PHYSICAL REVIEW A **71**, 024701 (2005)

Observation of small long-lived diatomic dications BeH^{2+} and BeD^{2+}

Klaus Franzreb, Richard C. Sobers, Jr., Jan Lörinčik, and Peter Williams*
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, USA

(Received 21 January 2004; published 24 February 2005)

The diatomic gas-phase dications BeH^{2+} and BeD^{2+} with only three electrons have been produced by Ar^+ sputtering of a Be metal foil with exposure of the surface to toluene (C_7H_8) or water (a mixture of D_2O and H_2O) vapor. BeH^{2+} and BeD^{2+} were observed and unambiguously identified by (mass)/(charge) determination in a magnetic sector mass spectrometer. They survived flight times of $\sim 4\ \mu s$. These observations confirm the discovery of BeD^{2+} in an atom-probe experiment by Barofsky and Müller [Surf. Sci. **10**, 177 (1968)] and support theoretical predictions of long-lived metastable BeH^{2+}.

DOI: 10.1103/PhysRevA.71.024701 PACS number(s): 32.80.Hd, 79.20.Rf, 36.40.−c, 61.80.Jh

Since the discovery of CO^{2+} and other dications more than 70 years ago [1–5], it has been known that long-lived diatomic dications can be observed in the gas phase. These dications provide an interesting theoretical challenge because the bonding in the electron-deficient molecule must outweigh the Coulomb repulsion of two positive charges a few angstroms apart.

The significance of such molecules in gas-phase and plasma chemistry, and the status of experimental molecular dication research have been addressed recently [6–11]. The atom probe technique developed by Müller *et al.* was particularly successful in producing various multiply charged diatomic molecules, with charge states as high as 4+ [12] (see also [13]). The interest in dications in theoretical chemistry goes back to 1933, when Pauling [14] predicted metastable He_2^{2+} half a century prior to its discovery in a charge-stripping experiment by Beynon *et al.* [15]. Due to the development of powerful computer codes, many efforts have been made during the last 20 years to calculate the electronic structures of homonuclear or heteronuclear diatomic dications and to understand their binding and predict their metastability versus dissociation into two fragment ions [16–20].

The metastable homonuclear molecule He_2^{2+} with two electrons (isoelectronic with H_2) is the diatomic dication with the fewest electrons that has an appreciable lifetime in the gas phase [14,15,21]. Its lifetime is $\geqslant 5\ \mu s$ [21]. The single-electron diatomic dication HeH^{2+} is short lived with a lifetime of only 4 ns [22]. It had been predicted by Bates and Carson in 1956 [23] and was observed after decay by coincidence detection of its fragment ions by Ben-Itzhak *et al.* in 1993 [24]. The diatomic dication with the fewest electrons that is predicted to be thermochemically stable is $BeHe^{2+}$ with four electrons [7,18,25]. BeH^{2+} and BeD^{2+} are the heteroatomic dication molecules with the fewest electrons that have a lifetime sufficient for direct observation by mass spectrometry. A faint signal corresponding to BeD^{2+} was first observed in 1968 by Barofsky and Műller [26], using a magnetic sector field-ion atom probe to identify ions formed by field evaporation from a beryllium tip exposed to a mixture of H_2 and D_2. Detection of BeH^{2+} was masked by an unresolved mass interference with D_2H^+ [26]. Later BeH^{2+} was reported by Műller and Tsong (raw data not shown) [12].

