Ab Initio Energies and Tunneling Lifetimes of the Doubly Charged AH^{2+} (A = Mg—Ar) Diatomics

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ABSTRACT .

Potential energy curves for the ground and low-lying excited states of the AH^{2+} (A = Mg—Ar) dications have been calculated using high-level ab initio methods with large atomic orbital basis sets. Quasi-bound potential energy curves with local minima and deprotonation barriers have been found for most of the dications studied. The energies, tunneling lifetimes, and widths of the quasi-bound states have been calculated by numerical solution of the radial Schrödinger equation using the Numeov method. All these dications except ArH^{2+} have low-lying states which support quasi-bound vibrational states. The ArH^{2+} dication has a ${}^{2}\Pi_{i}$ potential energy curve with a minimum so shallow that it does not support any quasi-bound vibrational states. Results of our calculations are compared with previous ab initio calculations and available experimental data. © 1995 John Wiley & Sons, Inc.

Introduction

Diatomic dications can form temporarily stable species in the gas phase even though strong Coulomb repulsion $(e^2/r = 7.2 \text{ eV} \text{ at } 2 \text{ Å} \text{ separation})$ exceeds conventional bond energies. A large number of AH²⁺ dications composed of first-or second-row atoms have been characterized both theoretically and experimentally [1–12]. Such species are usually thermodynamically unstable with respect to dissociation into two monocations, but significant kinetic stability may result if suffi-

ciently high barriers impede fragmentation. Barriers on the potential curves usually exist due to avoided crossings between states correlating diabatically with asymptotes of repulsive $(A^+ + H^+)$ and attractive $(H + A^{2+})$ character [13]. The accurate calculation of such barriers is important for determining the lifetimes of these dications.

In this article, we present results of high-quality complete active-space self-consistent-field calculations followed by configuration interaction with single and double excitations and approximate quadruple excitations [CASSCF-CISD(Q)] calculations of the potential energy curves of seven $AH^{2+}(A = Mg-Ar)$ dications using large atomic natural orbital (ANO) basis sets. These results were subsequently used for numerical solution of the onedimensional Schrodinger equation describing tunneling decay of these dications.

Computational Details

The complete active-space self-consistent-field method was used to generate a basis for further multireference all single- and double-excitation configuration interaction calculations (CASSCF-MRCISD) [14]. The final CASSCF-MRCISD energies were corrected by the Davidson method [15] [CASSCF-MRCISD(Q)] to account for the quadruple and higher-order excited configurations. For these calculations, we used large ANO basis sets [16, 17], and C_{2v} symmetry was used in all calculations. The active orbital space included $4a_1$, $2b_1$, $2b_2$, and 1a2 type orbitals for MgH2+, AlH2+, SiH2+, PH2+ and SH^{2+} ; $3a_1$, $2b_1$, $2b_2$, and $1a_2$ type orbitals for HCI^{2+} ; and $3a_1$, $1b_1$, $1b_2$, and $1a_2$ for HAr^{2+} . All valence electrons were considered as active in the CASSCF calculations, and the core orbitals were kept frozen in all subsequent MRCISD calculations. All these calculations have been performed using the MOLCAS II program [18].

For potential energy curves possessing a local minimum, the vibrational energy levels (and lifetimes for quasi-bound states) were calculated using the LEVEL 5.1 computer program of LeRoy [19]. The quasi-bound levels were calculated by numerical solution of a one-dimensional radial Schrödinger equation using the Numerov method [20] and by imposing an Airy function boundary condition at the third turning point, while the widths were calculated using a uniform semiclassical method.

Results and Discussion

MgH²⁺

The potential energy curve of this dication in the ground electronic state was previously studied by Gill and Radom using the unrestricted Hartree–Fock UHF/6-31G* method [7]. They found that the MgH²⁺ dication has a quasi-bound minimum at R = 2.22 Å and that it had an extraordinarily late deprotonation transition structure at R = 12.45 Å.

