

Alpha particle chemistry. On the formation of stable complexes between He^{2+} and other simple species: implications for atmospheric and interstellar chemistry

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Abstract The possibility that stable complexes may be formed between alpha particles (He^{2+}) and small molecules is investigated using QCISD quantum mechanical calculations. Implications for their presence in the terrestrial atmosphere and/or in interstellar space are discussed.

Keywords Alpha particle chemistry · Atmospheric chemistry · Interstellar chemistry · QCISD

Introduction

Radioactivity was first discovered by the French scientist Henri Becquerel in 1896 [1]. Not long after, the identification of multiple types of emanations was made, including experimental identification of the alpha particle as a helium nucleus, He^{2+} [2, 3].

The ultimate fate of terrestrial alpha particle decay is the formation of helium gas, as alpha particle decay is ultimately a charge-conserved process. However, it seems likely that the alpha particle does not extract two electrons from its own parent atom: indeed, the very existence of cloud and bubble chambers depends on the ability of the charged particle to ionize the molecules it passes through via collision, and many an induced nuclear reaction is dependent on the bombarding particles being doubly

ionized rather than being neutral helium atoms. Thus, it seems clear that the alpha particle enjoys a finite lifetime as a 2+-charged species.

The situation is more obvious in rarefied environments like interstellar space, where matter density ranges from 0.1 to 1,000 particles per cubic centimeter of space [4]. Unless an alpha particle (a minor component of the solar wind [5]) were to take two electrons from its parent atom, the chances of finding another species from which to take an electron are remote compared to the terrestrial atmosphere. Over time, however, the kinetic energy of an alpha particle should decrease as the number of interparticle collisions increases.

If the alpha particle does indeed have a finite lifetime, and if the frequency of interparticle collisions reduces the kinetic energy of the alpha particle before the electron capture process, the possibility arises that it may form stable complexes with surrounding species. In the terrestrial atmosphere, the potential species includes N_2 , O_2 , Ar, H_2O , and CO_2 ; in the interstellar environment, we can add H and H_2 as possible species with which an alpha particle can make a stable complex. Here, we present a computational study of the possible formation of stable complexes between alpha particles and small particles of atmospheric or interstellar interest.

The obvious answer to the question of what happens when an alpha particle encounters another species is electron transfer. Table 1 lists the ionization energies of all of the species given above as worth consideration, as listed in the NIST Chemistry Webbook [6]. For helium, both ionization energies are listed because of the need to consider the energetics involving He^{2+} . Table 1 clearly shows that the amount of energy liberated when an alpha particle accepts an electron, 54.392 eV, is substantially greater than the first ionization energies of all the other

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Table 1 Ionization energies of the species considered in this study

Species	Ionization energy (in eV)
He(I)	24.587
He(II)	54.392
Ar	15.759
CO ₂	13.777
H	13.598
H ₂	15.426
H ₂ O	12.65
N ₂	15.581
O ₂	12.070

reactant species. Thus, the easy answer is that an alpha particle will extract an electron from another atomic or molecular species.

However, this does not exclude the potential that a weak, short-lived complex might form, and that this molecular complex can have a 2+ charge distributed over the entire species M, or that a singly charged He⁺ might be interacting weakly with some other singly charged M⁺, where M is another atomic or molecular species. Indeed, this possibility has already been considered for HCN and HNC. In 2004, Maksić et al. published a study [7] on the possible existence of HeNCH²⁺ and HeCNH²⁺ using high level ab initio calculations. They described the thermodynamic consequences of comparing He²⁺/M, He⁺/M⁺, and He/M²⁺ systems but also pointed out that kinetic barriers might exist for such complexes, as is the case with the He₂²⁺ system (which has been determined to have a barrier for dissociation of 1.4 eV [8, 9]). Maksić found that the helium ion does attach itself to both HCN and HNC, claiming a “binding energy” of 4,101 kJ mol⁻¹ for the HCNHe²⁺ species. It is not clear if this value is meant to represent the strength of the N–He bond or simply the change in the total electronic energy between HCN and HCNHe²⁺, as it seems to be a fantastic bond energy. In any case, Maksić estimated a potential barrier of approximately 230 kJ mol⁻¹ for the loss of an H⁺ species from the complex, and concluded that the species HCNHe²⁺ and HNCHe²⁺ were stable and, at least at low vibrational states, would exist indefinitely.