Identification of multiply charged species is complicated by the possibility of mass spectrometric artifacts; it is desirable to verify such identification by isotopic labeling [27] or precise mass measurement. Sputtering solid targets in the presence of hydrogen-containing gases in a high-sensitivity, high-mass-resolution secondary-ion mass spectrometer is an effective method to demonstrate the existence of metastable dications [36]. We have used this approach to search for diatomic hydride dications ($BeH^{2+}, BeD^{2+}, LiH^{2+}$) with three of fewer electrons. No information on the stability of LiH^{2+} with two electrons seems to be available in the literature. Several theoretical studies have predicted the existence of long-lived metastable BeH^{2+} [18,28–31], apparently without knowledge of the prior discovery of BeD^{2+} [26] and BeH^{2+} [12]. In this paper we confirm the existence of long-lived BeH^{2+} and BeD^{2+} produced by sputtering a Be target in the presence of toluene or H_2O (D_2O) vapor. Attempts to detect LiH^{2+}, BH^{2+}, and to confirm $B_2{}^{2+}$ [32,33] and $B_2{}^{3+}$ [33], both of which were previously produced by accelerator mass spectrometry by stripping electrons from $B_2{}^-$, were unsuccessful. Here we present some arguments why we could not observe these ions, and we identify two distinct mechanisms that contribute to dication formation of BeH^{2+} by sputtering. In work reported elsewhere we have produced the dications $Mo_2{}^{2+}$ [34,35], SiH^{2+}, AlH^{2+} [36], and a few other diatomic dications and trications [13] by sputtering.

The experiments utilized the Cameca IMS-3f magnetic sector secondary-ion mass spectrometer at ASU. Ion flight times through this instrument are $t \approx (m/z)^{0.5} \times 1.79\ \mu s$ (4 μs for BeH^{2+}). An 8-keV $^{40}Ar^+$ primary-ion beam with a current of $\sim 1.5\ \mu A$ was rastered over an area of $250 \times 250\ \mu m^2$, and positive ions emitted from an area of 150 μm in diameter were analyzed for their mass-to-charge (m/z) ratio. Mass spectra were taken at a sample potential of $U = 4500$ V with an ion energy bandpass $\Delta E = \pm z \times 60$ eV and with maximum instrument transmission ($\sim 10\%$). In an additional experiment on BeH^{2+}, we closed the energy slit and step-scanned the sample potential [34] to obtain mass-resolved ion energy distribution data that revealed two ion formation mechanisms of BeH^{2+}. BeH^{2+} and BeD^{2+} were produced by Ar^+ sputtering of a beryllium foil with simultaneous exposure of the

---

*FAX: (1) 480 965 2747. Email address: pw@asu.edu

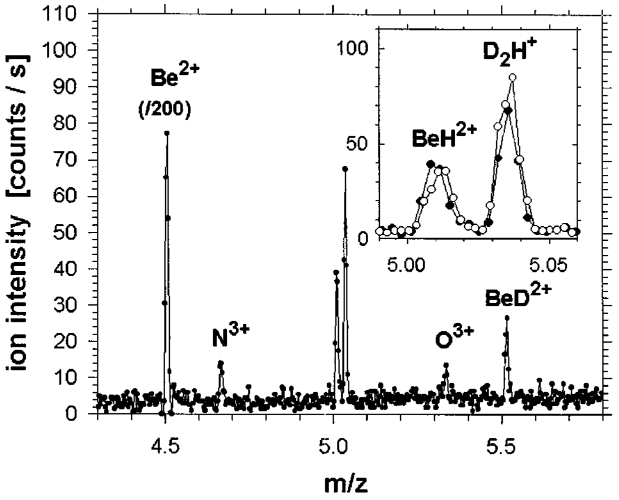

FIG. 1. Positive-ion mass spectrum for Ar$^+$ bombardment of Be with simultaneous exposure of the sputtered surface to water vapor. Both BeD^{2+} at m/z 5.5 and BeH^{2+} at m/z 5.01 (shown in the inset about -0.026 on the left of D$_2$H$^+$) were observed. The flood gas was D$_2$O with a H$_2$O contribution due to D-H exchange. The primary current density was ~ 2.4 mA/cm^2, the water vapor flood pressure was 4×10^{-5} torr, the sample potential was $U = 4500$ V, the ion energy window was $\Delta E = \pm z \times 60$ eV, and counting times were 2 or 4 s per data point.

surface to toluene vapor (C_7H_8, not isotopically enriched) or water vapor (D_2O with an H_2O contribution due to D-H exchange). A lithium metal foil, a polycrystalline piece of boron, and a few other samples were analyzed under similar bombarding conditions with and without toluene vapor flooding.