Because this dication has only one valence electron, we expected two low-energy electronic states ${}^{2}\Sigma^{+}(1\sigma^{1})$ and ${}^{2}\Pi(1\pi^{1})$ to exist. We carried out CI calculations including all single excitations (CIS) using $(17s12 p5d4f/7s7p5d4f)_{Mg}$ and $(8s4p3d/6s4p3d)_{H}$ basis sets. We found MgH²⁺ to have a ${}^{2}\Sigma^{+}$ ground electronic state and a ${}^{2}\Pi$ first excited state. The ground state has a local minimum at Re = 2.198 Å, lying 9.6 kcal/mol above the Mg⁺+ H⁺ dissociation limit (Table I).

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TABLE I

Dication	State	R _{min} (Å)	E _{tot} (au)	R _{max} (Å)	E _{tot} (au)	D _e (kcal / mol)	E [#] (kcal / mol)
MaH ²⁺	² Σ ⁺	2.198	- 199.355787	12.751	- 199.329899	-9.6	16.2
AIH ²⁺	¹ Σ ⁺	1.641	-241.633697	3.327	-241.577213	- 50.6	35.4
1.1.1.	³ Σ ⁺	2.220	-241.587939				
	1Π	2.071	-241.338242	3.624	-241.309876		17.8
SiH2+	² Σ ⁺	1.739	-288.586145	5.751	- 288.540284	- 33.1	28.8
	² Π	1.842	-288.446167	2.181	- 288.445190		0.6
	4П	2.120	-288.355194	3.646	-288.326538		18.0
	4Σ-	3.607	-288.309675				
PH ²⁺	¹ Σ ⁺	1.470	- 340.371857	3.373	- 340.269531	- 18.7	64.2
	³П	1.763	-340.306000	2.835	-340.290070		10.0
	1Π	1.984	-340.278276	3.181	-340.2613696		10.6
	³ Σ ⁺	3.264	-340.222132				
SH2+	2П	1.442	-397.107324	2.658	- 397.052765	-70.2	34.2
CIH2+	³ Σ ⁻	1.458	- 459.054504	2.231	-459.033814	- 101.5	13.0
	1Δ	1.455	-458.998047	2.204	- 458.978363		12.4
	¹ Σ ⁺	1.470	-458.950012	2.057	- 458.937653		7.8
ArH ²⁺	² Π	1.543	- 526,259065	1.611	- 526.258154	- 136.2	0.6

ENERGIES AND LIFETIMES OF AH2+ (A = Mg-Ar) DIATOMICS



FIGURE 1. Total energies (au) for lowest two states of MgH²⁺.

The first excited ${}^{2}\Pi$ state has a purely repulsive potential energy curve (see Fig. 1).

We found that the avoided crossing between two ${}^{2}\Sigma^{+}$ electronic states occurs between 13.0 and 13.5 Å. Because the deprotonation barrier is extremely wide, we used the VIBROT program in the MOLCAS II program to calculate the vibrational-rotational levels, treated as bound, and found a total of 12 levels, the lowest two of which are spaced by $\Delta G_{1/2} = 723$ cm⁻¹.

AIH²⁺

The potential energy curve of this dication in the ground electronic state ${}^{1}\Sigma^{+}$ $(1\sigma^{2})$ was previously studied by Gill and Radom using a variety of ab initio methods [8]. They found that AlH²⁺ has a quasi-bound minimum at R = 1.669 Å with a barrier for dissociation into Al⁺ + H⁺ located at R = 3.206 Å and lying 31.1 kcal/mol above the minimum. Gill and Radom [8] found that the wave function of AlH²⁺ has UHF instability in the region 1.6–3.9 Å, so the CISD method should be used to obtain more reliable results.

Because this dication has only two valence electrons, we expected four low-energy electronic states ${}^{1}\Sigma^{+}(1\sigma^{2})$, ${}^{3}\Sigma^{+}(1\sigma^{1}2\sigma^{1})$, ${}^{3}\Pi(1\sigma^{1}1\pi^{1})$, and ${}^{1}\Pi(1\sigma^{1}1\pi^{1})$ to exist for this dication. Calculations were carried out using the CASSCF-MRCISD method and the $(17s12p5d4f/7s7p5d4f)_{Al}$ and

