Lifetime of a Chemically Bound Helium Compound

Galina M. Chaban*, Jan Lundell† & R. Benny Gerber[≠,§]

*NASA Ames Research Center, Mail Stop 230-3, Moffett Field, CA 94035-1000, USA

†Laboratory of Physical Chemistry, University of Helsinki, P.O.Box 55 (A.I.Virtasen aukio 1), FIN-00014, Finland

[≠]Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel

[§]Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

The rare-gas atoms are chemically inert, to an extent unique among all elements. This is due to the stable electronic structure of the atoms. Stable molecules with chemically bound rare-gas atoms are, however, known. A first such compound, $XePtF_6$, was prepared in 1962[1] and since then a range of molecules containing radon, xenon and krypton have been obtained[2-7]. Most recently, a first stable chemically bound compound of argon was prepared[8], leaving neon and helium as the only elements for which stable chemically bound molecules are not yet known. Electronic structure calculations predict that a metastable species HHeF exists[9,10], but significance of the result depends on the unknown lifetime. Here we report quantum dynamics calculations of the lifetime of HHeF, using accurate interactions computed from electronic structure theory. HHeF is shown to disintegrate by tunneling through energy barriers into He + HF and H + He + F, the first channel greatly dominating. The lifetime of HHeF is more than 120 picoseconds, that of DHeF is 14 nanoseconds. The relatively long lifetimes are encouraging for the preparation prospects of this first chemically bound helium compound.

To predict theoretically the existence of a long-lived molecular species, several issues must be considered. First, as a necessary condition, the species must be shown to correspond to a local minimum of the potential energy surface of the system. In the case of HHeF this was already done by Wong[9] and by Lundell et al.[10] using accurate ab initio methods. Second, the potential surface regions that describe the decomposition pathways of the species must be determined. At least the potential along the path of minimum energy leading from the species to its decomposition products is necessary for a good estimate of the lifetime. To carry out a calculation of the molecule's lifetime, it is essential to compute its zero-point vibrational energy and wave function. If the molecule does not have at least one vibrational energy level under the top of the potential barrier that separates it from the product, then it is unstable and if somehow prepared will disintegrate instantaneously. If the zero-point energy lies under the top of the barrier, then in principle the species will decay by quantum-mechanical tunneling into the products of lower energy. The calculation of the tunneling process from the zero-point vibrational state of the molecular species yields the lifetime. Molecules that have extremely long tunneling decay times on laboratory timescales will appear experimentally stable.

Fig. 1 shows the equilibrium structure of HHeF, computed from MP2 electronic structure theory[11]. Calculations with higher level CCSD(T) method[11] were also carried out and are in good agreement with MP2 results. The short bond distances are characteristic of a chemically bound species, rather than of a van der Waals complex. Analysis shows that the bonding is partly ionic and partly covalent[10]. The fundamental vibrational frequencies of the HHeF species are high (H-He stretch 2124 cm^{-1}; F-He stretch 983 cm^{-1}; bending 519 cm^{-1}), again in the range characteristic of chemically bound molecules. These values were computed at a level of accuracy beyond the harmonic approximation, using the Correlation-Corrected Vibrational Self-Consistent Field (CC-VSCF) method[12], in an algorithm that uses directly points of the potential energy

surface obtained from electronic structure calculations in computing the vibrational energy levels[13]. Also the zero point vibrational energies used in the calculations of the lifetime in this paper were computed with the CC-VSCF method, since the accuracy of this method is important for reliable tunneling estimates.

Fig.2 shows the potential energy along the minimum energy path (also known as the Intrinsic Reaction Coordinate, IRC[11,14]) leading from the equilibrium structure to the energetically far more stable products He + HF. The IRC calculation[14,15] was carried out using the electronic structure package GAMESS[16] at the MP2 level of ab initio theory (MP2/aug-cc-pVTZ[11,16]). The potential energy points along the IRC were also computed using MCQDPT2[17], which is a method based on multi-configurational electronic structure theory (specifically, the method and the basis set used are MCQDPT2/MCSCF(10,6)/aug-cc-pVTZ[16]). The objective was to test if the MP2 results remain valid also away from the equilibrium configuration of HHeF, and the finding was that the two calculations gave virtually the same potential energy values along the IRC. This confirmed the validity of the single-configurational MP2 method in this case. The IRC corresponds approximately to motion along the bending coordinate of HHeF, especially near the equilibrium configuration of this species. The transition state in Fig.2 is of energy of 7.8 kcal/mol from the potential value for the equilibrium structure of HHeF. The tunneling lifetime of the species is exponentially sensitive to the potential energy barrier along the IRC, and in particular to the barrier height. The configuration corresponding to the transition state is shown in Fig.3. Beyond this geometry and as the system moves along the IRC towards the He + HF products, the effective charge on the He atom drops quickly to zero, that atom assumes a closed shell electronic structure, and the H-F bond starts to form. The lifetime calculation assumed a model of one-dimensional decomposition of HHeF by tunneling along the IRC. The effective mass associated with the IRC was employed[15] for the tunneling dynamics. The HHeF species was taken to be initially in the vibrational ground state. Within the

