(\text{He}) \quad (1)$$

The full counterpoise (CP) method [14] was used to correct the stabilization energy from the inherent basis set superposition error (BSSE). To gain insight into the nature of interactions, interaction energies of the $\text{NO}_2^+ \text{He}_n$ complexes were decomposed using the localized molecular orbital-energy decomposition energy (LMOEDA) method [15]. According to LMOEDA, the interaction energy of a supermolecule system can be separated into the following energy terms:

$$E_{\text{int}} = E_{\text{elst}} + E_{\text{exch-rep}} + E_{\text{pol}} + E_{\text{disp}} \quad (2)$$

where E_{elst} , $E_{\text{exch-rep}}$, E_{pol} and E_{disp} correspond to electrostatic, exchange-repulsion, polarization and dispersion energy terms, respectively. The electron densities of the complexes were analyzed using the atoms in molecules (AIM) methodology [16] by means of AIM2000 [17] program.

RESULTS AND DISCUSSION

Association of NO_2^+ with one to seven He atoms results in different structures with different stabilities (Fig. 1). Geometry searches were carried out for a number of possible isomers to ensure the location of the local minima. All of the possible interactions between He atoms and N or O atom of NO_2^+ have been considered here. It means that all the possible positions for locating He atoms surrounding NO_2^+ was considered as initial structures for optimization, then full geometry optimization without symmetry constrain was carried out to obtain local minima. The geometries and stabilities of global minima, located on the potential energy surface (PES) of the studied complexes are discussed in the following section. The geometry and stability of less stable structures located as local minima on the PES of the studied complexes are presented in the supplementary data.

The calculated bond length of N=O at MP2/aug-cc-pVTZ (1.138 Å) compared with QCISD/aug-cc-pVTZ (1.116 Å) is in good agreement with the experimental value (1.154 Å) [18], so the selected level of theory can be trusted for investigation of the whole group of the studied complexes. The optimized N=O bond lengths and O=N=O angles are shown for all the studied complexes in Table 1.

As Fig. 1 indicates, MP2 calculations predict a T-shape structure for the $[\text{NO}_2^+ \text{He}]$ complex, with N-He bond length of 2.675 Å. Note that the addition of He atom does not change the N=O bond lengths of NO_2^+ . Adding the second He atom to this complex results in the A(2) structure with C_{2v} symmetry (Fig. 1). The obtained results indicate that both He atoms are 2.654 Å far from the nitrogen atom of NO_2^+ .

In the A(3) complex, with C_{2v} symmetry, all of the He atoms are interacting with the N atom of NO_2^+ with bond length of 2.651 Å (Fig. 1). After adding the fourth He, the A(4) complex is formed which is also characterized by C_{2v} symmetry. In this structure, the N-He bond lengths are calculated to be about 2.653 and 2.657 Å, slightly longer than those of A(3). Continuously, adding the fifth atom completes the formation of A type complexes in the studied complexes. So, a regular pentagonal structure with D_{5h} symmetry is formed.

