SEQUESTRATION OF NOBLE GASES BY H$_3^+$ IN PROTOPLANETARY DISKS 
AND OUTER SOLAR SYSTEM COMPOSITION

O. MOUSIS
Institut UTINAM, CNRS-UMR 6213, Observatoire de Besançon, BP 1615, 25010 Besançon Cedex, France; the HOLMES collaboration; olivier.mousis@obs-besancon.fr

F. PAUZAT AND Y. ELLINGER
Laboratoire de Chimie Théorique (LCT/LETMEX), CNRS-UMR 7616, Université Pierre et Marie Curie, 4, Place Jussieu, 75252 Paris Cedex 05, France

AND

C. CECCARELLI
Laboratoire d’Astrophysique, Observatoire de Grenoble, BP 53, 38041 Grenoble Cedex 09, France
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ABSTRACT

We study the efficiency of the noble gas sequestration by the ion H$_3^+$ in the form of XH$_3^+$ complexes (with X = argon, krypton, or xenon) in gas-phase conditions similar to those encountered during the cooling of protoplanetary disks. We show that XH$_3^+$ complexes form very stable structures in the gas phase and that their binding energies are much higher than those involved in the structures of X-H$_2$O hydrates or pure X-X condensates. This implies that in the presence of H$_3^+$ ions, argon, krypton, or xenon are likely to remain sequestered in the form of XH$_3^+$ complexes embedded in the gas phase rather than forming ices during the cooling of protoplanetary disks. The amount of the deficiency depends on how much H$_3^+$ is available and efficient in capturing noble gases. In the dense gas of the mid-plane of solar nebula H$_3^+$ is formed by the ionization of H$_2$ from energetic particles such as those in cosmic rays or those ejected by the young Sun. Even using the largest estimate of the cosmic-ray ionization rate, we compute that the H$_3^+$ abundance is 2 and 3 orders of magnitude lower than the xenon and krypton abundance, respectively. Estimating the ionization induced by the young Sun, on the other hand, is very uncertain but leaves the possibility of having enough H$_3^+$ to make krypton and xenon trapping efficient. This may cause a deficiency of Kr, Xe, and to a lower extent of Ar, in the forming icy planetesimals. We then suggest that this sequestration mechanism may explain the deficiency of Titan in noble gases revealed by the Huygens probe measurements. Similarly, comets formed from crystalline water ice in the outer nebula should be also deficient in krypton and xenon, and to a lower extent in argon, in agreement with some recent observations.

Subject headings: astrochemistry — comets: general — planetary systems: protoplanetary disks — planets and satellites: formation — solar system: formation

1. INTRODUCTION

Noble gases are an important component of the atomic population in the universe. Even if helium is by far the most abundant, representing about 10% of hydrogen, the abundances of the heavier noble gases are not negligible compared with other elements such as carbon or oxygen. Moreover, noble gases seem to be widespread in the bodies of the solar system located at heliocentric distances up to ~5 AU. Indeed, these compounds have been measured in situ in the atmospheres of Earth, Mars, and Venus, as well as in meteorites (Owen et al. 1992). The abundances of argon, krypton, and xenon were also measured over solar by the GCMS aboard the Galileo probe in the atmosphere of Jupiter (Owen et al. 1999).

However, even if there is a deficiency of accurate measurements, the situation is likely to be different in bodies presumably formed at further heliocentric distances. Indeed, an unexpected feature of the atmosphere of Titan is that no noble gases other than argon were detected by the Gas Chromatograph Mass Spectrometer (GCMS) aboard the Huygens probe during its descent on 2005 January 14. The detected argon includes primordial $^{36}$Ar (the main isotope) and the radiogenic isotope $^{40}$Ar, which is a decay product of $^{40}$K (Niemann et al. 2005). The other primordial noble gases $^{38}$Ar, Kr, and Xe were not detected by the GCMS instrument. Besides, $^{36}$Ar/$^{14}$N is about 6 orders of magnitude lower than the solar value, indicating that the amount of trapped $^{36}$Ar is poor within Titan (Niemann et al. 2005). The apparent deficiency of noble gases in Titan is surprising since this satellite was expected to be made from the same building blocks as those accreted by Saturn (Mousis et al. 2002) and share a composition similar to that of the noble gases—rich planetesimals that took part in the formation of Jupiter, if the gas-phase conditions were homogeneous in the solar nebula (Alibert et al. 2005).

Regarding comets there is no firm detection of noble gases, in part due to the difficulty of obtaining the observations, which need out-of-the-atmosphere instruments. Stern et al. (2000) claimed the detection of argon in comet C/1995 O1 Hale-Bopp, but the signal-to-noise ratio is very low (Weaver et al. 2002; Iro et al. 2003). On the contrary, Weaver et al. (2002) did not detect $^{36}$Ar in comets C/1999 T1 (McNaught-Hartley), C/2001 A2 (LINEAR), or C/2000 WM1 (LINEAR), using the Far Ultraviolet Spectroscopic Explorer (FUSE). The upper limits they obtained for C/2001 A2 and C/2000 WM1 correspond to Ar/O ratios less than 10% of the solar value. In summary, although the apparent $^{36}$Ar is poor within Titan (Niemann et al. 2005). The apparent deficiency of noble gases in Titan is surprising since this satellite was expected to be made from the same building blocks as those accreted by Saturn (Mousis et al. 2002) and share a composition similar to that of the noble gases—rich planetesimals that took part in the formation of Jupiter, if the gas-phase conditions were homogeneous in the solar nebula (Alibert et al. 2005).

1 The resonance transitions of the noble gases lie in the far-ultraviolet spectral region ($\lambda \leq 1200$ Å).
2 The Ar/O upper limit for C/1999 T1 is essentially the solar value. However, the measurement was much less significant in that case, due to the fact that most of the data were accumulated during the daytime portion of the FUSE orbit and suffered some contamination from terrestrial dayglow emissions (Weaver et al. 2002).
deficiency of noble gases in comets needs confirmation, current observations point to some process that affected their trapping capabilities during their formation or evolution.