approximations made, only the zero-point energy corresponding to the bending mode (IRC motion) is relevant to the process. The latter can be obtained as the difference between the total zero-point energy of the equilibrium structure and that of the transition state of HHeF, 540 cm^{-1} by the CC-VSCF calculations. In the tunneling lifetime calculations, the two-fold degeneracy of the bending (and indeed of the IRC) motion must be kept in mind. With this, the tunneling rate was computed using a semiclassical expression (WKB)[18], yielding a lifetime of 120 picoseconds. A calculation by direct numerical integration of the time-dependent Schrödinger equation gave a similar result. The calculations for DHeF gave a lifetime of at least 14 nanoseconds, much larger than for HHeF since the effective mass along the tunneling path is larger by a factor of 2. Error estimates for the lifetimes are hard to give, since the errors are expected to be mostly due to the remaining inaccuracy of the computed potential, and due to the fact that a one-dimensional tunneling model was used. Calculations of the lifetime including all degrees of freedom of HHeF require a sufficiently accurate potential function in full (3D) dimensionality, which is not currently available.

HHeF has also an additional decay channel: HHeF $\rightarrow$ H + He + F. The potential along the IRC for this channel is shown in Fig. 4. The calculations for this process require an electronic structure theory that uses multi-configurational wave function and also includes perturbation-theoretic corrections for electron correlation effects, like MCQDPT2 method used here[17]. MCSCF[11], a multi-configurational theory, was used to compute the IRC path, but in the absence of dynamical electron correlation effects this level of electronic structure theory predicts HHeF to be unstable, decaying instantaneously into the 3-body channel H + He + F. At the level of MCQDPT2, which we expect to be quite reliable here, a barrier of 9.8 kcal/mol for the 3-body decay is found. The dissociation products are 15.8 kcal/mol below the HHeF equilibrium structure. The dissociation motion in this case is collinear, not the bending type as in Fig. 2. The decay rate is computed to be orders of magnitude slower than that leading to

He + HF. This is due to the somewhat higher barrier, and also because the effective mass associated with the 3-body decomposition is much larger. The contribution of this channel to the lifetime of HHeF can be completely ignored.

The results found for the lifetimes of HHeF and DHeF are in a sense gratifying: for modern experimental techniques, these lifetimes are long enough to permit identification of the molecular species and study of its decay process. There should be good prospects for experimental discovery of this very exotic species and for exploration of its properties.

1. Bartlett, N. Xenon hexafluoroplatinate(V) $Xe^{+}[PtF_6]^{-}$. *Proc. Chem. Soc.* 218 (1962).

2. Turner, J. J. & Pimentel, G. C. Krypton fluoride: preparation by the matrix isolation technique. *Science* **140**, 974-975 (1963).

3. Stein, L. Removal of xenon and radon from contaminated atmospheres with dioxygenyl hexafluoroantimonate, O_2SbF_6. *Nature* **243**, 30-32 (1973).

4. Holloway, J. H. & Hope, E. G. Recent advances in noble-gas chemistry. *Adv. Inorg. Chem.* **46**, 51-100 (1999).

5. Pettersson, M., Lundell, J. & Räsänen, M. New rare-gas-containing neutral molecules. *Eur. J. Inorg. Chem.* 729-737 (1999).

6. Lundell, J., Khriachtchev, L., Pettersson, M. & Räsänen, M. Formation and characterization of neutral krypton and xenon hydrides, *Low Temp. Phys.* **26**, 680-690 (2000).

7. Christe, K. O. A Renaissance in Noble Gas Chemistry, *Angew. Chem. Int. Ed.* **40**, 1419-1421 (2001).

8. Khriachtchev, L., Pettersson, M., Runeberg, N., Lundell, J. & Räsänen, M. A stable argon compound. *Nature* **406**, 874-876 (2000).

9. Wong, M. W. Prediction of a metastable helium compound: HHeF. *J. Am. Chem. Soc.* **122**, 6289-6290 (2000).

10. Lundell, J., Chaban, G. M. & Gerber, R. B. Combined ab initio and anharmonic vibrational spectroscopy calculations for rare gas containing fluorohydrides, HRgF. *Chem. Phys. Lett.* **331**, 308-316 (2000).

11. Jensen, F. *Introduction to Computational Chemistry*, Wiley, Chichester, England (1999).

12. Jung, J. O. & Gerber, R. B. Vibrational wavefunctions and spectroscopy of $(H_2O)_n$, n=2,3,4,5: vibrational self-consistent field with correlation corrections. *J. Chem. Phys.* **105**, 10332-10347 (1996).