In A(5)B(1) structure, the formation of B type

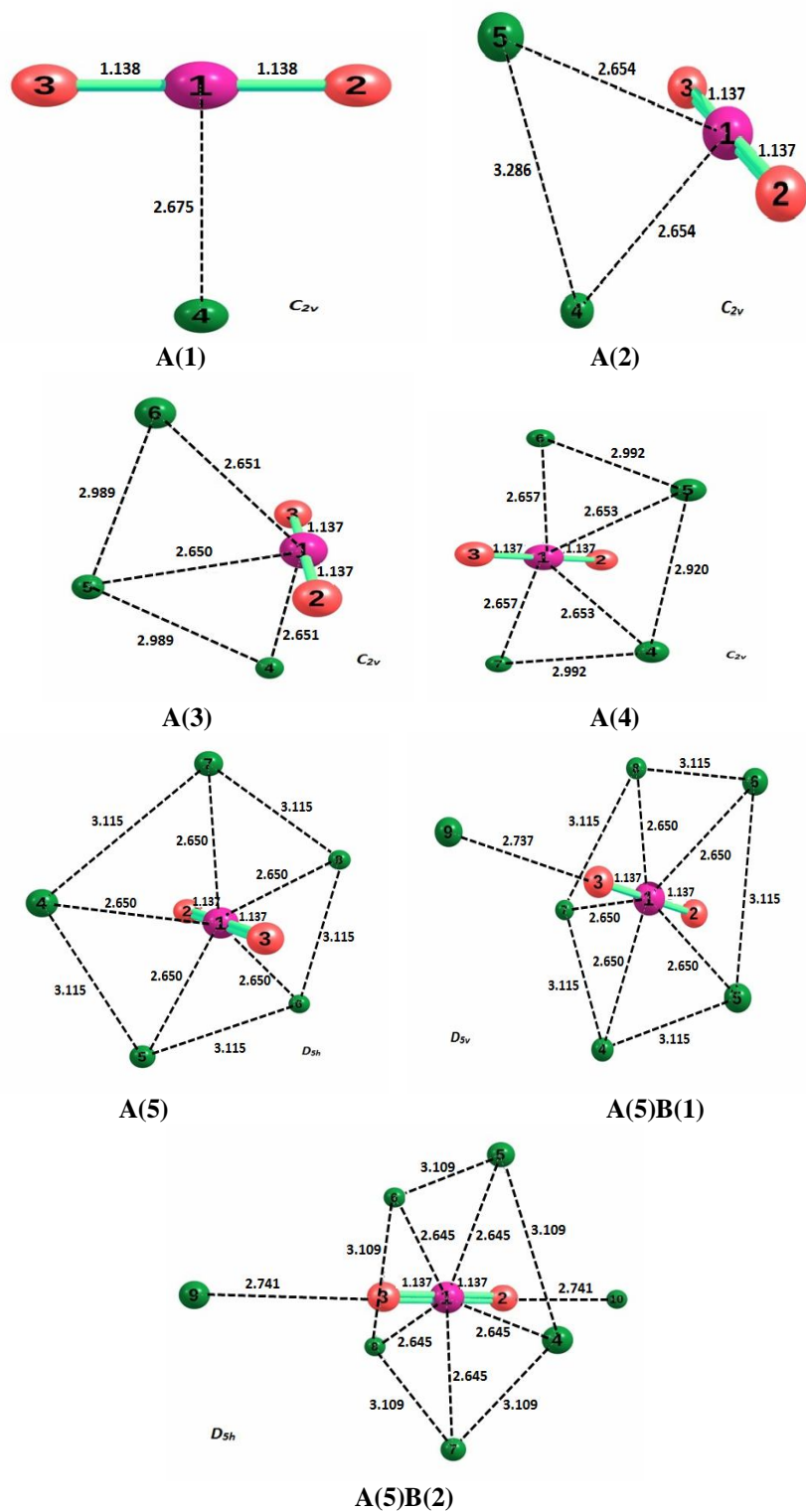


Fig. 1. Optimized structures of $[\text{NO}_2^+ \text{He}_n]$ ($n = 1-7$) clusters with helium atoms forming the A and B type complexes. All distances are in Å.

Table 1. Calculated Bond Length (Å) and Angle (°) for the [NO₂⁺ He_n] (n =1-7) Complexes at MP2/aug-cc-pVTZ Level

Structure	N=O	O=N=O
NO ₂ ⁺	1.138	180.0
A(1)	1.138	179.9
A(2)	1.137	179.3
A(3)	1.137	179.9
A(4)	1.137	179.9
A(5)	1.137	180.0
A(5)B(1)	1.137	180.0
A(5)B(2)	1.137	180.0

Table 2. Calculated Stabilization Energies Corrected with BSSE and ZPE for the [NO₂⁺ He_n] (n =1-7) Complexes (kJ mol⁻¹) Using MP2 and QCISD Methods with aug-cc-pVTZ Basis Set

n	Numbers of local minimas	Global minimas	Symmetry	MP2/aug-cc-pVTZ		QCISD/aug-cc-pVTZ
				ΔE(BSSE)	ΔE(BSSE+ZPE)	ΔE(BSSE)
1	2	A(1)	C _{2v}	2.61	1.59	2.63
2	3	A(2)	C _{2v}	5.24	2.99	5.30
3	2	A(3)	C _{2v}	7.85	4.17	7.94
4	1	A(4)	C _{2v}	10.46	5.48	10.58
5	1	A(5)	D _{5h}	13.13	6.91	13.29
6	1	A(5)B(1)	C _{5v}	14.16	7.34	14.20
7	1	A(5)B(2)	D _{5h}	15.17	7.64	15.10

complexes is started with addition of the 6th helium atom *via* interaction with O of NO_2^+ instead of N. Finally, the B type complexes are completed with addition of the 7th helium atom while interacting with the second oxygen atom of NO_2^+ in A(5)B(2) structure.