 $(8s4p3d/6s4p3d)_{\rm H}$ basis sets. The CASSCF expansions included 17 $({}^{1}\Sigma^{+})$, 8 $({}^{3}\Sigma^{+})$, 10 $({}^{3}\Pi)$, and 10 $({}^{1}\Pi)$ configurations, which represent all possible distributions of the two valence electrons among the (4, 2, 2, 1) active orbitals of a_1 , b_1 , b_2 , and a_2 C_{2v} symmetry, respectively. All single and double excitations from these CASSCF configurations were than included in the MRCISD calculations, giving 1815 $({}^{1}\Sigma^{+})$, 3233 $({}^{3}\Sigma^{+})$, 2730 $({}^{3}\Pi)$, and 1482 $({}^{1}\Pi)$ MRCISD configurations. The potential energy curves are shown in Figure 2.

According to our calculations, the ${}^{1}\Sigma^{+}$ state is the lowest electronic state and has a local minimum at R = 1.641 Å and a barrier at R = 3.33 Å. The height of the barrier for dissociation to Al⁺ (${}^{1}S, 3s^{2}$) + H⁺ is 35.4 kcal/mol (Table I). The dissociation energy of the AlH²⁺ (${}^{1}\Sigma^{+}$) to Al⁺ (${}^{1}S$) + H⁺ is -50.6 kcal/mol (-2.19 eV). All these results are quite close to the data of Gill and Radom (see above).

The MRCISD wave function is well represented by the Hartree–Fock wave function (CHF = 0.95-0.99) in the region R (Al—H) = 1.0-10.0 Å. The maximum contribution from the other configurations occurs in the region of the barrier at R = 2.0-4.0 Å. For the lowest electronic state, we found 11 quasi-bound vibrational states (Table II) The lowest six have very long lifetimes and, hence, very small widths. Because of the long lifetimes, this dication could be studied experimentally.



FIGURE 2. Total energies (au) for lowest four states of AIH²⁺.

The lowest excited ${}^{3}\Sigma^{+}$ state of AlH²⁺ has an attractive potential energy curve whose minimum lies below the Al²⁺ (${}^{2}s, 3s^{1}3p^{0}$) + H(${}^{2}s$) dissociation limit. This state has a minimum at R = 2.220Å and a harmonic vibrational frequency of $\omega_{e} =$ 1047 cm⁻¹ (Table I). The vertical and adiabatic ${}^{1}\Sigma^{+} \rightarrow {}^{3}\Sigma^{+}$ excitation energies were found to be 2.3 and 1.25 eV, respectively. The minimum of the potential energy curve of the ${}^{3}\Sigma^{+}$ state is located below the top of the barrier of the ground electronic state. Therefore, while the potential energy curve of the ${}^{3}\Sigma^{+}$ state has its minimum lying below its dissociation limit, decay may happen through nonadiabatic transition to the underlying ${}^{1}\Sigma^{+}$ electronic state. As a result of these nonadiabatic interactions, the highest quasi-bound vibrational-rotational levels of the ground electronic state and the lowest vibrational-rotational levels of the ${}^{3}\Sigma^{+}$ state could be substantially perturbed.

The ${}^{3}\Pi$ excited state has the Al⁺ (${}^{3}P, 3s^{1}3p^{1}$) + H⁺ dissociation limit. Its potential energy curve lies above the dissociation limit, although it has a very local minimum at R = 2.158 Å that is not able to support any quasi-bound vibrational state. The MRCISD wave function of this state is well represented by the Hartree–Fock function ($C_{\rm HF} = 0.99$) in the region R = 1.0-10.0 Å.

The ¹ Π excited state has the Al⁺ (¹P, 3s¹3p¹) + H⁺ dissociation limit. The potential energy curve for this state has a local minimum at R = 2.071 Å and a dissociation barrier at 3.624 Å, with the height of the barrier being 17.8 kcal/mol. Eight

quasi-bound vibrational levels were found for this state (Table III). The ${}^{1}\Sigma^{+} \rightarrow {}^{1}\Pi$ vertical and adiabatic excitation energies were found to be 8.5 and 8.0 eV, respectively. Again, the MRCISD wave function is well represented by the Hartree–Fock wave function ($C_{\rm HF} = 0.98$) in the region R = 1.0-10.0Å. Because the ${}^{1}\Sigma^{+} \rightarrow {}^{1}\Pi$ excitation is not spinforbidden, it might be interesting to study in vibration resolution the electron excitation spectrum and thus to obtain experimental molecular parameters for the AlH²⁺ dication.

