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E. Zicler, Marie-Christine Bacchus-Montabonel, F. Pauzat, P. Chaquin, Y. Ellinger. Communication: The formation of $\text{CHe}2+$ by radiative association. *The Journal of Chemical Physics*, 2016, 144 (11), pp.111103. 10.1063/1.4943979 . hal-02110638

HAL Id: hal-02110638

<https://hal.science/hal-02110638>

Submitted on 22 Jan 2021

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Cite as: J. Chem. Phys. **144**, 111103 (2016); <https://doi.org/10.1063/1.4943979>

Submitted: 07 February 2016 . Accepted: 02 March 2016 . Published Online: 16 March 2016

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Communication: The formation of CHe^{2+} by radiative association

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(Received 7 February 2016; accepted 2 March 2016; published online 16 March 2016)

The detection of ArH^+ has revived the interest in the search for noble gas containing species. Despite helium being the second most abundant element in the universe ($\text{He}/\text{H} \sim 1/10$), it has never been observed in any other form than that of a neutral/ionized atom in the interstellar medium. Because He is the “most noble” gas, its non-observation as part of neutral molecular systems is understandable. It is more surprising for charged species, especially HeH^+ whose spectral signatures are well documented in the laboratory. The purpose of this work was to find a simple positive ion containing He, and likely to be observed as an alternative to undetected HeH^+ . Among the HeX^{2+} diatomics formed with first row atoms, we focused on $\text{X} = \text{C}$ because of both its relative abundance and the magnitude of its ionization potentials with respect to He. The formation of CHe^{2+} by radiative association is the center of this study. The question was addressed by means of numerical simulations using high level *ab initio* calculations of the CHe^{2+} potential surface, followed by a quantum chemical determination of the rate coefficients for the corresponding radiative association in the range of 10 to 1000K. The radiative association path shows a potential well deep enough to accommodate 20 vibrational levels, and no barrier to oppose the reaction. The rate coefficient varies from $\sim 4.5 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ to $\sim 2.5 \times 10^{-22} \text{ cm}^3 \text{ s}^{-1}$ for the temperatures considered. The present study suggests that the existence of this species has to be searched for mainly in highly irradiated regions. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4943979>]

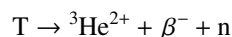
I. INTRODUCTION

The detection of the noble gas molecular ion, $^{36}\text{ArH}^+$, in the Crab nebula¹ put an end to years of unsuccessful search for noble gas containing molecular structures in space. Due to the large abundance of He with respect to the other noble gases, Ne, Ar, Kr, and Xe, it seems natural to look for He containing molecular structures. However, He is the most noble of all the noble gases. It has the highest ionization potential (24.59 eV) and the lowest polarizability (0.205 \AA^3) of the elements of the periodic chart, which makes it difficult to find a neutral partner for chemical bonding. Even if it seems able to form weak bonds with beryllium, as in HeBeO ,² this kind of structure is irrelevant to the chemistry in which we are interested here due to the abundance ratio $\text{Be}/\text{He} \sim 10^{-10}$.

The situation is totally different for ionic species where helium, the second most abundant element in the universe ($\text{He}/\text{H} \sim 1/10$) was shown capable of forming stable entities with ionic partners. A completely new kind of chemistry was predicted in the late 1980s,³⁻⁵ soon extended to the Ne and Ar light noble gases.^{6,7} These strong helium bonds are well-known in ionized species although none of them has ever been detected in the interstellar medium, even the simplest one, HeH^+ , whose structure, stability, and spectral signatures are known from laboratory experiments. Numerous examples of singly and multi-charged molecules can be found in the extensive review of ionic species in helium chemistry

by Grandinetti.⁸ Fundamental studies have been carried out recently for a better understanding of the generation of helium bonds⁹ and a chemical/topological analysis of their electronic density has been presented by Fourré *et al.*¹⁰ in which H atoms were systematically replaced by isoelectronic He^+ .

With a completely filled valence shell, only electron withdrawal can lead to the formation of a chemical bond with He. The possibility of *in situ* generation of He by a nuclear reaction transforming a Tritium atom (^3H), already present in an organic structure, as follows:

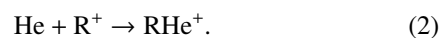
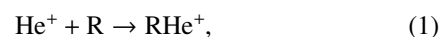


is beyond the scope of this study and was not considered.

