AIP | The Journal of Chemical Physics

Lifetime and decomposition pathways of a chemically bound helium compound

Galina M. Chaban, Jan Lundell, and R. Benny Gerber

Citation: The Journal of Chemical Physics **115**, 7341 (2001); doi: 10.1063/1.1412467
View online: http://dx.doi.org/10.1063/1.1412467
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/115/16?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Experimental and theoretical study of the pyrrole cluster photochemistry: Closing the π σ * dissociation pathway by complexation
J. Chem. Phys. **127**, 064307 (2007); 10.1063/1.2754687

Decomposition of solid amorphous hydrogen peroxide by ion irradiation
J. Chem. Phys. **124**, 104702 (2006); 10.1063/1.2171967

On the existence and lifetimes of Cu 2 + complexes with water, ammonia, and hydrogen cyanide
J. Chem. Phys. **123**, 014315 (2005); 10.1063/1.1950607

Stability of a chemically bound helium compound in high-pressure solid helium
J. Chem. Phys. **117**, 5105 (2002); 10.1063/1.1506150

Mechanism of chemical decomposition in a shocked condensed explosive
AIP Conf. Proc. **429**, 813 (1998); 10.1063/1.55506

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.248.9.8 On: Tue, 23 Dec 2014 13:26:50

JOURNAL OF CHEMICAL PHYSICS VOLUME 115, NUMBER 16 22 OCTOBER 2001

COMMUNICATIONS

Lifetime and decomposition pathways of a chemically bound helium compound

Galina M. Chaban
NASA Ames Research Center, Moffett Field, California 94035-1000

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

R. Benny Gerber[a]
Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel and
Department of Chemistry, University of California, Irvine, California 92697-2025

(Received 10 July 2001; accepted 29 August 2001)

HHeF, a first predicted chemically-bound helium compound, is a metastable species that disintegrates by tunneling through energy barriers into He+HF and H+He+F. The reaction paths for these decomposition processes are calculated with single-configurational Møller-Plesset (MP2) and multiconfigurational quasidegenerate MCQDPT2/MCSCF(10,6) electronic structure methods. The lifetime of HHeF, estimated using a one-dimensional model along the minimum energy path and the semiclassical WKB approximation, is more than 120 ps, that of DHeF is 14 ns. The relatively long lifetimes are encouraging for the preparation prospects of this helium compound. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1412467]

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 the significance of the result depends upon the unknown lifetime. Here we report quantum dynamics calculations of the lifetime of HHeF, using accurate interactions computed from electronic structure theory.

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 principal 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 time scales will appear experimentally stable.

Figure 1 shows the equilibrium structure of HHeF, computed at the second-order Møller–Plesset (MP2) level of electronic structure theory[11] with augmented correlation-consistent valence triple-ζ (aug-cc-pVTZ) basis set.[12] Calculations with the higher level coupled-cluster method CCSD(T)[13] 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,[14] in an algorithm that directly uses points of the potential energy surface obtained from electronic structure calculations in computing the vibrational energy levels.[15] Also the zero point vibrational energies used in the calculations of the lifetime in this

---

[a] Electronic mail: bgerber@uci.edu

0021-9606/2001/115(16)/7341/3/$18.00

© 2001 American Institute of Physics

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.248.9.8 On: Tue, 23 Dec 2014 13:26:50

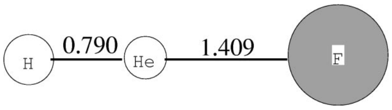

FIG. 1. Equilibrium geometry of HHeF (bond distances are given in angstroms).

paper were computed with the CC-VSCF method, since the accuracy of this method is important for reliable tunneling estimates.

Figure 2 shows the potential energy along the minimum energy path (MEP) leading from the equilibrium structure to the energetically far more stable products He+HF. This MEP is calculated using the intrinsic reaction coordinate method (IRC)[16] with the second order Gonzalez–Schlegel algorithm[17] and a step size of 0.1 amu$^{1/2}\cdot$bohr. The IRC calculation was carried out using the electronic structure package GAMESS[18] at the MP2/aug-cc-pVTZ level of *ab initio* theory. The potential energy points along the IRC were also computed using the second-order multiconfigurational perturbation theory MCQDPT2 method,[19] based on the CASSCF reference wave function that included 10 active electrons and 6 active orbitals. This is a full valence active space and is denoted as MCSCF(10,6). The same aug-cc-pVTZ basis set was used for multiconfigurational calculations as for single-configurational ones. The objective of the MCQDPT2 study was to test if the MP2 results also remain valid 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[17] 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 twofold 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),[20] yielding a lifetime of 120 ps. 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 ns, 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.