BeH^{2+} is metastable with respect to dissociation into Be$^+$ and H$^+$. The $X\,^2\Sigma^+$ ground state of BeH$^+$ was calculated by several groups [18,28–31]. Its local energy minimum is 2.75 ± 0.1 eV [18,29,31] above the level of completely separated Be$^+$ and H$^+$; it is ≈ 0.84 eV deep [18,29,31] and supports eight vibrational levels. Due to the high and broad energy barrier, the tunneling lifetimes for the lowest six vibrational levels were predicted to be sufficient (greater than microseconds [18,29]) to allow detection of BeH^{2+} for typical ion flight times in mass spectrometers. In particular, the tunneling lifetimes of the lowest three vibrational levels [18,29] are very large compared to the flight times of BeH^{2+} or BeD^{2+} of 4.0 or 4.2 μs in our experiment.

Figure 1 shows a positive-ion mass spectrum obtained for ^{40}Ar$^+$ sputtering of a Be metal surface with flooding with water (a mixture of D_2O with some H_2O) vapor. Ions detected at m/z 4.5, 4.67, 5.036, and 5.33 were identified as Be^{2+}, N^{3+}, D$_2$H$^+$, and O^{3+}, respectively, and serve as markers for accurate mass scale calibration. Both BeD^{2+} at m/z 5.5 and BeH^{2+} at m/z 5.01 were observed. The BeH^{2+}-D$_2$H$^+$ mass doublet at m/z 5 (inset in Fig. 1) was unambiguously identified by the mass difference of 0.026 ± 0.002 (tabulated m/z difference 0.026 024; there is no other conceivable mass doublet at this m/z value with this mass difference; in particular ^{10}B^{2+} is ruled out). The combined observation of BeD^{2+} at m/z 5.5 and of BeH^{2+} at m/z 5.01 unambiguously confirms the identification of these diatomic dications.

Replacing water vapor as a source of hydrogen with toluene vapor (C_7H_8, not D enriched) for similar bombarding conditions provided a factor of 3 more intense signal of BeH^{2+} (~ 100 counts/s at m/z 5.01), while no signal of D$_2$H$^+$ nor any signal at m/z 5.5 could be detected. The nonobservation of a peak at m/z 5.5 again rules out any contribution by a boron contamination (^{10}B^{2+}, ^{11}B^{2+}), and is additional evidence that the assignment of the peak at m/z 5.5 in Fig. 1 to BeD^{2+} is correct. Mass spectra for other samples [e.g., C, Li, Si (with the exception of B)] under similar sputtering and toluene flooding conditions did not reveal any ion features at m/z 5 or 5.5.

A search for other small diatomic dications was unsuccessful. We could not detect ^{7}LiH^{2+} at m/z 4 from an Ar$^+$-sputtered Li metal foil with toluene flooding. Similarly we could not detect ^{11}BH^{2+} at m/z 6 for an Ar$^+$-sputtered, toluene-flooded sample of crystalline boron. It seems unlikely that LiH^{2+} is metastable [51]. Calculations by Nicolaides *et al.* predicted the local energy minimum of BH^{2+} to be too shallow to support any vibrational levels [18]. We have also searched for bigger dication gas-phase dimers that had been observed before by other groups with other production techniques. We could confirm the existence [35,36,13] of the long-lived metastable gas-phase molecules Mo$_2$$^{2+}$ [37,38,17,34] and SiH^{2+} [39–42,19], but we failed to confirm the observation of B$_2$$^{2+}$ [32,33] and B$_2$$^{3+}$ [33].