The formation of RHe^{n+} molecules with $n = 1, 2$, where R represents an organic residue, is different according the level of ionization of the resulting species as follows:

(i) *Formation of singly ionized compounds: RHe^+*

The formation of these species that can be seen as analogues of protonated molecules in which H has been replaced by isoelectronic He^+ (for example, HeCN^+ in place of HCN), may proceed in either of the following two ways:



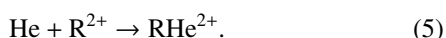
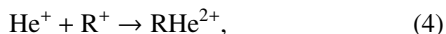
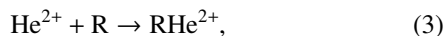
However, reactions of the first type will, most probably, not lead to the desired product; they involve He^+ that is known to be important in charge transfer reactions in space;¹¹ in addition, it should be remembered that it is the key ion used

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to ionize organic systems in penning ionization spectroscopy. Reactions of the second type yield to RHe^+ compounds whose lowest dissociation energies are small, meaning fragile helium bonds.⁵

(ii) *Formation of doubly ionized compounds: RHe^{2+}*

The formation of these species is more promising because the electron transfer between helium and the organic residue is much larger than in singly ionized species. It can be formally possible in three different ways:

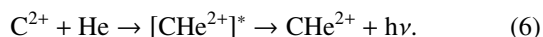


Reactions of the first type imply doubly ionized helium: on the one hand, the α particles of high energy present in cosmic-rays are totally inadequate to any sort of chemical reactivity; on the other hand, double ionization *in situ* would require up to 54.5 eV that would leave little chance for the organic residue to survive (at least as a neutral species). The second type of reaction is a repulsive situation in which charge transfer is not possible in a long distance approach, and by consequence, the formation of a covalent bond seems impossible. The third type of reaction is an attractive process that leads to a minimum energy structure whose stability depends on the strength of the donor-acceptor interaction between the fragments. In fact, the possibility of reaction depends on the relative position of the first ionization potential of He with respect to the second ionization potential of R on the energy scale, in other words, of the relative position of the $He + R^{2+}$ and $He^+ + R^+$ dissociation limits. Only R with second ionization potential below 24.5 eV can guarantee that the dissociation limit of reaction (5) is below that of reaction (4). In these conditions, there is no curve crossing between the potential surfaces describing the above two reactions. A full discussion of the open possibilities can be found in Frenking *et al.*⁵

The aim of this paper being the detection of helium bearing compounds *in fine*, we looked for the simplest system possible, i.e., a diatomic molecule. The only element satisfying the condition on the dissociation limit and abundant enough with respect to helium is carbon¹² with an abundance ratio $C/He \sim 10^{-3}$. It is the reason why we focused on CHe^{2+} .

II. RADIATIVE ASSOCIATION: COMPUTATIONAL BACKGROUND

The radiative association can be formally described by the following reaction:



During this reaction, the collision between C^{2+} and He leads to the creation of a $[CHe^{2+}]^*$ entity, for which we will only consider vibrational excitations. Then, CHe^{2+} is obtained from successive deexcitations of this excited species on the rovibrational levels of its ground state. The formation of the species under its excited form is considered as a quick step, so that the whole radiative association process is characterized by the last step of Equation (6) and the associated rate coefficient $k(T)$.

The calculations have been carried out here in the quantum approach used previously by Bacchus-Montabonel *et al.*¹³ In this approach,^{14,15} the quantum expression of the cross section at a given relative collision energy E of the colliding fragments is given by

$$\sigma(E) = \sum_J \sigma_J(E), \quad (7)$$

in which

$$\sigma_J(E) = \sum_{v'J'} \frac{64 \pi^5}{3} \frac{g}{c^3} \frac{g}{2\mu E} v_{E,v'J'}^3 S_{JJ'} M_{EJ,v'J'}^2, \quad (8)$$

where μ is the reduced mass of the system, g a parameter accounting for the degeneracy of the electronic state (here $g = 1$), $S_{JJ'}$ the Höln-London coefficients characteristic of the J and J' pair of rotational levels obtained as

$$S_{JJ'} = JM_{EJ,v'(J-1)}^2 + (J+1)M_{EJ,v'(J+1)}^2. \quad (9)$$

In this expression, $M_{EJ,v'J'}^2$ is the free-bound transition moment matrix element of the dipole moment $D(R)$ between the energy normalized function f_{EJ} of the continuum and the bound rovibrational function $\phi_{v'J'}$ for the same potential, evaluated from

$$M_{EJ,v'J'} = \int_0^\infty f_{EJ}(R) D(R) \Phi_{v'J'}(R) dR. \quad (10)$$

The frequency of the photon emitted, $\nu_{E,v'J'}$, corresponding to the energy difference between the continuum level of energy E and the rovibrational bound state of energy $E_{v'J'}$ is given by

$$\Delta E = h\nu_{v'J'} = E - E_{v'J'}.$$

Finally, the rate constants are calculated as the average over the cross sections weighted with a Maxwellian velocity distribution at temperature T ,¹⁵⁻¹⁷

$$k(T) = \left(\frac{8}{\pi\mu}\right)^{1/2} \left(\frac{1}{k_B T}\right)^{3/2} \int_0^\infty E \sigma(E) e^{-E/k_B T} dE. \quad (11)$$

The rovibrational bound states can be evaluated for diatomic systems, together with the corresponding free-bound dipole transition moments, so that a rigorous quantum chemical treatment can be carried out.