In this article, we explore the possibility that the observed deficit in the aforementioned bodies is due to the sequestration of the noble gases by H$_3^+$ during the early stages of the solar nebula. The idea is that at the epoch of formation of the icy planetesimals by accretion of the dust grains in the outer solar nebula a significant fraction of noble gases were sequestrated by the H$_3^+$ ion in the gas phase. As a result, they were not incorporated in the forming ices during the cooling of the solar nebula, giving rise to noble gas–deprived planetesimals. From calculations of the H$_3^+$ abundance in young protoplanetary disks, we suggest that the proposed sequestration scenario might explain the observed deficit of Kr, Xe, and to a small extent, that of Ar.

For many years after they were discovered, it was believed that noble gases were chemically inert and unable to participate in molecular structures. Counterexamples can be found in X-halides species (Christe 2001) and in a recently discovered novel class of noble gas insertion compounds that is unlikely to form in space (Gerber 2004). Besides, van der Waals complexes of noble gases were also characterized, but their stability due to neutral-neutral dispersion forces is very weak and can hardly resist turbulence.

However, this statement may not be relevant when positive ions are involved, especially in 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 in the gas phase plays the role taken by H$_3$O$^+$ in the aqueous phase on Earth.

The fact that H$_3^+$ may be a possible partner for accreting noble gases is a reasonable assumption since it is the simplest ion derived from the most abundant molecule in the universe, H$_2$. This assumption is confirmed by recent detection of this molecular ion in a large variety of environments: in star-forming regions (Geballe & Oka 1996), in diffuse interstellar media (McCall et al. 2002), and at the poles of Jupiter (Maillard et al. 1990) and of the other giant planets (Miller et al. 2000). In particular, and relevant to the subject of this article, it has also been detected under its deuterated form H$_3^+$ in protoplanetary disks (Ceccarelli et al. 2004). All these observations show that H$_3^+$ and its deuterated forms (H$_3^+$, H$_2$D$^+$, and D$_3^+$) are likely the most abundant positive charge carriers in cold and dense gas, as it is the case in protoplanetary disks.

The formation of molecular complexes of composition (H$_2$)$_n$H$_3^+$ is well known in the laboratory (Clampitt & Gowland, 1969; van Deursen & Reuss 1973; van Limig & Reuss 1978; Hiraoka 1987). Concerning noble gases, Hiraoka & Mori (1989) obtained thermochemical data on ArH$_3^+$ and an estimation of the binding energy of NeH$_3^+$. Apart from the latter examples, very little is known on these complexes, mainly because of extreme difficulties in setting the proper experiments. In such conditions, numerical simulations using state of the art methods of quantum chemistry can be a valuable alternative.

In what follows in this interdisciplinary report (§2), we show that molecular complexes with H$_3^+$ are stable enough to trap noble gases and serve as a means for maintaining these species in the gas phase. We assume here a two-body reaction, where H$_3^+$ and the noble gas combine via radiative association. Since we are dealing with protoplanetary disk conditions, the stability of these complexes in the presence of H$_2$O also has to be addressed. Model calculations lead to the conclusion that the transfer of the noble gas from XH$_3^+$ compounds (where X is Ne, Ar, Kr, or Xe) to the X-H$_2$O complex or to the pure X-X condensate is unlikely. In §3, we discuss a possible implication of the production of such stable complexes formed by H$_3^+$ and noble gases for the composition of bodies formed in the outer solar nebula. Since H$_3^+$ results from H$_2$ ionization by cosmic rays, it is expected to be among the most abundant ions in the outer part of protoplanetary disks, including the outer solar nebula. Hence, H$_3^+$ could play a major role in the gas-phase chemistry leading to the formation of icy planetesimals in the outer regions of the solar nebula (Pauzat et al. 2006). We conclude in §4. Finally, an Appendix is devoted to the description of the theoretical spectra that would allow identification of XH$_3^+$ complexes in the laboratory.

2. CHEMICAL ASPECT OF THE COMPLEXATION OF NOBLE GASES BY H$_3^+$

The quantum chemistry study presented below is a follow-up of a previous work that considered argon as a case study in a systematic investigation involving possible multiple complexation of H$_3^+$ by this noble gas (Pauzat & Ellinger 2005). Elaborate ab initio methods of coupled cluster type (CCSD, CCSD[T]) and density functional theory (DFT) methods using the BH&HLYP functionals were employed. For X = Ne, Ar, and Kr, the basis sets used are extended basis with high flexibility in the valence shell (cc-pVTZ to Aug-cc-pVQZ); the same basis sets, associated with relativistic pseudo potentials, were used for Xe.

The details of the calculations, well beyond the scope of this report, can be found in the aforementioned paper and for specific technical points (correction for basis set superposition error, role of the extension of the basis sets, and levels of excitation considered in the treatment of the electronic correlation) in a specialized paper (Pauzat & Ellinger 2007).

Consequently, only the results the most pertinent to the present study, i.e., those obtained at the post Hartree-Fock CCSD-T level of theory using the cc-pVQZ extended basis set are reported here. The outline of the computational procedure can be briefly summarized as follows:

1. Optimization of all stationary points (minima and transition states) and verification of their stability conditions through vibrational analysis.
2. Reconstruction of the potential energy surface around the minima by means of the counterpoise method (Boys & Bernardi 1970) in order to correct for the artifact known as basis set superposition error (BSSE) and notably large for weakly bound complexes.
3. Calculation of the rotational constants B$_r$.
4. Calculation of the infrared spectra within the harmonic approximation and scaling of the frequencies relative to the hydrogenated fragment to account for inharmonic effects and incompleteness in the basis set. No rovibrational corrections are evaluated.

All calculations were performed using methods and basis sets as implemented in the Gaussian package.$^3$

2.1. Structure and Stability of XH$_3^+$ Complexes

The major result of this theoretical study is that all XH$_3^+$ are stable with respect to dissociation. An important point to be mentioned is the gradual evolution of the complex (Fig. 1) that changes from a noble gas atom interacting with an almost unchanged H$_3^+$ ion (I) to a protonated noble gas slightly elongated by interaction with a neutral H$_2$ (II). It is illustrated by the self-explanatory Table 1 in which the geometries of the complexes together with those of the constituting fragments are reported.