As such, there is precedent for studying compounds that contain He²⁺. However, with some exceptions, there has been little work on exploring the possibility of such stable cations. By far the greatest amount of work has been performed on the He/H diatomic system. In some cases, the interest is in identifying the cations that exist in a mixed H/He plasma [10]; other studies recognize that HeH (of any charge) is one of the smallest molecular systems and thus a good target for calculational studies [11]. There is also some work, though not as much, on a substance with the formula HeH₂, though mostly as the theoretical helium dihydride rather than an alpha particle complex with a

hydrogen molecule. Kalinin et al. [12] claimed to detect the He–H₂ van der Waals complex in a cryogenic free jet expansion of H₂/He mixtures. However, we have been unable to find any work on the He²⁺–H₂ ionic complex.

Work on the He/O₂ system is related mostly to semiconductor etching studies. However, Groenenboom and Struniewicz performed a study of the interaction of neutral He with O₂ [13]. They found a global minimum in the three-dimensional potential energy surface at a T-shaped complex, with the distance between the H and O₂ being about 3.17 Å and the energy of interaction a mere 0.33 kJ mol⁻¹. They did not consider a 2⁺ charged species.

The sole report of an interaction between He²⁺ and N₂ is by Cooper and Wilson, who performed a study [14] of the bonding of helium ions with small atoms and molecules of varying overall charge, having a motivation similar to that presented here. Using SCF techniques and an unspecified basis set, they concluded that the HeN₂²⁺ is also a T-shape, with a 92.3° bond angle and a 1.50 Å bond distance to one of the N atoms. They also calculated a dissociation energy relative to He and N₂²⁺ (not, curiously, He²⁺ and N₂) of 360 kJ mol⁻¹—a substantial value.

Studies of He and Ar are limited to mixtures of these two gases. We have not been able to find any work on HeH₂O²⁺ or HeCO₂²⁺. Interestingly, Cooper and Wilson [14] did perform some calculations in which an He⁺ ion is substituted for an H atom in CH₄, NH₃, and H₂O to make isoelectronic molecules.

Here, we present the results of our studies on finding stable structures of an alpha particle interacting with five atmospheric species: N₂, O₂, Ar, H₂O, and CO₂. To make the study more relevant to interstellar substances, we include the interactions of He²⁺ with H and H₂.

Computational details

All calculations were performed using Gaussian 03 [15] on a desktop personal computer. The molecular systems were optimized using the quadratic configuration interaction method [16] with single and double excitations (QCISD) using the 6–311+(2*d*,*p*) basis set. All systems were assumed to have singlet electronic ground states except for the complex with oxygen, which was assumed to have a triplet electronic ground state. Vibrational frequencies were calculated to ensure that the minimum-energy geometries, if found, corresponded to true minima. For substances in which an energy minimum was found, a potential energy scan was performed by first decreasing the X–He bond by 0.5 Å and then determining the energy of the molecule at 0.1 Å radial increments. The depth of the potential energy well was taken to be the bond strength between the alpha particle and the other moiety, and is the energy difference

between the energy minimum and the total energy as the distance approaches infinity.

Results and discussion

Optimized geometries

$H-He^{2+}$

Results of calculations on this system showed that the single electron from the hydrogen atom transferred to the helium ion, followed by the two positive fragments repelling each other. No minimum-energy geometry was obtained.

H_2-He^{2+}

Calculations showed that a system with this formula and charge spontaneously emitted an H^+ ion, and the H^+ and HHe^+ fragments subsequently repelled each other in space. As such, no minimum-energy geometry for a stable H_2-He^{2+} complex was found. The HHe^+ fragment (electronic state $^1\Sigma^+$) optimized with an interatomic radius of 0.7887 Å, an unscaled vibrational frequency of 3161.0 cm^{-1} , and a rotational constant of 1,009.2148 GHz. The optimized interatomic radius is consistent with the value determined by Coxon and Hajigeorgiou [17], who used a 19-parameter fitting to determine an equilibrium bond distance of 1.46 a_0 (0.772 Å) for HeH^+ .