SiH2+

This dication was experimentally studied by Porter et al. [9a] and later by Koch, Frenking, Schwarz, Maquin, and Stahl (KFSMS) [9b]. Both groups found SiH²⁺ to be a metastable species with a very long lifetime [9a, c]. A few ab initio studies [9b-e] were performed earlier for the lower electronic states. Koch, Frenking, and Chang (KFC) [9d] found that the $X^2\Sigma^+$ ground electronic state has a deep minimum at 1.75 Å, using MRD-CI and CASSCF methods and a valence triple-zeta + polarization basis set. The charge distribution in the ground $X^2\Sigma^+$ electronic state can approximately be described as Si2+H0. At large internuclear distances (around 5.5 Å), this state begins to interact with the $B^2\Sigma^+$ state, whose charge distribution may be approximated as Si⁺H⁺, and the two states undergo an avoided crossing. As a result, the ground-state potential energy curve has

Quasi-bound levels of the '2,' state of AIH-'.				
Levels	<i>E</i> (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)	
$\nu = 0, J = 0$	766.9	∞	0	
v = 0, J = 1	779.7	∞	0	
$\nu = 0, J = 2$	805.1	α,	0	
$\nu=1,J=0$	2242.2	œ	0	
$\nu = 1, J = 1$	2254.4	œ	0	
$\nu = 1, J = 2$	2278.7	œ	0	
$\nu=2,J=0$	3638.3	œ	0	
$\nu = 2, J = 1$	3650.0	×. ∞	0	
$\nu = 2, J = 2$	3673.3	œ	0	
$\nu = 3, J = 0$	4960.6	œ	0	
$\nu = 3, J = 1$	4971.7	œ	0	
$\nu = 3, J = 2$	4994.0	œ	0	
$\nu=4, \ J=0$	6207.3	œ	0	
$\nu = 4, J = 1$	6217.9	œ	0	
$\nu = 4, J = 2$	6239.2	∞ ,	0	
$\nu = 5, J = 0$	7371.2	$0.3 \times 10^{+10}$	0.2×10^{-20}	
$\nu = 5, J = 1$	7381.4	$0.2 \times 10^{+10}$	0.2×10^{-20}	
$\nu = 5, J = 2$	7401.8	$0.2 \times 10^{+10}$	0.3×10^{-20}	
$\nu=6, \ J=0$	8462.7	0.7 × 10 ⁺⁰⁴	0.7×10^{-15}	
$\nu = 6, J = 1$	8472.5	0.7 × 10 ⁺⁰⁴	0.8×10^{-15}	
$\nu = 6, J = 2$	8492.1	$0.6 \times 10^{+10}$	0.9×10^{-15}	
$\nu = 7, J = 0$	9473.4	0.1	0.5×10^{-10}	
$\nu = 7, J = 1$	9482.7	0.1	0.5×10^{-10}	
$\nu = 7, J = 2$	9501.4	0.9×10^{-01}	0.6×10^{-10}	
$\nu = 8, J = 0$	10406.6	0.7×10^{-05}	0.8×10^{-06}	
$\nu = 8, J = 1$	10415.5	0.6×10^{-05}	0.8×10^{-06}	
$\nu = 8, J = 2$	10461.6	0.4×10^{-05}	0.1×10^{-05}	
$\nu = 9, J = 0$	11253.0	0.2×10^{-08}	0.3×10^{-02}	
$\nu = 9, J = 1$	11261.3	0.2×10^{-08}	0.3×10^{-02}	
$\nu = 9, J = 2$	11277.8	0.2×10^{-08}	0.4×10^{-02}	
v = 10, J = 0	11991.0	0.2×10^{-11}	2.6	
v = 10, J = 1	11998.4	0.2×10^{-11}	2.7	
v = 10, J = 2	12013.0	0.2×10^{-11}	2.9	
v = 10, J = 2	12013.0	0.2 × 10	2.9	

TABLE II ______ Quasi-bound levels of the ${}^{1}\Sigma^{+}$ state of AlH²⁺.