$^3$ Gaussian 03 Quantum Chemistry package, Gaussian Inc., Pittsburg 2004.
From an energetic point of view, two dissociation mechanisms are relevant to this study, namely

\[ \text{XH}_3^+ \rightarrow X + H_3^+ \]  \hspace{1cm} (1)
\[ \text{XH}_3^+ \rightarrow \text{XH}^+ + H_2 \]  \hspace{1cm} (2)

The values listed in Table 2 show that all complexes are stable with respect to either dissociation routes, which suggests that \( \text{H}_3^+ \) could possibly act as a sink for noble gases. Looking in more details at dissociation energies \( D_e \), it can be seen that the family of the noble gases splits in two. The first two complexes with Ne and Ar dissociate according to reaction (1) while the last two complexes with Kr and Xe follow reaction (2). It is a direct consequence of the relative order of the proton affinity (PA) of the noble gases with respect to molecular hydrogen (Dixon & Lias 1984; Klein & Rosmus 1984): PA (Ne) values in parentheses).

In view of the available experiments, comparison of binding energies can essentially be done for argon. From spectroscopic studies, Bogey et al. (1988) were able to estimate \( D_e \) at 6.6 or 9.9 kcal mol\(^{-1}\) according to the shape of the energy potential used to analyze the data while Hiraoka & Mori (1989) proposed a value of \( D_e = 6.69 \text{ kcal mol}^{-1}\) for ArH\(^+_3\) using thermochemistry plots deduced from the mass spectrometry experiments. For neon, the same technique provided an estimation of \( D_e \) at \( \approx 0.4 \text{ kcal mol}^{-1}\). The theoretical values of 7.27 and 0.98 kcal mol\(^{-1}\) obtained at the CCSD(T)/cc-pVQZ level for ArH\(^+_3\) and NeH\(^+_3\), respectively, are both \( \approx 0.6 \text{ kcal mol}^{-1}\) higher than those estimated from mass spectroscopy. The predictions for the other dissociation energies of Table 2 should be equally accurate.

A point also worth mentioning is that H\(^+_3\) is able to trap more than one atom of noble gas, although the binding energies of the second, \( D_e(2) \) and third \( D_e(3) \) atoms are weaker than that of the first one. In the case of argon, the values deduced by Hiraoka & Mori (1989) from the thermochemistry plots \( [D_e(2) = 4.6 \text{ and } D_e(3) = 4.3 \text{ kcal mol}^{-1}] \) and confirmed by Pauzat & Ellinger (2005) at the CCSD/cc-pVQZ level of theory \( [D_e(2) = 3.9 \text{ and } D_e(3) = 3.5 \text{ kcal mol}^{-1}] \) are still large enough to support the hypothesis of multiple trapping.

### 2.2. Stability of \( \text{XH}_3^+ \) Complexes in Presence of Ices

In this section, we explore the stability of \( \text{XH}_3^+ \) complexes in presence of different kind of ices (noble gases trapped in clathrate hydrates structures or in the form of pure condensates) that can be found at low temperature in protoplanetary disks (see § 3.1). It is worthwhile to mention that for other volatiles, for example CO and CO\(_2\), H\(^+_3\) will probably react to form the already known protonated derivatives HCO\(^+\) (Buhl & Snyder 1970) and HOCO\(^+\) (Thaddeus et al. 1981) because of the higher proton affinity of the neutral parents compared to H\(_2\).

The case of H\(_2\)O is more relevant to this study in view of the general clathrates formula: \((\text{H}_2\text{O})_n\). At this point, it should first be noted that the binding energy of noble gases to the water molecule is about an order of magnitude smaller than their binding energy to H\(^+_3\). The case of neon, however, should be considered more carefully since the NeH\(^+_3\) complex may be too weakly bound to resist turbulence even at temperatures below 30 K.

Furthermore, the high proton affinity of H\(_2\)O compared to H\(_2\) (\( \sim 170 \text{ compared to } \sim 101.4 \text{ kcal mol}^{-1}\)) suggests that \( \text{XH}_3^+ \) and H\(_2\)O may not exist together: \( \text{XH}_3^+ \) could react with H\(_2\)O, giving H\(_2\)O\(^+\) + H\(_2\) + X in an exothermic process (between \( \sim 50 \) and \( \sim 70 \text{ kcal mol}^{-1}\) for Ne to Xe). Such an energy released in the clathrate hydrate is an order of magnitude larger than the 5.02 kcal mol\(^{-1}\) binding energy between two water molecules (Tschumper et al. 2002) and about 5 times larger than the cohesion energy of crystalline ice (Casassa et al. 2005). One can assume in these conditions that \( \text{XH}_3^+ \) cannot be sequestrated in clathrates as such. Its destruction could even lead to their erosion through the process detailed above (this phenomenon is currently under investigation).

A second aspect to consider is the cohesion of pure noble gas solids; the values (in kcal mol\(^{-1}\)) known for cfc crystals are

| Complex | X-H\(_X\) (Å) | H\(_X\)-H (Å) | H-H (Å) |
|---------|-------------|--------------|--------|
| NeH\(_3^+\) | 1.7939 | 0.8821 | 0.8607 |
| Ne\(^+\) | 0.9886 (0.9912\(^a\)) | ... | ... |
| ArH\(_3^+\) | 1.8306 | 0.9342 | 0.8280 |
| KrH\(_3^+\) | 1.2800 (1.2804\(^a\)) | ... | ... |
| Kr\(^+\) | 1.7236 | 1.0575 | 0.7954 |
| XeH\(_3^+\) | 1.4155 (1.4212\(^a\)) | ... | ... |
| Xe\(^+\) | 1.6451 | 1.5304 | 0.7581 |
| H\(_3^+\) | 1.5909 (1.6028\(^a\)) | ... | ... |
| H\(^+\) | ... | 0.8737 | 0.8737 (0.8734\(^a\)) |
| H\(_2\) | ... | ... | 0.7416 (0.7414\(^a\)) |

Note.—Optimized geometries (Å) of \( \text{XH}_3^+ \) (\( \text{X} = \text{Ne} \) to \( \text{Xe} \)) after full correction of BSSE together with those of the constituting fragments (experimental values in parentheses).

\(^{a}\) Ram et al. (1985).
\(^{b}\) Johns (1984).
\(^{c}\) Warner et al. (1984).
\(^{d}\) Rogers et al. (1987).
\(^{e}\) Cencek et al. (1998).
\(^{f}\) Huber & Herzberg (1979).
4.6 (Ne), 1.84 (Ar), 2.67 (Kr), and 3.91 (Xe). Compared to
the binding energies of X to \( \text{H}_2^+ \) reported in Table 2, they are
4–6 times smaller, implying the idea that noble gases will remain
in the form of \( \text{XH}_2^+ \) complexes. Another point to be mentioned at
this level is the fact that the binding energy of \( \text{XH}_2^+ \) is also more
than an order of magnitude larger than that of any XX noble gas
dimmer.