The nonobservation of B$_2$$^{2+}$ was puzzling and motivated us to study diatomic dication formation mechanisms during sputtering in some detail. The main difficulty with the production of dications or trications by sputtering is the competition with fast and very efficient reneutralization processes that result from electron transfer from the surface as the ions depart. Therefore it is very likely that sputtered diatomic dications are formed in the gas phase sufficiently far from the surface that reneutralization by resonant transfer of surface electrons becomes inefficient. This distance to minimize reneutralization was estimated in [43] to be ~ 0.3 nm. We identified recently two mechanisms that allow formation of diatomic dications during Ar$^+$ sputtering in the gas phase beyond this reneutralization distance. Sputtered Mo$_2$$^{2+}$ and SiH^{2+} serve as examples to explain these two particular formation processes, labeled (*A*) and (*B*).

(*A*) Ionization by resonant or near-resonant electron transfer between an emitted singly charged sputtered molecular ion and an incoming projectile ion, such as the formation of Mo$_2^{2+}$ in gas-phase collisions of $\mathrm{Mo_2}^+ + \mathrm{Ar}^+ \rightarrow \mathrm{Mo_2}^{2+} + \mathrm{Ar}$ [35].

(*B*) Auger deexcitation of sputter-ejected core-excited neutralized molecules with electron shake-off, such as the formation of SiH^{2+} by Auger decay of $\mathrm{Si}^*(2p^{-1})\mathrm{H} \rightarrow \mathrm{SiH}^{2+} + 2e^-$ [36,44].

These two ion formation mechanisms can be distinguished in measurements of diatomic dication energy distributions made in the presence of the strong ion extraction field of ~ 1 V/μm in our instrument. Collisional electron transfer ionization (*A*) takes place for soft (large impact parameter) collisions at locations up to several 100 μm away from the sputtered surface [34]. Relative to ions accelerated from the sample surface, ions created in such gas-phase collisions enter the mass spectrometer with an energy deficit

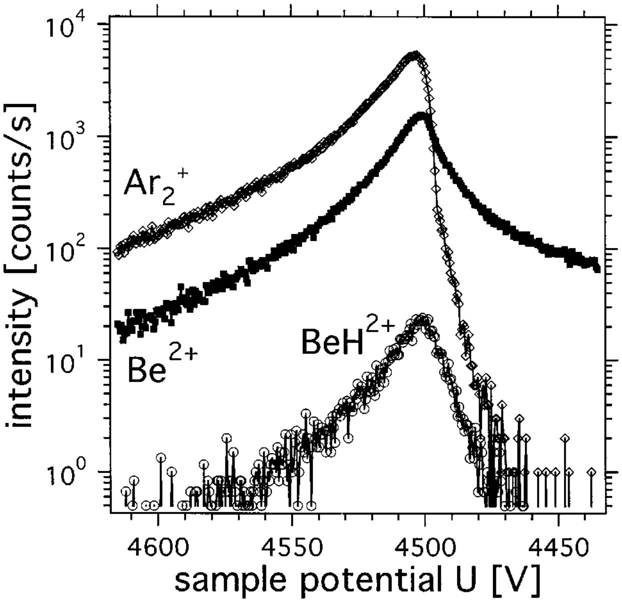

FIG. 2. Mass-resolved ion energy distribution of the diatomic dication of BeH^{2+} produced by Ar^+ sputtering of Be with toluene flooding. Corresponding data for Be^{2+} and $Ar_2{}^+$ are included for comparison. The counting time for BeH^{2+} at m/z 5 was 6 s per data point. The primary-ion current density was ~2.2 mA/cm^2 and the toluene flood pressure was 1×10^{-5} torr. See text for further details.

~d eV, where d is the distance (in micrometers) above the surface at which the ion is formed. Ionization by Auger decay with shake-off (B) takes place at much shorter distances of several nanometers from the surface owing to the relatively short core lifetimes, and the ions experience essentially the full potential drop from the sample to ground. The intensity of BeH^{2+} of ~100 counts/s for toluene vapor flooding was sufficient to allow a measurement of its ion energy distribution. For this purpose, the energy slit was closed to allow only accelerated ions with kinetic energy $z\times(4500\pm4)$ eV to pass through the energy-resolving slit, and the sample potential U was scanned. The result for BeH^{2+} is shown in Fig. 2. Ions observed at $U>4500$ V were formed in the gas phase in front of the sample surface. The ion energy distributions of Be^{2+} and $Ar_2{}^+$ are included in Fig. 2 for comparison. $Ar_2{}^+$ is formed exclusively in the gas phase by resonant electron transfer ($Ar_2+Ar^+\rightarrow Ar_2{}^++Ar$) [34], similar to the dication formation process (A).