III. DETERMINATION OF RATE COEFFICIENTS

The accurate determination of rate coefficients rely first on the quality of the potential energy surface (PES) for reaction (6). Preceding calculations by Koch *et al.*⁴ gave an equilibrium distance $R_e(C-He) = 1.566 \text{ \AA}$ using a complete active space (CAS) SCF formalism. Two other points are worth mentioning. First, the lowest energy dissociation limit of CHe^{2+} into $C^{2+} (^1S) + He (^1S)$ is estimated at 0.767 eV above the energy minimum,⁵ and it can be reached only from the diatomic ground state. Second, the closest charge separation dissociation into $C^+ (^2S) + He^+ (^2S)$ has experimentally been found to be above 0.21 eV,¹⁸ which justifies the use of a single reference in the configuration interaction calculations.

The PES of reaction (6) was then calculated using high levels of theory, namely, Coupled Cluster treatments

TABLE I. Equilibrium distances (\AA) and potential depth ΔE (kcal/mol) for CHe^{2+} ($^1\Sigma^+$).

	$R_e(\text{C-He})$	ΔE
CCSD/aug-cc-pV5Z	1.546	18.973
CCSD(T)/aug-cc-pV5Z	1.538	19.895
CCSD(T)/aug-cc-pV5Z + BSSE	1.542	19.619

including single and double (CCSD) excitations to which a perturbative treatment of triple CCSD(T) excitations was added. The atomic basis set is a large split-valence polarized basis of quintuple-zeta quality (cc-pV5Z) augmented with diffuse functions. All the calculations were performed using methods and basis sets as implemented in the GAUSSIAN09 package.¹⁹ The results are presented in Table I and Figure 1.

From the exhaustive mapping of reaction (6) performed, it can be seen that, at that point of sophistication, the equilibrium distance is practically insensitive to the level of theory, which is not entirely true of the well depth. The variation of the bond length between CCSD and CCSD(T) shows a shortening of the equilibrium distance by 0.008 \AA due to the extra electronic correlation provided

TABLE II. Radiative association rate coefficients for CHe^{2+} .

T (K)	k ($\text{cm}^3 \text{s}^{-1}$)
10	4.5×10^{-20}
20	6.1×10^{-20}
30	7.0×10^{-20}
40	7.4×10^{-20}
50	7.6×10^{-20}
60	7.6×10^{-20}
70	7.5×10^{-20}
80	7.3×10^{-20}
90	7.0×10^{-20}
100	6.8×10^{-20}
150	5.4×10^{-20}
200	4.3×10^{-20}
300	2.9×10^{-20}
500	1.6×10^{-20}
1000	6.8×10^{-21}
5000	6.9×10^{-22}
10000	2.5×10^{-22}

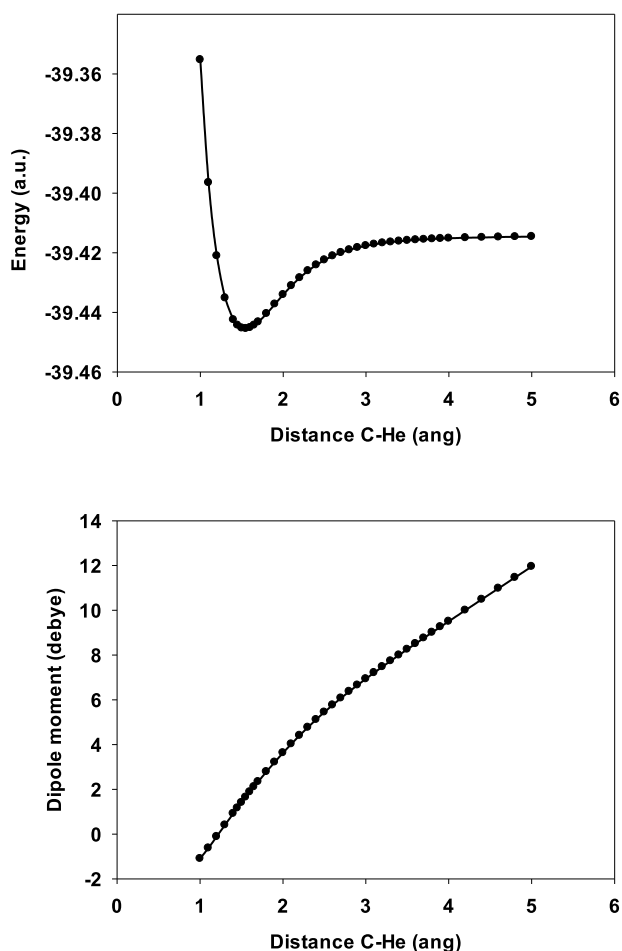


FIG. 1. Top: Potential energy curve for CHe^{2+} . The energy increases by 0.0002 a.u. beyond 5 \AA (not represented). Bottom: Dipole moment for each point of the energy curve. The dipole moment increases linearly beyond 5 \AA (not represented).