3. IMPLICATIONS FOR THE OUTER SOLAR
SYSTEM COMPOSITION

In this section, we explore the possibility that the mechanism
described previously, namely trapping of noble gases by the \( \text{H}_2^+ \)
ions, is responsible for the deficiency of Ar, Xe, and Kr observed
in Titan and possibly in comets, as suggested in § 1. The idea is
that ices entering the “vaporization line” at about 30 AU sub-
limate in the early and hot nebula and later form clathrate hydrates
deficient in noble gases, these latter being sequestered by the
\( \text{H}_2^+ \) ion at higher heliocentric distances than \(-5\) AU (the current
Jupiter orbit, neglecting the possibility of migration during its for-
mation in the nebula). A critical point in this picture is the \( \text{H}_2^+ \)
abundance across the inner 30 AU of the solar nebula at the time
of the planetesimals formation. We address these two aspects in
the next two paragraphs. The last two paragraphs discuss the pos-
sible consequences when the theory is applied to Titan and the
comets’ formation respectively.

3.1. Formation of Planetesimals and the Influence
of \( \text{H}_2^+ \) Trapping

Formation scenarios of the protoplanetary nebula invoke two
main reservoirs of ices that took part in the production of icy plan-
etesimals. One reservoir, located within 30 AU of the Sun, contains
ices (mostly water ice) originating from the interstellar medium
(ISM), which due to their proximity to the Sun are initially vapor-
ized (Chick & Cassen 1997). With time, the decrease of tempera-
ture and pressure conditions allowed the water in this reservoir
to condense at \(-150\) K in the form of microscopic crystalline
ice (Kouchi et al. 1994). It is then considered that most other
volatile species were trapped as clathrate hydrates, and eventu-
al pure condensates,4 within 30 AU in the outer solar nebula
(Mousis et al. 2000). The other reservoir, located at larger helio-
centric distances, is composed of ices originating from ISM that
did not vaporize when entering the disk. In this reservoir, water ice
was essentially in the amorphous form and the other volatiles
remained trapped in the amorphous matrix (Owen et al. 1999;
Notesco & Bar-Nun 2005). Consequently, icy planetesimals for-
med interior to 30 AU mainly agglomerated from clathrate
hydrates, while in contrast those produced at higher heliocentric
distances (i.e., in the cold outer part of the solar nebula) are ex-
pected to be formed from primordial amorphous ice originating
from ISM and containing noble gases trapped in the amorphous
water ice matrix.

In order to quantify this effect, we computed the ice abundance
in the cooling solar nebula following the model described in
Mousis et al. (2006), with and without the trapping of noble gases
by \( \text{H}_2^+ \). The composition of ices formed within 30 AU in the solar
nebula is determined using the clathrate hydrate trapping theory
as presented, e.g., in Mousis et al. (2006). With time, the decrease
of temperature and pressure conditions in the solar nebula leads
to the trapping of volatile species as hydrates or clathrate hydrates,
as illustrated in Figure 2. The trapping of volatiles is calculated
using the stability curves of hydrates or clathrate hydrates and the
evolutionary tracks of temperature and pressure (hereafter cooling
curves) at given heliocentric distances, taken from a solar nebula
model (Alibert et al. 2005). The cooling curves intercept the sta-
bility curves of the different ices at some given temperature and
pressure conditions. For each considered ice, the domain of sta-
bility is the region located below its corresponding stability curve.
As a result, in gas-phase conditions where the presence of \( \text{H}_2^+ \)
is neglected, all major species,5 including Ar, Kr, and Xe, are pre-
sumed to be trapped in the form of hydrates or clathrate hydrates
during the cooling of the solar nebula (provided the abundance
of water is large enough).

On the other hand, assuming that Ar, Kr, and Xe have been
sequestrated by \( \text{H}_2^+ \) in the form of \( \text{XH}_2^+ \) complexes in the gas
phase, and following the considerations developed in § 2.2, they
are expected to have been preserved from the trapping as clathrate
hydrates by crystalline water at low temperature and pressure con-
ditions in the nebula. As a result, icy planetesimals formed in the
presence of a large concentration of \( \text{H}_2^+ \) in the gas phase may not
contain Ar, Kr, and Xe, albeit they trapped most of the other
major volatile species.

3.2. The \( \text{H}_2^+ \) Abundance in the Inner 30 AU

The ionization structure of the inner 30 AU protoplanetary
disks, which are supposed to be a good description of the solar
nebula at the time of the planetesimal formation, have been com-
puted by a few authors, giving somewhat different results (see,
e.g., the discussion in Markwick et al. 2002). The most recent
computations by Semenov et al. (2004) predict ionization fractions
between \( 1 \times 10^{-15} \) and \( 1 \times 10^{-10} \) in the plane of the disk, where
the only source of ionization is the cosmic rays. In this region the
positive charge carrier is \( \text{HCO}^+ \), and \( \text{H}_2^+ \) is somewhat lower in
abundance. Although the overall ionization degree is a rather com-
plex problem to solve, the abundance of \( \text{H}_2^+ \) in the inner 30 AU
region is relatively simple to compute, in principle. In fact, \( \text{H}_2^+ \)
is formed by the ionization of \( \text{H}_2 \) from energetic (\( \leq 100 \) MeV) par-
ticles, such as those in the cosmic rays or those emitted by the
young Sun, at a rate \( \zeta_{\text{ep}} \), and destroyed by the reactions with the
most abundant molecules, namely CO and H2O, at a rate \( k_{\text{CO}} \)
and \( k_{\text{H}_2\text{O}} \), respectively. At steady state, the formation and de-
struction rates balance, and this provides a relation between the
\( \text{H}_2^+ \) abundance (\( x_{\text{H}_2^+} \)) and the CO and H2O abundances
(\( x_{\text{CO}} \) and \( x_{\text{H}_2\text{O}} \)) with respect to \( \text{H}_2 \), the \( \text{H}_2 \) density \( n_{\text{H}_2} \), and the \( \text{H}_2 \) ioniza-
tion rate \( \zeta_{\text{ep}} \), as follows:

\[
x_{\text{H}_2^+} = \frac{\zeta_{\text{ep}}}{n_{\text{H}_2}(k_{\text{CO}}x_{\text{CO}} + k_{\text{H}_2\text{O}}x_{\text{H}_2\text{O}})}.
\]