The energy distributions of both BeH^{2+} and Be^{2+} in Fig. 2 show evidence of two ion formation processes. We attribute formation of BeH^{2+} and Be^{2+} at $U\leqslant4500$ V to sputtering of core-excited or core-ionized diatomic molecules $Be^*(1s^{-1})H$, $Be^{+*}(1s^{-1})H$ and atoms $Be^*(1s^{-1})$, $Be^{+*}(1s^{-1})$ with a Be 1s core hole and excess kinetic energy typical of the sputtering process, followed by Auger shake-off decay. This dication formation mechanism of BeH^{2+} via $Be^*(1s^{-1})H\rightarrow BeH^{2+}+2e^-$ is analogous to process (B). The Be 1s core lifetime of $\tau[Be(1s^{-1})]$ is extrapolated from calculations in [45] to be ~40 fs, i.e., a factor of ~2 larger than that for boron, $\tau[B(1s^{-1})]=20$ fs [45]. The shorter 1s core lifetime of boron might explain why we were unable to detect $B_2{}^{2+}$ or $B_2{}^{3+}$. Core-excited $B_2{}^*$ with a typical energy of 10 eV travels only 0.2 nm in 20 fs. This distance is not sufficient to avoid efficient surface reneutralization of B_2 subsequent to Auger deexcitation. For the larger core lifetime and lighter mass of BeH^*, the travel distance from the surface is roughly a factor of 3 larger. This significantly reduces the efficiency of reneutralization losses of BeH^{2+}. The above arguments are based on calculated core lifetimes of atoms in the gas phase [45]. The presence of adsorbates at the surface and of molecular binding might increase such core lifetimes, as had been found in [43] for surface oxygen. The binding energies for the 1s electron in Be or B are 111 or 188 eV, respectively [46], sufficient to allow dication formation by Auger decay with shake-off. It was shown by *KLL* Auger electron detection that sputtered core-excited atoms of $Be^*(1s^{-1})$ are produced efficiently for Ar^+ sputtering of Be at 8 keV impact energy and even lower [47]. We found for boron that the signal of B^{2+} in the mass spectrum was a factor of ~100 lower than that of Be^{2+}.

The energy distribution data for BeH^{2+} and Be^{2+} in Fig. 2 at $U>4500$ V show that ion formation also takes place in the gas phase up to several tens of micrometers away from the sputtered surface. The corresponding slopes of BeH^{2+}, Be^{2+}, and Ar_2^+ are nearly identical. In the case of Be^{2+}, (double) ionization of Be atoms as well as of Be^+ ions in hard collisions with energetic incoming projectile ions of Ar^+ is the most likely process. However, dication formation of BeH^{2+} from the parents BeH^+ or BeH must be restricted to soft collisions, since minimum momentum transfer is necessary to avoid its dissociation. It is tempting to consider resonant electron capture in grazing collisions of $BeH^++Ar^+\rightarrow BeH^{2+}+Ar$, analogous to the dication formation process (A) for $Mo_2{}^{2+}$. However, the dissociation energy of the ground state $X\,{}^1\Sigma^+$ of the molecule BeH^+ is 3.14 eV with respect to the energy level of the separated ground-state fragments of Be^+ and H [48]. Thus the adiabatic ionization energy to form BeH^{2+} from BeH^+ is ~19.5 eV, well above a possible resonance with the ionization energy of argon (15.8 eV). Hence, the formation process A can be ruled out for BeH^{2+} because of the energetics. BeH^{2+} formation by electron impact ionization of sputtered BeH or BeH^+ is unlikely, since energetic (~100 eV) Be *KLL* or *KVV* electrons are decelerated in the positive ion extraction field. A suggested formation process is attachment of H^+ onto Be^+ and/or H onto Be^{2+} in three-body association collisions (proton or hydrogen stripping) between Be^{k+} (with $k=1$, 2) and a toluene molecule or water in the gas phase above the sample. This is supported by the constant intensity ratio of $BeH^{2+}:Be^{2+}$ of about 1% for $U\geqslant4500$ V in Fig. 2. Such diatomic dication formation in association reactions (process C) has been reported recently for collisions of $Ar^{2+}+X_2\rightarrow ArX^{2+}+X$ (with X=N, O) [49,50].