$Ar-He^{2+}$

Figure 1a shows the optimized structure of a stable $Ar-He^{2+}$ ($^1\Sigma^+$) diatomic complex. The complex optimized with a bond distance of 1.399 Å—an eminently reasonable bond distance and close to the bond distance of 1.27 Å for the isoelectronic HCl molecule. [18] Other characteristics of this complex will be discussed below.

O_2-He^{2+}

All calculations with diatomic oxygen interacting with He^{2+} , with O_2 in a triplet electronic state, showed a completely repulsive potential energy surface. The final calculation in the optimization sequence showed the diatomic oxygen molecule and helium ion over ca. 30 Å apart. Furthermore, the computational output indicated that the helium atom had a +1 charge while the diatomic oxygen molecule also had a +1 charge. We conclude from this that, for this system, an electron transfer occurs and the two resulting positively charged fragments repel each other, rather than form a 2+-charged molecular ion.

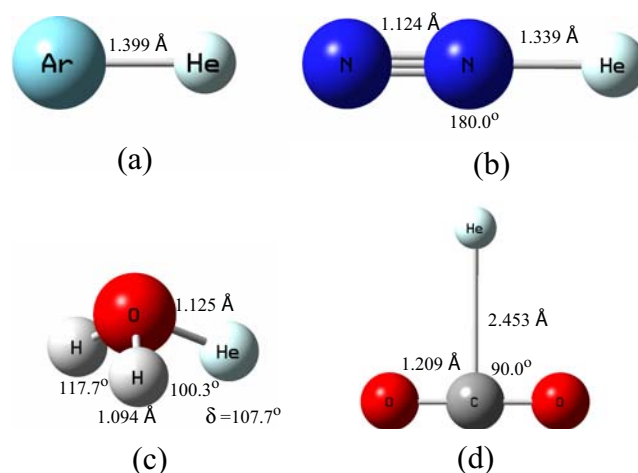


Fig. 1 Optimized geometries of stable alpha particle complexes. **a** $Ar-He^{2+}$ ($^1\Sigma^+$) diatomic complex, **b** N_2He^{2+} complex, **c** H_2OHe^{2+} complex, **d** CO_2He^{2+} complex

N_2-He^{2+}

Figure 1b shows the optimized structure of a stable N_2He^{2+} complex. The complex is linear, with a 1.124 Å N–N bond distance and a 1.339 Å N–He distance. Similar calculations on the N_2 molecule shows an N–N bond distance of 1.098 Å, so the binding of the He^{2+} ion has caused the N–N bond distance to increase by 0.026 Å. The ground electronic state is predicted to be $^1\Sigma$. Other characteristics of this complex will be discussed below.

H_2O-He^{2+}

Figure 1c shows the optimized structure of a stable H_2OHe^{2+} complex, in which the He^{2+} ion is assumed to bond to the oxygen atom. The complex has a plane of symmetry, with two equivalent O–H bonds and the O–He bond lying in the symmetry plane. The O–H bond lengths are 1.094 Å, an increase of 0.135 Å from the O–H bonds in the free water molecule calculated using the same method. The H–O–H bond angle in the complex is 117.7°, again an increase from the 104.8° bond angle calculated for the free water molecule. The O–He bond distance is 1.125 Å, slightly longer than the O–H bond distance, with the O–He bond making a dihedral angle of 108.9° with respect to the H–O–H plane. Other characteristics of this complex are discussed below.

CO_2-He^{2+}

Figure 1d shows the optimized structure of a stable CO_2He^{2+} complex. Curiously, rather than bonding with one of the oxygen atoms, the He nucleus adopts a position midway between the two oxygen atoms, as if it were bonding to the

carbon atom. At 2.453 Å, the bond distance between the helium nucleus and the next closest atom is the longest of all the complexes reported here. This suggests a tenuous bond, at best. The structure of the CO₂ moiety changes little upon complexation, with the O–C–O bond angle staying at 180° and the C–O bond distance increasing slightly, from 1.161 Å in free CO₂ to 1.209 Å in the complex. Other characteristics of this complex are discussed below.