Now let us discuss the stabilization energies of the title complexes. Table 2 shows the calculated stabilization energies corrected with BSSE and zero point energy (ZPE) of the $[\text{NO}_2^+-\text{He}_n]$ complexes at MP2 level. When studying interactions of He atoms, it would be advisable for confirmatory calculations to be carried out with more sophisticated correlated methods. Coupled cluster (CC) methods have become a primary tool for high-accuracy calculations of atomic and molecular properties. In general, the results of CC calculations are better than those of configuration interaction (CI) or many-body perturbation theory (MBPT) calculations obtained with the same basis set and the same type of excitations. QCISD is established by adding quadratic terms to the CISD projection equations. In this way, QCISD becomes size-extensive at the cost of losing the variation character of a CI method. One can consider QCISD as a simplified CCSD method that does not contain cubic and quartic terms and, therefore, is somewhat easier to implement and to carry out than the CCSD method.

New optimizations with a more complete treatment of electron correlation at QCISD/aug-cc-pVTZ computational level were carried out and the results compared with those of MP2 calculations (Table 2). As Fig. 2 indicates, there is a nice correlation between the BSSE-corrected stabilization energy at MP2 level and the number of helium atoms in the complexes. Figure 2 also shows a progressive weakening as He atoms are added, even in the first shell. A nice linear correlation is established between the results at MP2 and QCISD level as depicted in Fig. 3.

Vibrational frequencies were calculated for isolated NO_2^+ and $[\text{NO}_2^+-\text{He}_n]$ complexes at MP2/aug-cc-pVTZ level. Upon complex formation, a small blue shift between 1-10 cm^{-1} is predicted for stretching and bending vibrational modes of NO_2^+ . It should be noted that the calculated vibrational frequencies are based on harmonic oscillator approximation, so there is an error in these calculations. On the other hand we should mention the special nature of the bosonic He atoms in such clusters; their ZPE values are usually large and, even in ions, the outer atoms in the outer

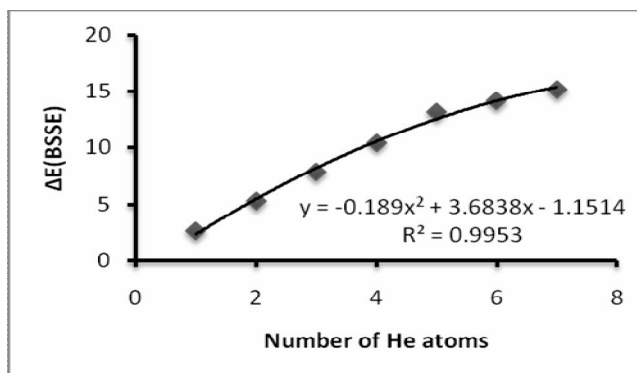


Fig. 2. Correlation between $\Delta E_{(\text{BSSE})}$ (in kJ mol^{-1}) and the number of helium atoms at MP2/aug-cc-pVTZ level.

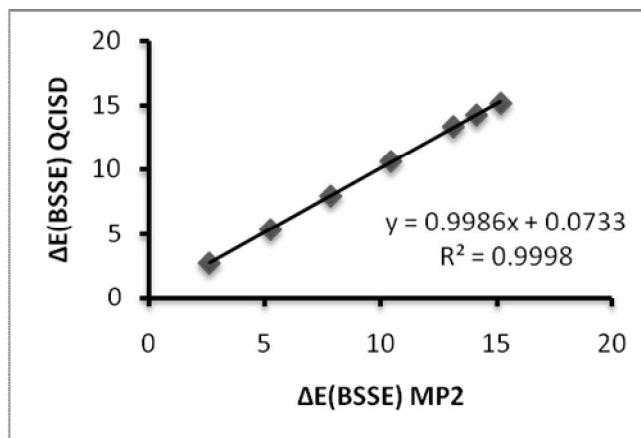


Fig. 3. Correlation of the stabilization energies (in kJ mol^{-1}) obtained at QCISD level with those of MP2 (in kJ mol^{-1}).

shells can undergo tunneling by bosonic exchanges; none of them were included in the calculations.

All interactions between NO_2^+ cation and He atoms were established from the results of AIM analysis. Application of AIM analysis to all the complexes allowed us to locate bond critical points, BCPs, and analyze their properties based on the electron density (ρ_{BCP}) and its Laplacian ($\nabla^2\rho_{\text{BCP}}$). The analysis of the electron density within the AIM methodology shows the presence of BCPs between the interacting atoms (Table 3). The electron densities at the BCPs are in the range of 0.0030-0.0046 a.u. On the other hand, the values of the Laplacian at the BCPs are all

positive corresponding to a local depletion of the electron density from the bonding region. Nature of interactions (closed shell/electrostatic) in studied complexes is concluded from the results of AIM analysis.