Note that in the inner 30 AU, the temperature in the midplane is
considered larger than the temperature required for the condensa-
tion of ices so that the abundances of CO and H2O are set equal to
\( 1 \times 10^{-4} \), namely approximately their gas-phase abundances
in the solar nebula (Mousis et al. 2006). The reaction rates \( k_{\text{CO}} \)
and \( k_{\text{H}_2\text{O}} \) are respectively \( 1.7 \times 10^{-9} \) and \( 5.9 \times 10^{-9} \text{ cm}^3\text{s}^{-1} \) (from the
UMIST database).6

4 It is usually assumed that the local abundance of water is high enough to
trap all the major volatiles in the form of clathrate hydrates in the outer solar nebula
(Alibert et al. 2005; Mousis et al. 2006). In the contrary case, remaining volatiles
that have not been trapped by water form pure condensates at lower temperatures
in the nebula (\(-20–30\) K).

5 Except the unique cases of CO2 and Ne. CO2 crystallizes as a pure con-
densate prior to being trapped by water to form a clathrate hydrate in the solar
nebula (Alibert et al. 2005; Mousis et al. 2006) and Ne is a poor clathrate hydrate
former (Lunine & Stevenson 1985).

6 See http://www.rate99.co.uk.
Equation (3) shows that the H$_3^+$ abundance is inversely proportional to the H$_2$ density and linearly depends on the ionization rate $\zeta_{ep}$. We emphasize that equation (3) only applies to the disk midplane where the electronic abundance is less than $\sim 5 \times 10^{-7}$; otherwise the H$_3^+$ recombination would be a major route of H$_3^+$ destruction, lowering the H$_3^+$ abundance. As mentioned above, there are at least two known sources of H$_3^+$ formation from the H$_2$ ionization: the cosmic rays and the energetic particles emitted from the young Sun. A third source could be a nearby supernova that exploded during the solar system formation (e.g., Ouellette et al. [2007] for a recent discussion of this hypothesis). Note that X-rays, although copiously emitted from the young Sun, do not significantly affect the ionization in the midplane, as they cannot penetrate so deeply (e.g., Glassgold et al. 1997). In the following, we will discuss the first three sources of H$_3^+$ formation.

The cosmic-ray ionization rate has been estimated in different regions, giving somewhat different results. A lower limit has been estimated to be around few times $10^{-17}$ s$^{-1}$ (e.g., Webber 1998), whereas the upper limit is around $1 \times 10^{-15}$ s$^{-1}$ (Payne et al. 1984). Here we adopt the high value to consider the most optimistic case for the H$_3^+$ abundance. Figure 3 shows the computed H$_3^+$ abundance with respect to H$_2$ in the disk midplane as a function of the distance from the center for such high value. In these computations, we have used the structure of a 0.001 $M_\odot$ disk surrounding a 0.5 $M_\odot$ star with a luminosity of 0.5 $L_\odot$ and a temperature $T_{\text{eff}}$ of 3630 K (namely a typical T Tau star, believed to be a good representative of the Sun in the early phases of the solar system formation). The average grain size is assumed to be 1 $\mu$m, namely dust that started to coagulate on the disk midplane. For reference, such a disk has a H$_2$ density of $\sim 10^6$ cm$^{-3}$ at around 30 AU and its physical structure has been reported in Ceccarelli & Dominik (2005). Figure 3 shows that the H$_3^+$ production by the cosmic rays only is (at least) three orders of magnitude lower than the Kr solar abundance reported in Table 3.

That other sources of energetic particles existed in the early phase of the solar system formation is testified by the presence of radionuclides with half-lives less than 1 Myr in the calcium-aluminum–rich inclusions (CAIs) in meteorites (see for example the recent review by McKeegan & Davis 2005). This includes light atoms, such as $^{10}$Be and heavy atoms, such as $^{60}$Fe. These two extremes, $^{10}$Be and $^{60}$Fe, imply two different origins: an inner and an external production of energetic particles, respectively. By the inner origin we mean irradiation of energetic particles

![Figure 3](image-url)
from the young Sun (e.g., Lee et al. 1998; Gounelle et al. 2001, 2006), whereas by external origin we mean the presence of a nearby supernova during the solar system formation (e.g., Busso et al. 2003; Tachibana & Huss 2003). The other short-lived radionuclides (e.g., $^{26}$Al, $^{36}$Ca, and $^{41}$Ca) can be produced by models considering both origins with a different “mix” (see for example the discussion in Gounelle et al. 2006). The analysis of the observed X-rays luminosities and spectra in young stellar objects implies a flux of energetic particles about $1 \times 10^3$ times that of the Sun today (Feigelson et al. 2002), with flares exceeding $1 \times 10^3$ times more (Leya et al. 2003). However, the exact value of the flux of energetic particles through the disk as well as its spectrum and the influence on the disk ionization and chemical composition are highly uncertain. For this reason, instead of trying to model the two scenarios, the inner and external irradiation of energetic particles respectively, we computed the minimum enhancement of energetic particles flux with respect to the cosmic rays in order to make the $H_2$ abundance larger than the krypton abundance. This is the minimum to make $H_2$ able to trap krypton, assuming that the process has an efficiency close to unity. The results of these computations are shown in Figure 3: the flux of energetic particles has to be at least three orders of magnitude larger than the cosmic-ray flux. If these conditions apply to the young Sun—which may not be unreasonable—trapping of krypton (and even more xenon) by $H_2$ might be an efficient mechanism able to explain the deficiency of these two elements, and to a lower extent that of $Ar$ in some bodies of the outer solar system. In the following, we will assume that this is the case and explore this possibility in more detail.