Vibrational frequencies

All four of the stable complexes detailed above had positive vibrational frequencies. Table 2 lists the unscaled values of the calculated frequencies, along with the shift of the similar vibration found in the parent molecule, if available.

The diatomic Ar–He²⁺ complex has a single vibration with a frequency of 1,192.9 cm⁻¹. This is much lower than the harmonic vibrational frequency of HCl, which is isoelectronic with Ar–He²⁺ and has a harmonic frequency of 2,991.0 cm⁻¹ [20]. The force constants are rather different as well, with Ar–He²⁺ having a *k* of 16.0 N m⁻¹, as opposed to 51.7 N m⁻¹ for HCl. The N₂–He²⁺ complex has three vibrations, one of which corresponds to the N–N stretching mode. Table 2 shows that this vibration in the complex has shifted 403.9 cm⁻¹ down from the N–N stretch calculated for the free N₂ molecule using the same calculational method, showing the influence of the additional mass attached to one end of the N₂ moiety.

The H₂O–He²⁺ complex has six vibrational frequencies. The H–O–H bending mode has decreased in frequency by over 680 cm⁻¹, while the symmetric and asymmetric stretches are affected very differently by complexation of the He²⁺ ion. The symmetric O–H stretch is significantly red-shifted to 2,298 cm⁻¹, while the asymmetric O–H stretch is only red-shifted by 541 cm⁻¹. The opposite effect is seen in the stretching motions of the CO₂ molecule. The symmetric C–O stretch is shifted down by only 246 cm⁻¹, while the asymmetric C–O stretch is significantly shifted, from 2,383.7 cm⁻¹ in the free CO₂ molecule to 1,140.0 cm⁻¹ in the complex. What was the doubly degenerate O–C–O bending motion splits into two nonde-

generate frequencies. The out-of-plane bending motion is affected more by the presence of the He ion, shifting down over 389 cm⁻¹ to 295.5 cm⁻¹, while the in-plane bending motion shifts only 225 cm⁻¹, from 684.7 cm⁻¹ in free CO₂ to 459.4 cm⁻¹ in the complex. The size of the shifts from the parent molecules to the complexes suggests that the bonding between the He²⁺ ion and the other molecules are not trivial interactions.

Rotational frequencies

All of the stable complexes found have a non-zero dipole moment. Therefore, based on quantum-mechanical selection rules, their pure rotational spectrum should be observable. Table 3 lists the rotational constants calculated for the optimum nuclear geometries. Linear complexes have only one unique rotational constant that defines both degrees of rotation, while non-linear complexes have three unique rotational constants, insofar as the nonlinear complexes noted here are asymmetric tops. Although asymmetric top molecules do not have any simple theory for their rotational spectra, diatomic and other linear molecules should show a spectrum showing a series of equally spaced absorption or emission lines. [19] The values in Table 3 are, therefore, markers to look for in radio or microwave spectra in interstellar space, should these complexes be of astrochemical interest. Molecular beams may also be a way to generate such species and measure their rotational spectra.

Bond energies

The bond energies were determined from the potential energy diagrams plotted by moving the He atom from slightly shorter than its equilibrium distance to a distance of ca. 5–7 Å away, approximating the asymptotic limit of an infinite distance between the atom/molecule and the He²⁺ ion. Figure 2 shows the potential energy curves for the four stable complexes. All of the plots show a normal one-dimensional potential energy curve for a bonding interaction: high, repulsive energies at very close distances, decreasing to a minimum energy at the equilibrium bond distance, then increasing in energy to an approximate

Table 2 Calculated vibrational frequencies of the alpha particle complexes

Complex	Calculated vibrational frequencies (unscaled; cm ⁻¹)
Ar–He ²⁺	1,192.9
N ₂ –He ²⁺	138.6, 1,017.5, 1,979.3 (–403.9)
H ₂ O–He ²⁺	942.6 (–682.2), 1,556.0, 1,385.2, 1,601.0, 2,298.7 (–1,541.9), 3,411.1 (–541.5)
CO ₂ –He ²⁺	113.5, 182.5, 295.5 (–389.2), 459.4 (–225.3), 1,139.1 (–246.5), 1,140.0 (–1,243.7)