by triple excitations. This same correlation effect increases the depth of the potential well by almost 1 kcal/mol. A further refinement of the potential energy surface is obtained by including the correction for the basis set superposition error (BSSE), which has been done according to Boys and Bernardi²⁰ for each point of the surface. The best estimate of the PES obtained after correction, i.e., CCSD(T)/aug-cc-pV5Z + BSSE, gives an equilibrium $R_e(\text{C-He}) = 1.542 \text{ \AA}$ and a well depth of 0.8508 eV (19.619 kcal/mol), marginally different from the non-corrected results (Table I).

The values of the dipole moment have been obtained in a quadratic configuration interaction calculations using a basis of configuration composed of all single and double (QCISD) excitations from the reference ground state. It should be reminded that, because CHe^{2+} is not neutral, the dipole moment depends on the origin of the coordinates which was taken at the center of mass for each value of the reaction coordinate $R(\text{C-He})$.

The CCSD(T)/aug-cc-pV5Z PES including the BSSE correction is represented in Figure 1, together with the dipole moment function. In this well, we found 20 vibrational levels ($v = 0-19$). The corresponding radiative association rate constants are reported in Table II for temperatures in the range 10–10 000 K that covers all temperatures from cold dense clouds in the interstellar medium (ISM) to highly ionized regions. The radiative association cross sections have been summed over the rotational levels ($J = 0-19$), including all the rovibrational levels in the calculation (Table II).

IV. CONCLUDING REMARKS

The present study shows that the doubly ionized diatomic, CHe^{2+} can be formed in a radiative association reaction without activation barrier. Though the value of the rate constant is rather small, which suggests that CHe^{2+} may be no more than a laboratory curiosity, we cannot neglect

the possible interest for this ion in astrophysics. The radiative association to form another important ion in astrophysics, CH^+ , was considered previously.²¹ Although CH^+ and CHe^{2+} are isoelectronic, the reactive surfaces are fundamentally different. All surfaces but the ($^1\Sigma^+$) ground state are repulsive at long distances⁴ for CHe^{2+} , whereas the lowest three are attractive for CH^+ , which justifies considering the role of the excited states. Should the calculations be limited to the ($^1\Sigma^+$) surfaces, the difference between the potential depths (98 vs 19 kcal/mol for CH^+ and CHe^{2+} , respectively), would give a significantly larger rate for CH^+ . The question is, where would it be possible to find both neutral He and C^{2+} present in the same region?

The situation requires a double ionisation of the carbon atom while helium remains neutral. This can be obtained in [HII] regions with radiation flux comprised between the 13.6 eV necessary to ionize H and 25.6 eV corresponding to the first ionization of helium. Since the first and second ionization potentials of carbon are 11.26 eV and 24.34 eV, respectively, reaching C^{2+} from C^+ needs less energy than H ionization. Doubly ionized C^{2+} is not totally unusual. For example, it has been observed in the plasma tail of comet Kudo-Fujikawa.²² The formation of C^{2+} by ionization of C^+ has also been proposed recently by Langer and Pineda²³ to explain how X-ray sources may affect the carbon ionization balance, with the direct consequence of reducing the C^+ luminosity used to probe the star formation rate in galaxies. Following the same authors, we can deduce that ionization of C^+ leading to C^{2+} should be looked at in the warm interstellar medium (WIM) and in the Galactic center molecular zone (CMZ).

The survival of CHe^{2+} should also be considered. According to Frenking *et al.*,⁵ it lies at ca. 33 eV above HeC^+ ($^2\Pi$), which itself has actually been observed in laboratory experiments²⁴ in spite of a very weak energy dissociation energy of 0.9 kcal/mol.

However, reaction with electrons will give rise to the exothermal reaction sequence: $\text{CHe}^{2+} + e^- \rightarrow \text{C}^+ + \text{He}$. Any species with an ionization potential less than ca. 33 eV would also play the same role as the electron.

At all events, finding CHe^{2+} in space should rely on a thorough study of its spectral signatures in the laboratory, which is certainly a challenging task.

ACKNOWLEDGMENTS

This work was supported by CNRS national program PCMI (Physics and Chemistry of the Interstellar Medium) and COST Action CM No. 1401, "Astrochemical History". We acknowledge computational resources from the CCIN2P3 in Villeurbanne.

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