3.3. Interpreting the Noble Gases Deficiency in Titan

Several different scenarios interpreting the deficiency of Titan’s atmosphere in primordial noble gases have been recently proposed. These scenarios can be regrouped in two different approaches. The first category of scenarios postulates that Titan initially incorporated primordial noble gases during its formation but that subsequent processes prevented their detection in its atmosphere. For example, Jacovi et al. (2005) suggested that the aerosols observed in Titan’s atmosphere may have cleared its content of noble gases, assuming they were produced from the aggregation of polymers. Alternatively, Osegovic & Max (2005) proposed that clathrate hydrates formed from hydrocarbons and nitrogen on the surface of Titan are possibly a sink for primordial Ar, Kr, and Xe absent from its atmosphere. On the other hand, Thomas et al. (2007) reinvestigated the conclusions of Osegovic & Max (2005) and demonstrated that Ar is a poor clathrate hydrate former on the surface of Titan, in contrast to Kr and Xe. These authors then concluded that an alternative scenario must be proposed in order to explain the Ar deficiency in the atmosphere of Titan. The second category of scenarios, which is favored in this work, postulates that the noble gases deficiency in Titan’s atmosphere results from processes that occurred either during its accretion or during the formation of its planetesimals. These scenarios have the advantage in explaining in a self-consistent way the current characteristics of Titan’s atmosphere and not only its apparent deficiency in noble gases. In this way, in order to interpret the observed properties of Titan’s atmosphere, ignoring the possibility of formation of $XH_2$ complexes in the gas phase, Alibert & Mousis (2007) proposed that its building blocks were produced in Saturn’s feeding zone and/or in its surrounding subdisk. They then argued that during their formation these planetesimals would have incorporated all the main volatile compounds, including noble gases, by following the clathration sequence described in Figure 2. During their migration within the subnebula, the planetesimals that led to the formation of Titan would have suffered a partial vaporization, due to the higher temperature and pressure conditions encountered in the gas phase on their pathway, thus leading to their impoverishment in clathrate hydrates whose dissociation temperatures are the lowest. As a result, Titan would be formed from planetesimals deficient in CO and in noble gases, in agreement with its observed properties.

Following the scenario proposed by Alibert & Mousis (2007), and similarly to Jupiter, the abundances of noble gases within Saturn’s atmosphere should be over solar since the giant planet accreted volatile-rich planetesimals produced in its feeding zone. Table 4 reproduces the enrichment in volatiles predicted in Saturn by Mousis et al. (2006) for a nominal solar nebula gas-phase composition ($CO_2:CO:CH_4 = 30:10:1$ and $N_2:NH_3 = 1$), in agreement with the scenario of Alibert & Mousis (2007), assuming that the amount of available crystalline water was sufficient to trap all the main volatile species.

On the other hand, if the sequestration of noble gases by $H_2$ was efficient at the heliocentric distance of 10 AU in the solar nebula gas phase, Ar, Kr, and Xe should be poorly trapped in icy

### TABLE 3

**Protosolar Abundances of Noble Gases**

| Species | Abundance |
|---------|-----------|
| Ar      | $3.02 \times 10^{-6}$ |
| Kr      | $3.82 \times 10^{-9}$ |
| Xe      | $3.72 \times 10^{-10}$ |

**Note:** Protosolar abundances (molar mixing ratio with respect to $H_2$) of noble gases of interest (from Grevesse et al. 2005).

### TABLE 4

**Observed and Calculated Carbon Enrichment in Saturn**

| Species | Observed | Mousis et al. (2006) | This Work |
|---------|----------|----------------------|-----------|
| C       | 8.8 ± 1.7 | 7.1                  | 7.1       |
| N       | ...      | 6.5                  | 6.5       |
| S       | ...      | 5.6                  | 5.5       |
| Ar      | ...      | 5.1                  | 1 to 5.1* |
| Kr      | ...      | 5.6                  | 1         |
| Xe      | ...      | 6.7                  | 1         |

**Note:** Observed carbon enrichment in Saturn (Flasar et al. 2005), and calculated enrichments in volatiles assuming a full clathration of noble gases by crystalline water (Mousis et al. 2006) or their full sequestration in the form of $XH_2$ complexes in the solar nebula gas phase (this work). Enrichments are calculated using the nominal gas-phase conditions given in Mousis et al. (2006; $CO_2:CO:CH_4 = 30:10:1$ and $N_2:NH_3 = 1$) and are calibrated on the observed carbon enrichment.

* As a function of the assumed argon trapping scenario (see text).

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7 It is important to note that even if the $H_2$ abundance is postulated high enough in the disk to allow an efficient trapping of argon (at least $10^{-8}$ times the $H_2$ abundance), then the dissociative reaction $H_3^+ + e^- \rightarrow H_2 + H$, with a reaction rate of $\approx 10^{-2} \text{ cm}^3 \text{s}^{-1}$, becomes competitive. This can then further deplete $H_2$ in the disk and lead to the breakup of $Ar-H_2$ if its recombination rate is similar.
planetaryimals formed in this location. This hypothesis is fully compatible with the mechanism proposed by Alibert & Mousis (2007), namely a partial vaporization of its building blocks during their migration within the subnebula, which is required to explain at least the deficiency in CO in its atmosphere. In order to discriminate which of the two processes was likely at 10 AU in the solar nebula (sequestration of noble gases by H$_3^+$ or their full clathration by crystalline water), we predict that abundances of Kr and Xe should remain solar within Saturn’s atmosphere (see Table 4), if the formation of XH$_3^+$ complexes (with X = Kr or Xe) was efficient in the gas phase. Indeed, since these XH$_3^+$ complexes would stay coupled with the gas phase their molar mixing ratios relative to hydrogen should still remain constant, in particular within Saturn’s envelope which results from the accretion of gas and gas-coupled solids from the solar nebula.

The case of Ar is less straightforward since its solar abundance is at least 3 orders of magnitude higher than those of Kr and Xe (see Table 3). Following our discussion in § 3.2, requiring a H$_3^+$ abundance high enough to trap efficiently Ar in the solar nebula is probably unlikely. This is in agreement with the detection by Huygens of only $^{36}$Ar, among the primordial noble gases, in Titan. On the other hand, the Ar subsonal abundance measured in the satellite’s atmosphere suggests that it has been only partially trapped in planetesimals produced in Saturn’s feeding zone. As a result, we estimate that the corresponding Ar abundance within Saturn’s atmosphere is enclosed by two extreme values: a solar abundance and the oversolar prediction made by Mousis et al. (2006) (see Table 4). The inner and upper values correspond respectively to the full sequestration of Ar by H$_3^+$ in the solar nebula gas phase and a full trapping of the noble gas in the form of clathrate hydrate in the forming planetesimals.