Table 3 Rotational constants for the alpha particle complexes (in GHz)

	A	B	C
Ar–He ²⁺	70.9864683		
N ₂ –He ²⁺	23.4930554		
H ₂ O–He ²⁺	225.8612171	103.1840622	81.6688042
CO ₂ –He ²⁺	22.8646730	10.8001358	7.3353030

asymptotic limit. (We believe that the small dip in energy in Fig. 2a for the Ar–He²⁺ complex is a numerical artifact of the calculation and is not indicative of the overall trend.) The distance between the minimum energy and the asymptotic limit is taken by us to represent the bond energy of the X–He bond (X=Ar, N, O, and CO₂).

Table 4 lists the potential energy curve depths, as measured from the supposed asymptotic limit, for each complex. For three of the four complexes, the potential energy decrease upon complex formation suggests a covalent bond of well over 100 kJ mol⁻¹, well within the range of known covalent bonds. For the carbon dioxide–He²⁺ complex, a rather small energy decrease is found, only about 7 kJ mol⁻¹. However, when compared to a room temperature value of 2.48 kJ mol⁻¹, this still suggests that a real—though weak—chemical bond can form.

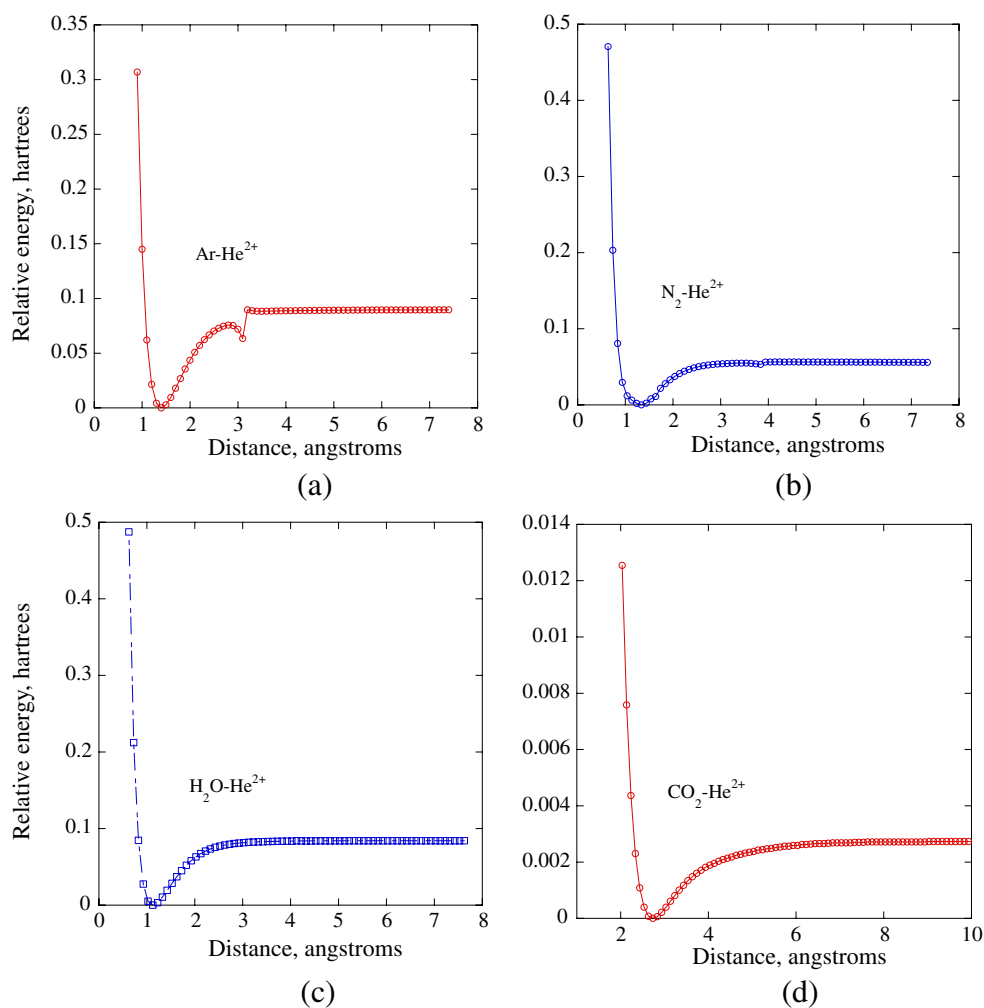
The potential energy wells suggest that relatively stable complexes can form between He²⁺ and at least three common atmospheric species: Ar, N₂, and H₂O. With CO₂, a complex is energetically possible, but predicted to be weakly bound. The first step, however, is for these