The calculated polarizability of the isolated NO_2^+ cation and He atom are reported in Table 4. The corresponding values of $[\text{NO}_2^+ \cdot \text{He}_n]$ complexes are also listed in this table.

The components of the polarizability tensor [19] are obtained as the second-order derivatives of the energy with respect to the Cartesian components ($i,j = x,y,z$) of the electric field, *viz.*

$$\alpha_{ij} = [d^2E/dF_i dF_j]_{F=0} \quad (2)$$

Table 3. Calculated AIM Parameters (in a.u.) of the $[\text{NO}_2^+ \cdot \text{He}_n]$ ($n = 1-7$) Complexes at MP2/aug-cc-pVTZ Level

n	$\rho_{1,4}/\nabla_{1,4}^2$	$\rho_{1,5}/\nabla_{1,5}^2$	$\rho_{1,6}/\nabla_{1,6}^2$	$\rho_{1,7}/\nabla_{1,7}^2$	$\rho_{1,8}/\nabla_{1,8}^2$	$\rho_{3,9}/\nabla_{3,9}^2$	$\rho_{2,10}/\nabla_{2,10}^2$
1	0.0042/0.0290						
2	0.0045/0.0307	0.0045/0.0307					
3	0.0045/0.0310	0.0045/0.0310	0.0045/0.0310				
4	0.0045/0.0307	0.0045/0.0308	0.0044/0.0304	0.0044/0.0304			
5	0.0045/0.0310	0.0045/0.0309	0.0045/0.0310	0.0045/0.0310	0.0045/0.0310		
6	0.0045/0.0310	0.0045/0.0310	0.0045/0.0310	0.0045/0.0130	0.0045/0.0310	0.0031/0.0206	
7	0.0046/0.0314	0.0046/0.0314	0.0046/0.0314	0.0046/0.0314	0.0046/0.0314	0.0030/0.0203	0.0030/0.0203

Table 4. Calculated Mean Dipole Polarizability (α) and Polarizability Anisotropy ($\Delta\alpha$) for each Complex at the MP2 Level (all in a.u.) at MP2/aug-cc-pVTZ Level

Structure	$\alpha(\text{au})$	$\Delta\alpha(\text{au})$
NO_2^+	13.98	16.13
He	1.35	0
A(1)	15.27	15.70
A(2)	16.55	15.23
A(3)	17.83	14.76
A(4)	19.11	14.29
A(5)	20.40	13.81
A(5)B(1)	21.84	14.39
A(5)B(2)	23.29	14.99

The derivatives are evaluated numerically by using the finite field method and the mean polarizability is calculated from the diagonal elements of the polarizability tensor as,

$$A = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

and polarizability anisotropy ($\Delta\alpha$) is defined as follows:

$$(\Delta\alpha)^2 = 1/2((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2) \quad (4)$$

As seen in Table 4, the polarizability increases monotonically with the number of He atoms in the clusters. For the calculated mean polarizability, when is plotted as a function of n , an excellent linear correlation is found with a correlation coefficient value of 0.99 (Fig. 4). This demonstrates that an additive effect is present in these clusters. Furthermore, it is evident that the calculated polarizability anisotropy of $[\text{NO}_2^+-\text{He}_{n=2-7}]$ complexes is smaller than the corresponding mean polarizability, indicating that the electron distribution on these complexes are almost symmetric.

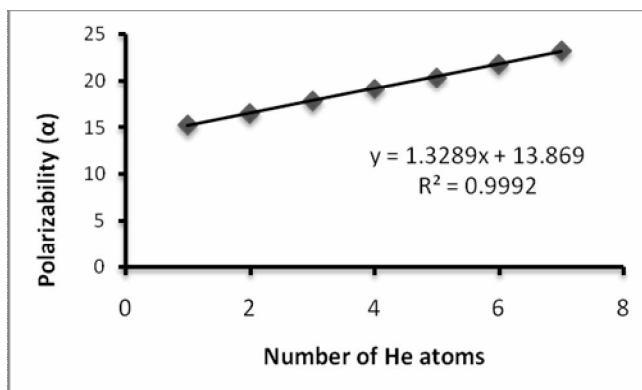


Fig. 4. Correlation between mean polarizability (α) and the number of helium atoms in the clusters at MP2 level.