3.4. Implications for Comets

The origin of comets in the solar nebula is still poorly constrained: Edgeworth-Kuiper belt comets are presumed to be formed at a distance further from 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. As a function of the considered formation scenario (see Horner et al. [2007] for a comprehensive review), comets may have formed either from clathrate hydrates in the initially hot part of the solar nebula (where the local gas temperature was initially high enough to vaporize the entering ices) or from amorphous ice at heliocentric distances higher than 30 AU. This implies that the content of comets in noble gases may vary as a function of their formation region. From the scenario proposed in § 3.1 and following the argumentation developed in the case of Ar in § 3.3, we propose that comets formed within the heliocentric distance of 30 AU should be depleted efficiently in Kr and Xe, and only partly in Ar, in agreement with the marginal detection of this species in comet C/1995 O1 Hale-Bopp by Stern et al. (2000). On the other hand, comets formed at higher heliocentric distances from an initially amorphous ice mixture should contain Ar, Kr, and Xe. In that context, subsequent measurements of noble gases abundances in comets should help to constrain the origin of the reservoirs of cometary bodies.

4. SUMMARY AND CONCLUSIONS

In this work, we have studied the efficiency of the noble gases sequestration by the H$_3^+$ ion in the form of XH$_3^+$ complexes (with X = argon, krypton, xenon, or neon) in gas-phase conditions similar to those encountered during the cooling of protoplanetary disks, and especially at the epoch of the planetesimals formation. We have calculated that the binding energy of noble gases to the water molecule is ~one order of magnitude lower than their binding energy to H$_3^+$, meaning that the XH$_3^+$ complex is more stable than a clathrate hydrate of species X. Similarly, we have shown that the binding energy of XH$_3^+$ complexes is more than one order of magnitude higher than that of pure condensates of noble gases. This implies that, provided H$_3^+$ is abundant enough, once argon, krypton, or xenon are sequestrated in the form of XH$_3^+$ complexes in the gas phase, they remain in this structure rather than forming ices during the cooling of protoplanetary disks. The case of neon should be considered more carefully since the NeH$_3^+$ complex may be too weakly bound to resist turbulence even at low temperatures in the nebula.

On the other hand, we have calculated that the abundance of H$_3^+$ in the 3–30 AU midplane region of disks is about $1 \times 10^{-12}$ at most, implying a poor noble gas sequestration (the abundances of xenon, krypton, and argon hold between $10^{-10}$ and $10^{-6}$). However, we have stressed that there is evidence that the solar nebula has been exposed to other sources of energetic particles. This is testified to by the presence of radionuclides with half-lives less than 1 Myr in the calcium-aluminum–rich inclusions in meteorites which could imply two different origins: an inner and an external production of energetic particles, respectively. By inner origin we mean irradiation of energetic particles from the young Sun, whereas by external origin we mean the presence of a nearby supernova during the solar system formation. If this hypothesis is correct, one associated effect might be an augmentation of the cosmic ionization rate in the disk by several orders of magnitude. From these statements, given the noble gas abundances in the solar nebula, Kr and Xe could be relatively easily trapped in regions where H$_3^+$ is at least ~$1 \times 10^{-9}$ times the H$_2$. Argon, with its higher abundance, may be more difficult to trap and requires a minimum H$_3^+$ abundance of ~$1 \times 10^{-6}$ times the H$_2$.

Taking into account these considerations, we have assumed that the H$_3^+$ abundance in the 10–30 AU region of the solar nebula was indeed effectively large enough to make possible at least the efficient trapping of xenon and krypton, and limited trapping of argon. Therefore, icy planetesimals formed from ices crystalized within this distance range in the solar nebula should be impoverished in krypton and xenon. This scenario allowed us to propose that the apparent deficiency of Titan’s atmosphere in noble gases can be explained if the satellite was formed from such solids. Since Titan is expected to be made from the same building blocks as those accreted by Saturn, the abundances of at least krypton and xenon should be solar in the giant planet. The case of argon is less straightforward since its isotope $^{36}$Ar is the only primordial noble gas detected (in subsolar abundance ratio) in Titan’s atmosphere. This is in agreement with the idea that argon has been sequestrated only partially by H$_3^+$ in the solar nebula.

Moreover, the proposed scenario allowed us to argue that comets formed from crystalline water ice in the outer solar nebula should be deficient in krypton and xenon, and to a lower extent in argon, in agreement with some recent observations. Following our scenario, we also predict that the abundances of Kr and Xe in Uranus and Neptune should be solar, provided that the two planets have accreted planetesimals aggglomated from ices crystalized in the solar nebula. A more direct way of testing this scenario would be to measure the abundances of noble gases in a significant sample of comets. Some measurements will be obtained from planned space missions toward Jupiter family comets, such as the Rosetta mission, whose target is the comet 67P/Churyumov-Gerasimenko. However, the determination of their composition could be ambiguous because such comets may have been initially formed from amorphous ice originating from the
presolar cloud and may not be relevant for the processes that occurred between 10 and 30 AU in the solar nebula. We note that in order to make our $\text{H}_3^+$ sequestration scenario compatible with the noble gases oversolar abundances measured within Jupiter atmosphere by the Galileo probe it is necessary to assume that the ion abundance was very low in the inner solar nebula up to the formation distance of the giant planet at least. This hypothesis needs to be tested in the near future.

Finally, we note that at temperatures greater than ~150 K in the solar nebula the capability of $\text{H}_3^+$ to trap the noble gases can be limited. Indeed, due to the different proton hopping reactions, such as those with $\text{H}_2\text{O}$, the lifetime of the $\text{XH}_3^+$ complex is very short (of the order of $10^3$ s) compared with the time taken to form ices in the disk (several hundreds of thousand of years). As a result, in these temperature conditions the sequestration of the noble gases by $\text{H}_3^+$ is probably not stable for sufficiently long periods of time against their re-release by proton hopping destruction for this to be truly effective. On the other hand, the lifetime of the $\text{XH}_3^+$ complex is expected to significantly increase once the condensation temperatures of the different species involved in its destruction are reached in the disk, provided that the noble gases still remain in the gas phase. For example, at temperatures lower than ~150 K in the outer nebula water ice is formed and the abundance of $\text{H}_2\text{O}$ molecule converges toward zero in the gas phase. This implies that the destruction rate of $\text{XH}_3^+$ by $\text{H}_2\text{O}$ becomes insignificant. In order to be validated, these considerations will require the development of a hybrid thermochemical and chemical-kinetic model of the protosolar nebula.