Table 4 Potential energy curve depths for the stable complexes

Complex	Depth, hartrees	Depth, kJ mol ⁻¹
Ar–He ²⁺	0.08966	235.4
N ₂ –He ²⁺	0.05600	147.0
H ₂ O–He ²⁺	0.08418	221.0
CO ₂ –He ²⁺	0.00273	7.17

molecules to first capture an alpha particle. Nucleus-emitted alpha particles typically have energies of 3–7 MeV upon emission [21]; this corresponds to velocities ranging from 12,000 and 18,400 km s⁻¹. If the alpha particle has more kinetic energy than its bond energy with the complex, it is likely that it will not bond with the atom or molecule. For the strongest X–He bond reported here, that means that the kinetic energy needs to be decreased to less than 3.9×10^{-19} J per particle, or an equivalent velocity of 10.8 km s⁻¹. This implies that the alpha particle must lose 99.9+% of its velocity before it can make a chemical bond (and much more than that if the bond is to be made to CO₂). Presumably it would do so through collisional de-

Fig. 2 Potential energy curves for **a** Ar–He²⁺, **b** N₂–He²⁺, **c** H₂O–He²⁺, and **d** CO₂–He²⁺. The graphs are not to the same scale



excitation, and it would have to do so without having an electron transferred to it. Although it seems unlikely that an alpha particle will do so in an environment of atmospheric pressure, given the results presented here, we must at least permit the possibility. In the interstellar space environment, however, conditions are different. Density and temperature are much lower, and the root mean distances between collisions are much higher: estimating a hard sphere diameter of 4 fm for the helium nucleus and a temperature of 2.7 K, kinetic theory of gases [18] calculates a mean free path of 1.9×10^{17} to 1.9×10^{21} m using the range of interstellar densities listed by Chaisson and McMillan [3]—2.1 to 2.1×10^4 light years. With an average speed of only 112 m s^{-1} under these conditions, the interstellar alpha particle can, for example, be significantly impacted by radiation pressure. Even at these velocities, the kinetic energy is low enough that an alpha particle can be captured by another atomic or molecular species. Thus, we suggest the possibility that alpha particle complexes might be more easily detected in an interstellar type of environment, rather than in a terrestrial one. The listing of rotational constants in Table 3 is meant to assist such a search.

Why were stable complexes found in some examples and not in others? A review of Table 1 and consideration of the systems that did not form stable complexes allows for a supposition. First, we see that a complex did not form with the species that had the lowest ionization energy: the oxygen molecule. Molecules with even slightly higher ionization energies—water, carbon dioxide—formed stable complexes. As such, we suggest that a minimum ionization energy is necessary, only above which will a stable complex form. Second, we note that a stable complex did not form with the H atom or the H₂ molecule, despite the fact that both of these species have ionization energies higher than H₂O, which did form a stable complex. This suggests a second criterion: the presence of enough molecular orbitals that would allow the distribution of a 2+ charge. For example, in the optimized H₂O–He²⁺ complex, the Mulliken charge distribution showed the helium atom and the oxygen atom with a partial charge of +0.4 and the hydrogen atoms with a partial charge of +0.6. It is likely that adequate distribution of the positive charge is another requirement to form a stable complex. While the oxygen molecule may have the orbitals to accommodate a

positive charge, its low ionization energy (see Table 1) supercedes this criterion. With this small population of examples, it is difficult to state conclusively which criterion are more important. Further study is suggested.

Given the data in Table 1, it appears clear that the ultimate product of alpha particle emission is neutral helium. The results here suggest, however, that complexes of alpha particles of finite lifetime are possible.

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