13. Chaban, G. M., Jung, J. O. & Gerber, R. B. Ab initio calculations of anharmonic vibrational states of polyatomic systems: electronic structure combined with vibrational self-consistent field. *J. Chem. Phys.* **111**, 1823-1829 (1999).

14. Baldridge, K. K., Gordon, M. S., Steckler, R. & Truhlar, D. G. Ab initio reaction paths and direct dynamics calculations. *J. Phys. Chem.* **93**, 5107-5119 (1989).

15. Gonzalez, C. & Schlegel, H. B. Reaction-path following in mass-weighted internal coordinates. *J. Phys. Chem.* **94**, 5523-5527 (1990).

16. Schmidt, M. W. et al. General atomic and molecular electronic structure system. *J. Comput. Chem.* **14**, 1347-1363 (1993).

17. Nakano, H. Quasi-degenerate perturbation theory with multiconfigurational self-consistent-field reference functions. *J. Chem. Phys.* **99**, 7983-7992 (1993).

18. Holstein, B. R. *Topics in Advanced Quantum Mechanics*. Addison-Wesley, California (1992). Chapter V.

We thank Dr. R. Baer and Professors C. Wittig and V. A. Apkarian for helpful comments. This work was supported by the DFG, Germany (project sfb450), by the Israel Science Foundation, by the Chemistry Division of the NSF (USA), and by the Academy of Finland.

Correspondence and requests for materials should be addressed to R. B. Gerber (e-mail: benny@fh.huji.ac.il).

Figure legends:

Figure 1. Equilibrium geometry of HHeF (bond distances are given in angstroms).

Figure 2. Potential along minimum energy path for HHeF → He + HF.

Figure 3. Transition state geometry for HHeF → He + HF.

Figure 4. Potential along minimum energy path for HHeF → H + He + F.

Fig. 1

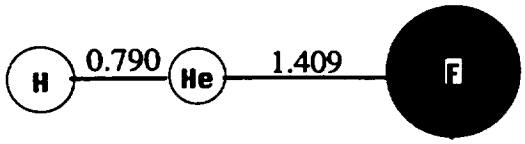


Fig. 2

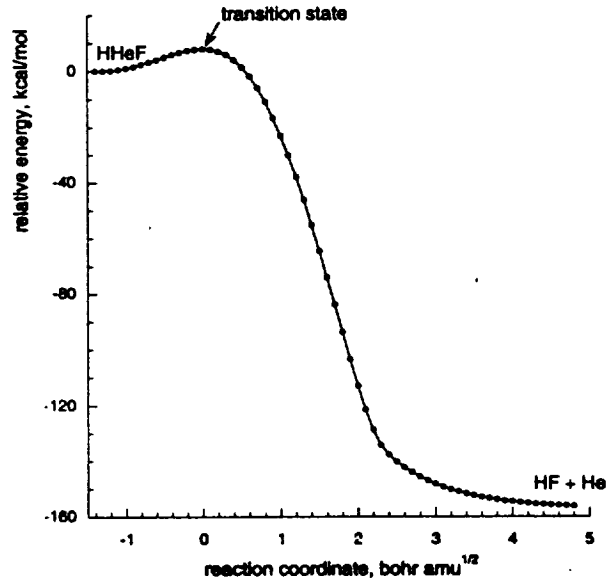

transition state
HHeF
HF + He
relative energy, kcal/mol
0
-40
-80
-120
-160
-1
0
1
2
3
4
5
reaction coordinate, bohr amu^1/2

Fig. 3

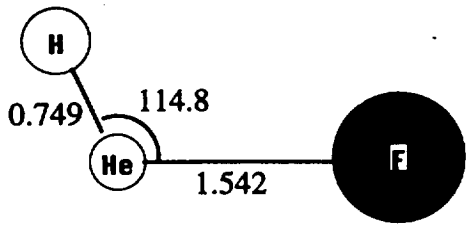
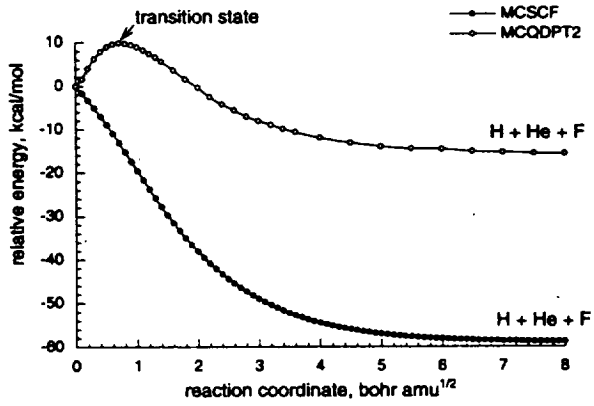


Fig. 4


transition state
MCSCF
MCQDPT2
H + He + F
H + He + F
relative energy, kcal/mol
reaction coordinate, bohr amu^1/2
10
0
-10
-20
-30
-40
-50
-60
0
1
2
3
4
5
6
7
8