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APPENDIX A

THEORETICAL SPECTRA

Every astrochemical model is based on observations or nonobservations of chemical species. In the present case observations of $\text{H}_3^+$ and $\text{H}_2\text{D}^+$ provided the incentive for this study. Now, observations of $\text{XH}^+$ and $\text{XH}_3^+$ complexes would be of utmost interest. At that point, it should be recalled that identification of a molecule in space relies on a perfect match between the observed lines and the spectrum of the same species in the laboratory. However, it is difficult to realize, especially for the type of unstable species we are dealing with. Generally indeed, unstable species are formed in the experiments together with a number of other molecules that may be isomers or even compounds with completely different chemical formulas. It is the purpose of the numerical simulations reported below to propose theoretical spectra that are precise enough to make possible an interpretation of the laboratory experiments to come and extract the spectra of the target molecules from the mixture of experimental values for comparison with further spatial observations.

A1. ROTATIONAL CONSTANTS

$\text{ArD}_3^+$ is the only complex for which spectroscopic data are available ($\text{ArH}_3^+$ is poorly characterized by a few lines). One has to keep in mind that rotational constants are not direct products of the experiments; like $D_e$, they are extracted from the very complex spectra of the clusters by searching for the best possible match between the measured spectra and the one deduced from phenomenological models. Three of those models, hereafter referred to as the rigid model (RM), semirigid model (SRM), and flexible model (FLM), were successively used. In these models the $\text{H}_3^+$ fragment was first constrained to a frozen equilateral triangle, then allowed to freely rotate and finally relax during rotation. Distances were then adjusted to reproduce the experimental data to the best possible extent.

The $A$ constant of $\text{ArH}_3^+$ was first estimated at $A = 1309.2$ GHz by scaling of the $\text{ArD}_3^+$ value according to the H/D ratio of the atomic masses within the RM approximation (Bogey et al. 1987); $B = 30.9623$ GHz and $C = 30.1378$ GHz were determined subsequently. Spectroscopic data on mixed H/D species made it possible to implement the SRM and FLM (Bogey et al. 1988). Adjusting the constants in the SRM gives the following set of experimental values: $A = 1310$ GHz, $B = 30.811$ GHz, $C = 30.155$ GHz. The FLM leads to a second set of experimental values: $A = 1490$ GHz, $B = 31.411$ GHz, $C = 30.750$ GHz.

It can be seen from Table 5 that the rotational constant $A$ corresponding to rotation about the $C_3$ axis of $\text{ArH}_3^+$ deduced from the FLM description is within ~2% of the theoretical value. The present quantum simulation shows that the RM and SRM approximations are clearly inadequate for determining the $A$ constant since the ~12% error in the RM and SRM descriptions is much larger than the maximum error expected for the type of CCSD(T) calculations performed here. In these conditions it is clear that the quality of the results of the quantum calculation is at least of equal quality to that of the so-called experimental values deduced from the various spectroscopic models. The values predicted for the cluster series reported in Table 5 should be accurate enough to stimulate new

| Complex   | $A$   | $B$   | $C$   | $\mu$ |
|-----------|-------|-------|-------|-------|
| NeH$_3^+$ | 1353.9| 35.147| 34.258| 7.9   |
| ArH$_3^+$ | 1463.0| 30.607| 29.979| 7.4   |
| KrH$_3^+$ | 1585.1| 29.502| 28.963| 6.5   |
| XeH$_3^+$ | 1745.0| 22.997| 22.698| 2.6   |

Note.—Rotational constants (GHz) and dipole moment (Debye) of $\text{XH}_3^+$ ($X = \text{Ne to Xe}$).
laboratory experiments and possible observations in the future. Apart from XeH$_2^+$, whose dipole moment ($\mu = 2.6$ D) is the weakest of the series, all other complexes with dipole moments in the range of $\sim 6$–8 D should be reasonable targets for detection by microwave spectroscopy.

A2. INFRARED SIGNATURES

The harmonic vibrational frequencies of XH$_2^+$ ($X = \text{Ne to Xe}$) are reported in Table 6 together with the corresponding absolute intensities. These best estimated frequencies were deduced from the CCSD(T)/cc-pVQZ level of theory using an appropriate scaling procedure.

The point to consider is that the spectrum of any of these molecules is clearly separated into two domains. At high frequencies one has the internal vibrations of each fragment; at low frequencies one finds the inter-fragment vibrations corresponding to the relative motions of the two interacting species. Whenever related experimental data are available, it is a well-admitted procedure to use the ratio of the calculated to observed frequencies for all vibrations higher than 2000 cm$^{-1}$ as a scaling factor to derive a best estimate of the frequencies to look at. In the present case, the frequencies of the individual fragments H$_2^+$ (Oka 1980; Ketterle et al. 1989) and H$_2$ (Stoicheff 1957; Huber & Herzberg 1979) are well known.

The scaling factors deduced from these values are then applied to the corresponding frequencies in the complexes. Not scaling lower frequencies is entirely justified in view of the raw spectrum calculated for ArD$_2^+$ (Pauzat & Ellinger 2005): $\nu_1 = 2542; \nu_2 = 1643; \nu_3 = 1504; \nu_4 = 570; \nu_5 = 437; \nu_6 = 351$ (values in cm$^{-1}$), for which the value obtained for the $\nu_6$ stretching frequency is in complete agreement with the 352 cm$^{-1}$ obtained for the only experimental frequency that could be estimated from the centrifugal distortion in the ArD$_2^+$ experiment (Bogey et al. 1988). The changes in the frequencies from the ion in isolation confirm the structural changes of the complexes when going from Ne to Xe. The most intense bands should be good candidates for more studies in the laboratory in view of possible application in space.

TABLE 6

| Frequency | Ne   | Ar   | Kr   | Xe   |
|-----------|------|------|------|------|
| $\nu_1$   | 3185 | 3311 | 3515 | 4181 |
| $\nu_2$   | 2484 | 2104 | 1791 | 1701 |
| $\nu_3$   | 2463 | 1925 | 1273 | 804  |
| $\nu_4$   | 429  | 803  | 919  | 579  |
| $\nu_5$   | 315  | 614  | 727  | 513  |
| $\nu_6$   | 314  | 478  | 618  | 404  |

**Note.**—IR frequencies (cm$^{-1}$) for XH$_2^+$ ($X = \text{Ne to Xe}$). Italic values correspond to absolute intensities (km mol$^{-1}$) as obtained at the CCSD/cc-pVQZ level.

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