SEQUESTRATION OF NOBLE GASES BY H_3^+ IN THE OUTER SOLAR NEBULA – IMPLICATIONS FOR THE FORMATION OF COMETS. F. Pauzat[1], Y. Ellinger[1] and O. Mousis[2], [1]Laboratoire de Chimie Théorique, UMR-CNRS 7616, 4 Place Jussieu, 75252 Paris cedex, France (pauzat@lct.jussieu.fr); [2]Observatoire de Besançon, UMR-CNRS 6091, 41 bis, Avenue de l'Observatoire, BP 1615 Besançon, France.

Astrophysical context: Noble gases are an important component of the atomic population in the universe. It is generally admitted that these elements are inert and do not participate in molecular structures. This statement certainly applies to space chemistry for interactions with neutral systems driven by Van der Waals forces are very weak and can hardly resist turbulence. It may not be relevant when positive ions are involved, especially is the case of the interstellar medium (ISM) where positive ions do exist in space as free flyers. These species are mainly protonated species, formed by proton transfer from H_3^+ that plays in the gas phase in space the role taken by HO_3^+ in the aqueous phase on Earth.

The fact that H_3^+ may be a possible partner for accreting noble gases in the gas-phase is a reasonable assumption since it is the simplest ion derived from the most abundant molecule in the universe. This assumption is comforted by recent detection of this molecular ion in a large variety of environments: in star forming regions [1], in diffuse interstellar media [2], at the poles of Jupiter [3] and of the other giant planets [4]; it has also been detected under its deuterated form H_2D^+ in proto-planetary disks [5].

The formation of molecular complexes of H_3^+ is well known in the laboratory. Among others, one may recall the early experiments using low energy electron impact on solid hydrogen that allowed to detecting the presence of hydrogen clusters up to H_{47}^+ [6]. More recently, the thermochemical stabilities of $(H_2)_n…H_3^+$ with n=1-9 (where … is a conventional representation of the weak bonding of the clusters) have been determined [7]. Concerning noble gases, thermochemical data on $Ar…H_3^+$ were obtained and the binding energy in $Ne…H_3^+$ was estimated [8].

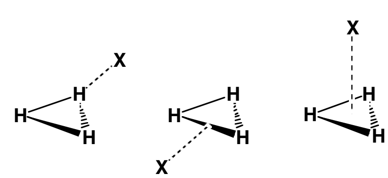
In this work, we discuss the implications of the production of stable complexes formed by H_3^+ and noble gases for the formation of comets in the outer solar nebula. Since H_3^+ is produced by the H_2 ionization of cosmic rays, it is expected to be the most abundant ion present in the outer part of protoplanetary disks, including the outer solar nebula [9]. Hence, H_3^+ could play a major role in the gas-phase chemistry in some regions of the solar nebula where comets are presumed to be formed.

Stability of X-H_3^+ complexes: In fact, very few is known on these complexes, mainly as a reason of extreme difficulties in setting the proper experiments. In such conditions, it has been shown that numerical simulation using "state of the art" methods of quantum molecular calculation can be a valuable alternative. The main goal of the theoretical investigation reported here is to probe whether molecular complexes with H_3^+ are stable enough to trap noble gases and serve as a mean for concentrating these atomic species in astrophysical objects.

Ab-initio methods of Coupled Cluster type and Density Functional Theory (DFT) methods using the BH&LYP formalisms have been employed. The description of the atoms relies on extended basis of atomic orbitals with high flexibility in the valence shell. In these calculations, all electrons are taken into account, with the exception of Xenon where core electrons are represented by effective core potentials. All energetical terms are exactly calculated and exchange and correlation effects are included.

The validity of the computing procedure has been demonstrated in a previous study in which we considered $Ar…H_3^+$ as a test case [10]; it is the only complex for which spectral signatures are known, to the best of our knowledge. Using appropriate basis sets, Coupled Cluster and density functional BH&HLYP levels of theory have been shown to reproduce the rotational constants within 0.3% together with the only known IR frequency on the test case of $Ar…D_3^+$. The strategy developed in this preliminary work is applied here to the noble gases from Neon to Xenon.