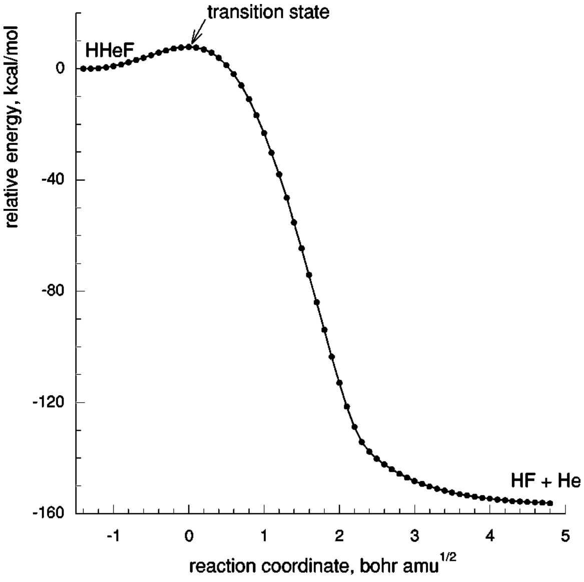

FIG. 2. Potential along minimum energy path for HHeF→He+HF.

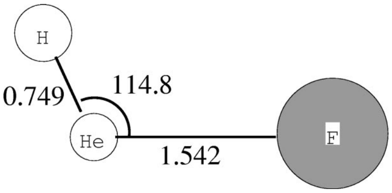

FIG. 3. Transiton state geometry for HHeF→He+HF.

HHeF also has an additional decay channel: HHeF→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 multiconfigurational

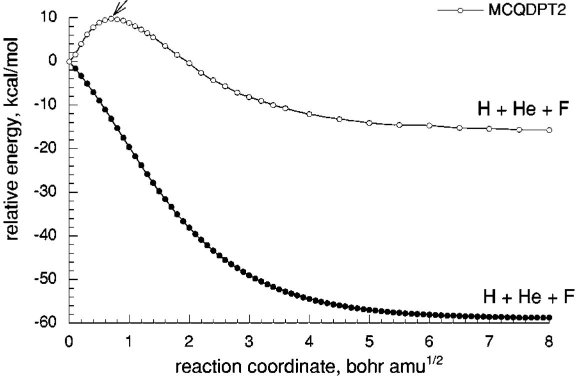

FIG. 4. Potential along minimum energy path for HHeF→H+He+F.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.248.9.8 On: Tue, 23 Dec 2014 13:26:50

wave function and also includes perturbation-theoretic corrections for electron correlation effects, like the MCQDPT2/MCSCF(10,6) method described above. MCSCF(10,6)/aug-cc-pVTZ level 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 geometry of this transition state is linear, with $R_{\mathrm{HHe}}=1.15$ Å and $R_{\mathrm{HeF}}=1.41$ Å. 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.

The authors thank Dr. R. Baer, Dr. D. Schwenke, Professor C. Wittig, and Professor 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 (Grant CHE-0101199), and by the Academy of Finland.

[1] N. Bartlett, Proc. Chem. Soc. **1962**, 218.
[2] J. J. Turner and G. C. Pimentel, Science **140**, 974 (1963).
[3] L. Stein, Nature (London) **243**, 30 (1973).
[4] J. H. Holloway and E. G. Hope, Adv. Inorg. Chem. **46**, 51 (1999).
[5] M. Pettersson, J. Lundell, and M. Räsänen, Eur. J. Inorg. Chem. **1999**, 729.
[6] J. Lundell, L. Khriachtchev, M. Pettersson, and M. Räsänen, Low Temp. Phys. **26**, 680 (2000).
[7] K. O. Christe, Angew. Chem. Int. Ed. Engl. **40**, 1419 (2001).
[8] L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, and M. Räsänen, Nature (London) **406**, 874 (2000).
[9] M. W. Wong, J. Am. Chem. Soc. **122**, 6289 (2000).
[10] J. Lundell, G. M. Chaban, and R. B. Gerber, Chem. Phys. Lett. **331**, 308 (2000).
[11] J. A. Pople, J. S. Binkley, and R. Seeger, Int. J. Quantum Chem. **10**, 1 (1976).
[12] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989); R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *ibid.* **96**, 6796 (1992).
[13] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[14] J. O. Jung and R. B. Gerber, J. Chem. Phys. **105**, 10332 (1996).
[15] G. M. Chaban, J. O. Jung, and R. B. Gerber, J. Chem. Phys. **111**, 1823 (1999).
[16] K. K. Baldridge, M. S. Gordon, R. Steckler, and D. G. Truhlar, J. Phys. Chem. **93**, 5107 (1989).
[17] C. Gonzalez and H. B. Schlegel, J. Phys. Chem. **94**, 5523 (1990).
[18] M. W. Schmidt, K. K. Baldridge, J. A. Boatz *et al.*, J. Comput. Chem. **14**, 1347 (1993).
[19] H. Nakano, J. Chem. Phys. **99**, 7983 (1993).
[20] B. R. Holstein, *Topics in Advanced Quantum Mechanics* (Addison-Wesley, Redwood City, CA, 1992), chap. V.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.248.9.8 On: Tue, 23 Dec 2014 13:26:50