The energy decomposition analysis of the title complexes can provide some helpful insight on the nature of the interactions. The interaction energies of the $[\text{NO}_2^+-\text{He}_n]$ complexes were decomposed using the LMOEDA scheme [17]. The results are listed in Table 5. One can see that polarization effects are the major source of the attraction in

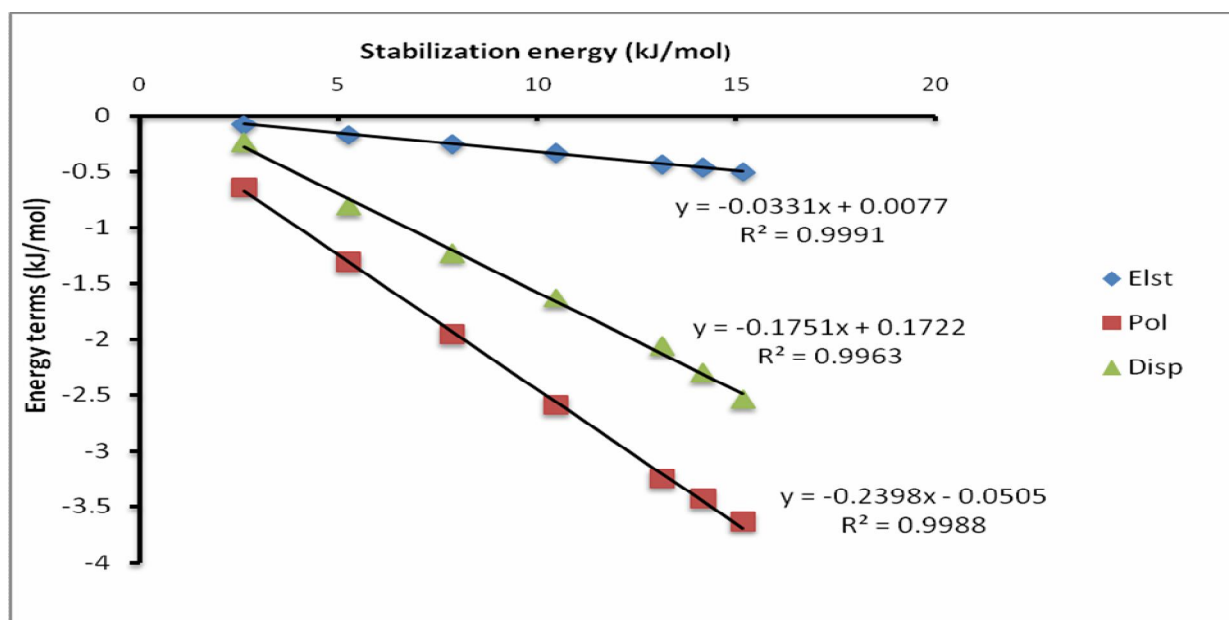


Fig. 5. Correlation between different terms of energy and stabilization energy in $[\text{NO}_2^+-\text{He}_n]$ complexes at MP2/aug-cc-pVTZ level.

Table 5. Calculated Binding Energy Components (in kJ mol⁻¹) for [NO₂⁺ He_n] (n = 1-7) at MP2/aug-cc-pVTZ Level

Structure	E _{elst}	E _{exch-rep}	E _{pol}	E _{disp}
A(1)	-0.08	0.48	-0.64	-0.24
A(2)	-0.17	1.05	-1.31	-0.81
A(3)	-0.25	1.59	-1.96	-1.23
A(4)	-0.33	2.08	-2.59	-1.63
A(5)	-0.43	2.66	-3.25	-2.06
A(5)B(1)	-0.46	2.87	-3.43	-2.30
A(5)B(2)	-0.50	3.13	-3.63	-2.54

these complexes. The second most important attraction term is dispersion energy (E_{disp}), which contributes to 25% of all the attractive terms in A(1) and increases its contribution, reaching to 38% in the A(5)B(2) complex. As in the case of stabilization energy, the dispersion energy becomes more negative as the number of He atoms in the clusters increases. On the other hand, the electrostatic energy (E_{elst}) corresponds to about 8% of the total attractive terms. We also consider the relationship between the different energy terms and stabilization energy of the title complexes. They represent a linear relationship as shown in Fig. 5.

CONCLUSIONS

In summary, ab initio calculations were performed to investigate the microsolvation of NO₂⁺ in the He_n clusters, where n = 1-7. The A shell is obtained while N atom of NO₂⁺ interacts with five He atoms. Finally, the addition of two other He atoms forms the B shell. A nice linear correlation was found between the BSSE-corrected stabilization energies at MP2 and QCISD levels. The attractive polarization and dispersion components make the major contribution to the stability of [NO₂⁺-He_n] complexes. The dispersion energy becomes more negative as the size of the clusters increases.

Supporting Information

Geometry and stability of less stable structures located as local minima on the PES of the studied complexes.

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