Three stationary points have been identified for these complexes (Figure 1). All the calculations, including a number of levels of theory not reported here, have shown the same energetical order of the three stationary points whatever the noble gas:



				Dissociation energy
Ne	0.0	0.32	0.61	1.42
Ar	0.0	4.0	5.6	7.2
Kr	0.0	7.5	10.2	13.3
Xe	0.0	15.4	19.2	22.8

Figure 1: Structures and relative energies (kcal/mol) of $X…H_3^+$ complexes at *CCSD/cc-pVTZ* level of theory.

The left structure is the stable structure (on-apex) with X attached to a summit of the H_3^+ triangle; all frequencies are real. The middle structure is a single dimension saddle point (on-side) with an imaginary frequency. It is a transition state on the in-plane transfer of X from a hydrogen to another. The right structure is a long distance structure III (on-top) where the X atom is above the H_3^+ triangle. This non-planar structure of C_{3v} symmetry is a maximum on the surface with two imaginary frequencies. These calculations show that the noble gas can all be trapped by H_3^+ to form stable complexes in the gas-phase; Neon however may be too weakly bound to resist in highly turbulent environments.

Formation of X-H_3^+ complexes in the solar nebula: Current scenarios of the formation of the solar nebula consider that most of ices falling from the presolar cloud onto the disk vaporized when entering in the early nebula and that H_2O ice vaporized within 30 AU in the solar nebula [11]. With time, the decrease of temperature and pressure conditions allowed the water to condense at 150 K in the form of microscopic crystalline ice [11] [12]. When temperature and pressure conditions reached values allowing the formation of amorphous ice, the remaining amount of water vapor was negligible. It is then considered that volatiles were incorporated into clathrate hydrates within 30 AU in the outer solar nebula. Clathrate hydrates subsequently agglomerated in order to form growing planetesimals. In contrast, planetesimals formed at higher heliocentric distances (i.e. in the cold outer part of the solar nebula) are expected to be formed from amorphous ice that were preserved from vaporization.

Observational evidences suggest that H_3^+ is present in the outer parts of proto-planetary disks [5] [9]. As a result, this ion can be presumed to have been also abundant in the outer solar nebula with a concentration increasing with the heliocentric distance. The calculations presented above suggest that H_3^+ acts as a sequestrator of noble gases in the solar nebula gas-phase. In other words, H_3^+ would impede the noble gases to be incorporated into clathrate hydrates during the cooling of the solar nebula. Indeed, X-H_3^+ complexes would remain in the solar nebula gas-phase up to its dissipation. This implies that clathrate hydrates formed just below the 30 AU region may not contain noble gases albeit they trapped most of the other major volatile species.

Implications for the formation of comets: Since comets may have formed either from clathrate hydrates in the initially hot outer part of the solar nebula (where the initial gas temperature was greater than 150 K) or from amorphous ice at heliocentric distances higher than 30 AU, their content in noble gases may vary as a function of their formation region. Up until now, noble gases have not yet been clearly detected in comets (the detection of Ar in Comet Hale-Bopp was claimed [13] but the signal to noise ratio is too low).

From our calculations, we propose the following scenario: comets formed within the heliocentric distance of 30 AU should be depleted in noble gases. On the other hand, comets formed at higher heliocentric distances from initially amorphous ice should contain Ar, Kr and Xe. The origin of comets in the solar nebula is still imprecise: Edgeworth-Kuiper belt comets are presumed to be formed at a distance further to the Sun than that of Neptune prior to its migration and the formation zone of Oort cloud comets varies, according to the different models, from near Jupiter and Saturn to heliocentric distances higher than 30 AU. In that context, subsequent measurements of noble gases abundances in comets should help to constrain the origin of the reservoirs of cometary bodies.

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