In summary, we have produced the long-lived diatomic dications BeH^{2+} and BeD^{2+} by sputtering a Be sample in the presence of toluene or water vapor. These metastable gas-phase ions were unambiguously identified by exact mass measurement and isotope labeling approaches confirming their experimental discovery by Műller's group [26,12]. These species contain the fewest electrons (three) of any long-lived heteroatomic dications yet reported. Formation of BeH^{2+} is suggested to occur in the gas phase above the sputtered surface by the following two processes.

(*B*) Auger deexcitation of a sputtered neutralized core-excited molecule or ion:

$$\mathrm{Be}^{*}(1s^{-1})\mathrm{H} \rightarrow \mathrm{BeH}^{2+} + 2e^{-}, \quad \mathrm{Be}^{*+}(1s^{-1})\mathrm{H} \rightarrow \mathrm{BeH}^{2+} + e^{-}.$$

(*C*) Proton or hydrogen atom stripping collisions between Be^{k+} $(k=1,2)$ and toluene (or water) molecules:

$$\mathrm{Be}^{k+} + \mathrm{C}_n\mathrm{H}_m \text{ (or } \mathrm{H_2O}) \rightarrow \mathrm{BeH}^{2+} + \text{rest}.$$

This work was supported by the National Science Foundation under Grant No. CHE 0111654. We thank Rick Hervig for his help during our work on the ASU SIMS instrument.

