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Lewis acid catalyzed stabilization of an excess electron on a molecular surface

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Abstract

In a recently developed molecular surface model we proposed that excess electrons could be stabilized in charge pockets. These hypothetical molecular species had a network of hydrogen bonding OH groups on one side of the surface and hydrogen atoms on the opposite side. The OH groups were unevenly distributed so as to permit the dipole moment of the system to increase which allows charge pockets to form that can attract excess electrons on molecular surfaces. In this work we report the ability of $AlCl_3$–NH_3 to stabilize excess electrons on molecular surfaces. The calculations reveal that the resulting anions are very stable with respect to electron detachment.

Keywords: $AlCl_3$; NH_3; Molecular surfaces; Charge pockets; VDE

1. Introduction

For a while Lewis acids have been known to act as catalysts in organic reactions. The types of reactions in which trivalent aluminum plays a catalytic role are many and varied. The Friedel–Crafts alkylation and acylation of aromatic rings, removal of *tert*-butyl groups from phenols, and the well-known Ziegler–Natta polymerization reactions are some examples where the aluminum trichloride acts as a catalyst. Several of these important compounds have been experimentally and theoretically studied [1–6]. The ability of Aluminum trihalide (AlX_3) to form stable complexes has also been the subject of experimental and theoretical works [7–24].

Alternatively, it is known that the binding interactions between a Lewis base (an electron pair donor such as NH_3) and a Lewis acid (an electron pair acceptor such as $AlCl_3$) plays an important role in many chemical processes. The reaction takes place with the formation of donor-acceptor complexes. The points that have been more substantially developed are conformational structure, complexation energy and charge transfer. Recently, Timoshkin et al. [25] have reported their investigations of the role of the terminal atoms in donor–acceptor complex formation of group 13 metals. They have shown that the dissociation energies of the $AlCl_3$–donor complexes are rather high and the complexes that form are indeed stable.

In this work we will show that molecular surfaces can adequately form stable anions by trapping excess electrons in charge pockets on molecular surfaces. In these investigations we computed molecular surfaces with a network of hydrogen bonded OH groups on one side coupled to hydrogen atoms on the opposite side of surface [26]. The uneven distribution of the OH groups coupled to the partial positive charge of the hydrogen atoms on the opposite side created charge pockets which were capable of stabilizing excess electrons in charge pockets on molecular surfaces. Our computed results demonstrated that the anions were stable with respect to electron detachment.

It is relatively well known that electrons can be stabilized in-between molecular species [27]. These anions have been identified as “Anions with Internally Suspended

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Electrons" or AISÉs for short which permit electrons to occupy the space in the cavity which separates two polar subunits. The resulting AISE anions formed have their dipole-moments facing each other which creates a pocket of positive charge capable of attracting excess electrons and localizing them forming electron bonds or e-bonds. These anions are metastable and short-lived species which can result from kinetic and thermodynamic factors.

The stability of the solvated molecular AISE anions depend on the stability of dipole-bound anions of the molecular complexes. The first step in AISE formation is the formation of a dipole-bound anion by one of the monomers in the dimer species. Then the second polar subunit attaches to the excess electron on the opposite side of where the first species is located. Therefore, in this work we will attempt to calculate stable AISE anions for an acid catalyzed molecular surface.

In our previous work we have shown that hydrated surfaces and other hydrated analogous can solvate excess electrons on molecular surfaces [28]. We have reported that ammonia (NH_3) can adequately solvate excess electrons on molecular surfaces [29,30]. Calculations reveal that complexes formed between NH_3 with BF_3 formed relatively stable dipole-bound anions [29] with a dipole moment of over 6.5 D (compared to the dipole moment of around 1.65 D for the isolated NH_3 species). It is evident that the primary stabilization force arises from charge transfer (CT) effects. Therefore, while the van der Waals complexes of such a species does not form very stable anions, the covalent molecular dimer does.

The purpose of the current study is to study the ability of $AlCl_3$ to catalyze an ammoniated surface yielding $AlCl_3$–NH_3 that acts to solvate the excess electron. We believe that basic experimental methods can be used to generate this species once the NH_3 molecular surfaces are formed. This work attempts to describe a situation whereby a Lewis acid can act to stabilize electrons in charge pockets on molecular surfaces.

2. Computational methods

All of the quantum chemical calculations performed in this work were carried out with the GAUSSIAN03 suite of codes [18]. Due to the fact that systems under consideration are rather large, geometry optimizations were performed with the spin-unrestricted Hartree–Fock (UHF) method. We coupled this to a 3-21G* basis set with six diffuse Gaussian sp-shells with exponents equal to 0.01, 0.002, 0.0004, 0.00008, 0.000016, and 0.000032, and a p-shell with exponent 0.036 that have been placed away from the molecular framework of the system.

Since we are only comparing the qualitative values of the vertical detachment energies (VDE) (which is defined as the difference in energy between the anion structure and the neutral structure at the anions geometry) it is not necessary to compute accurate energies are not necessary. These systems serve as hypothetical models for electron attachment and solvation of molecular surfaces.

We must be aware of the fact that the position of the excess basis functions was permitted to optimize in the minimization algorithm. The coordinates of these functions are defined at the point by which the lowest unoccupied molecular orbital (LUMO) for the neutral species is the most negative in energy. According to Koopmans theorem [27] the LUMO is an approximation to the electron affinity and the HOMO energy of the corresponding anion is an approximation to its vertical electron detachment energy. Because the basis functions are so diffuse it does not matter where they are placed the effects on the energy are minimal. The functions prevent the possibility of the excess electron to be confined to the molecular framework due to an overly confining basis set.

3. Results and discussion

3.1. Molecular surfaces and charge pockets

From our previous report on charge pocket formation on molecular surfaces we reported a series of eight cyclooctane and cyclohexane molecular frameworks [26]. The selected systems had OH groups on one side of the surface and hydrogen atoms on the opposite side. The uneven distribution of the OH groups were added to increase the dipole moment of the system and the attraction of excess electrons to the molecular surface. Smaller ringed systems were not large enough to permit adequate OH bonded networks to form due to the limited size of the framework. This limited surface area have reduced number of OH groups (as a result of their small frames) which prevents the formation of stable dipole-bound and AISE anions.

In our previous investigations we have shown that as the number of OH groups increases on the molecular surfaces so does the vertical detachment energies (VDE) of the resulting anions. Similar to our previous studies [26,28,30] we will use the same set of molecular systems to study the acid catalyzed solvation of excess electrons on molecular surfaces. It is important to note that the isolated molecular surface [26] only forms dipole-bound anions and therefore only has one value as can be seen in the table. We have considered the cyclooctane species with both 4 OH and 6 OH groups on the surface. Alternatively, the cyclohexane systems consists of six configurations. The first is the one cyclohexane ring (with 4 OH groups), two cyclohexane rings (containing 5 OH groups), three cyclohexane rings (with 6 OH groups), four cyclohexane rings (that has 8 OH groups), five cyclohexane rings (with 10 OH groups) and finally 11 OH, six cyclohexane ring species [31]. As previously mentioned the number of OH groups was added in order to increase the dipole-moment of the system. The OH groups used were the minimum number needed in order for the dipole moment to be high enough to attach an excess electron, if less than this number was selected this leads to unstable anion states. The cyclohex-