---

[1] J. J. Thomson, *Rays of Positive Electricity and their Application to Chemical Analysis*, 1st ed. (Longmans, Green, and Co., London, 1913).
[2] F. W. Aston, Philos. Mag. **40**, 628 (1920).
[3] R. Conrad, Phys. Z. **31**, 888 (1930).
[4] A. L. Vaughan, Phys. Rev. **38**, 1687 (1931).
[5] E. Friedländer *et al.*, Z. Phys. **76**, 70 (1932).
[6] S. D. Price, J. Chem. Soc., Faraday Trans. **93**, 2451 (1997).
[7] D. Schröder and H. Schwarz, J. Phys. Chem. A **103**, 7385 (1999).
[8] S. G. Cox *et al.*, Phys. Chem. Chem. Phys. **5**, 663 (2003).
[9] V. G. Nenajdenko *et al.*, Chem. Rev. (Washington, D.C.) **103**, 229 (2003).
[10] S. D. Price, Phys. Chem. Chem. Phys. **5**, 1717 (2003).
[11] D. Mathur, Phys. Rep. **391**, 1 (2004).
[12] E. W. Müller and T. T. Tsong, Prog. Surf. Sci. **4**, 1 (1973); E. W. Müller, S. V. Krishnaswamy, and S. B. McLane, Surf. Sci. **23**, 112 (1970).
[13] K. Franzreb *et al.*, J. Chem. Phys. **121**, 12293 (2004).
[14] L. Pauling, J. Chem. Phys. **1**, 56 (1933).
[15] M. Guilhaus *et al.*, J. Phys. B **17**, L605 (1984).
[16] M. W. Wong and L. Radom, J. Am. Chem. Soc. **110**, 2375 (1988).
[17] F. Liu *et al.*, Phys. Rev. Lett. **59**, 2562 (1987).
[18] C. A. Nicolaides, M. Chrysos, and P. Valtazanos, J. Phys. B **23**, 791 (1990).
[19] V. V. Nefedova, A. I. Boldyrev, and J. Simons, Int. J. Quantum Chem. **55**, 441 (1995).
[20] S. Petrie, J. Chem. Phys. **107**, 3042 (1997).
[21] A. Belkacem *et al.*, Phys. Rev. Lett. **63**, 2555 (1989).
[22] I. Ben-Itzhak *et al.*, Phys. Rev. A **49**, 1774 (1994).
[23] D. R. Bates and T. R. Carson, Proc. R. Soc. London, Ser. A **234**, 207 (1956).
[24] I. Ben-Itzhak *et al.*, Phys. Rev. Lett. **71**, 1347 (1993).
[25] G. Frenking *et al.*, J. Am. Chem. Soc. **110**, 8007 (1988).
[26] D. F. Barofsky and E. W. Müller, Surf. Sci. **10**, 177 (1968).
[27] S. N. Schauer, P. Williams, and R. N. Compton, Phys. Rev. Lett. **65**, 625 (1990).
[28] P. M. W. Gill and L. Radom, Chem. Phys. Lett. **147**, 213 (1988).
[29] F. R. Ornellas and F. B. C. Machado, J. Mol. Struct.: THEOCHEM **282**, 43 (1993).
[30] M. Chrysos, M. E. Alikhani, and M. Jacon, Int. J. Quantum Chem. **53**, 57 (1995).
[31] P. J. Bruna, G. A. DiLabio, and J. S. Wright, J. Phys. Chem. **96**, 6269 (1992); G. H. Lushington, P. J. Bruna, and F. Grein, Z. Phys. D: At., Mol. Clusters **36**, 301 (1996); F. H. Wang *et al.*, Chin. Phys. Lett. **15**, 715 (1998).
[32] A. Galindo-Uribarri, H. W. Lee, and K. H. Chang, J. Chem. Phys. **83**, 3685 (1985).
[33] D. L. Weathers *et al.*, Nucl. Instrum. Methods Phys. Res. B **56/57**, 889 (1991).
[34] K. Franzreb and P. Williams, Phys. Rev. Lett. **91**, 015501 (2003).
[35] K. Franzreb *et al.*, J. Chem. Phys. **120**, 7983 (2004).
[36] K. Franzreb *et al.*, Appl. Surf. Sci. **231-232**, 82 (2004).
[37] T. T. Tsong, J. Chem. Phys. **85**, 639 (1986).
[38] T. T. Tsong, Surf. Sci. **177**, 593 (1986).
[39] C. J. Porter *et al.*, Croat. Chem. Acta **54**, 407 (1982).
[40] C. R. M. Grovenor and G. D. W. Smith, Surf. Sci. **123**, L686 (1982).
[41] W. Koch *et al.*, J. Chem. Soc., Perkin Trans. 2 **5**, 757 (1986).
[42] W. Koch, G. Frenking, and C. C. Chang, J. Chem. Phys. **84**, 2703 (1986).
[43] S. N. Schauer and P. Williams, Phys. Rev. B **46**, 15 452 (1992).
[44] K. Wittmaack, Phys. Rev. Lett. **43**, 872 (1979).
[45] D. L. Walters and C. P. Bhalla, Phys. Rev. A **3**, 1919 (1971).
[46] *CRC Handbook of Chemistry and Physics*, edited by R. C. Weast, 59th ed. (CRC Press, Boca Raton, FL, 1979), Tables E-191 and E-68.
[47] O. Grizzi and R. A. Baragiola, Phys. Rev. A **30**, 2297 (1984).
[48] F. B. C. Machado and F. R. Ornellas, J. Chem. Phys. **94**, 7237 (1991).
[49] P. Tosi *et al.*, Phys. Rev. Lett. **82**, 450 (1999).
[50] D. Ascenzi *et al.*, J. Chem. Phys. **118**, 2159 (2003).
[51] LiH^{+2} is expected to be unstable with purely repulsive potential curves according to P. J. Bruna (private communication).