the characteristic quasi-bound shape with a local minimum and a deprotonation barrier. Their barrier for deprotonation is quite high (24.7 kcal/mol at the MRD-CI level and 24.4 kcal/mol at the CASSCF level). The so-called reverse activation energy [computed as the barrier on the Si⁺ (²*P*) + H⁺ \rightarrow SiH²⁺ ($X^2\Sigma^+$) curve] is 57.7 kcal/mol at the MRD-CI level and 57.0 kcal/mol at the CASSCF level, both which agree well with the experimental value of 55.8 kcal/mol. The experimental determinations are made by measuring the kinetic energy released (T_h) when the AH²⁺ species fragments into A⁺+ H⁺, assuming most of the product ion flux to derive from levels near the barrier on the PES.

An excited state of SiH²⁺ was also observed in the experiments. In line with experimental observation, KFC found a weak minimum on the $A^2\Pi$ potential curve- with an interatomic distance of 1.85 Å. However, KFC did not report the deprotonation barrier for this state. The $X^2\Sigma^+$ and $A^2\Pi$ states have the same dissociation limit because the 2σ - and 1π -MOS become degenerate at large internuclear distances.

Park and Sun (PS) recently repeated ab initio calculations of the ground and excited states of SiH^{2+} [9e]. They used the second-order effective valence-shell Hamiltonian based on quasi-degenerate many-body perturbation theory and

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TABLE	111	100					
Quasi-b	ound	levels	of the	¹ Π	state o	f AIH ²⁺ .	

Levels	<i>E</i> (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)
v = 0, J = 0	460.3	8	0
$\nu = 0, J = 1$	468.3	8	0
v = 0, J = 2	484.4	8	0
$\nu = 1, J = 0$	1375.3	8	. 0
$\nu = 1, J = 1$	1383.0	œ	0
$\nu = 1, J = 2$	1398.6	8	0
v = 2, J = 0	2250.3	$0.5 \times 10^{+06}$	0.1×10^{-16}
v = 2, J = 1	2257.7	$0.4 \times 10^{+06}$	0.1×10^{-16}
v = 2, J = 2	2272.7	$0.4 \times 10^{+06}$	0.1×10^{-16}
v = 3, J = 0	3085.0	$0.1 \times 10^{+02}$	0.4×10^{-12}
$\nu = 3, J = 1$	3092.0	$0.1 \times 10^{+02}$	0.4×10^{-12}
$\nu = 3, J = 2$	3106.4	$0.1 \times 10^{+02}$	0.4×10^{-12}
v = 4, J = 0	3877.6	0.1×10^{-02}	0.4×10^{-08}
$\nu = 4, J = 1$	3884.3	0.1×10^{-02}	0.4×10^{-08}
$\nu = 4, J = 2$	3897.9	0.1×10^{-02}	0.4×10^{-08}
$\nu = 5, J = 0$	4623.6	0.4×10^{-06}	0.1×10^{-04}
$\nu = 5, J = 1$	4629.9	0.4×10^{-06}	0.1×10^{-04}
$\nu = 5, J = 2$	4642.7	0.4×10^{-06}	0.1×10^{-04}
$\nu = 6, J = 0$	5313.5	0.3×10^{-09}	0.2×10^{-01}
v = 6, J = 1	5319.4	0.3×10^{-09}	0.2×10^{-01}
$\nu = 6, J = 2$	5331.2	0.3×10^{-09}	0.2×10^{-01}
v = 7, J = 0	5921.9	0.1×10^{-11}	4.9
$\nu = 7, J = 1$	5927.1	0.1×10^{-11}	5.0
v = 7, J = 2	5937.6	0.1×10^{-11}	5.2

double-zeta basis sets augmented by diffuse and double sets of polarization functions. PS studied the ground and the 12 lowest excited states of SiH^{2+} . Their spectroscopic constants, deprotonation energies, and deprotonation activation energies for the lowest states are in good agreement with KFC data.

We performed ab initio calculations for SiH²⁺ at higher ab initio levels using larger basis sets. We studied five $X^2\Sigma^+$ $(1\sigma^22\sigma^1)$, $^2\Pi$ $(1\sigma^21\pi^1)$, $^4\Pi$ $(1\sigma^12\sigma^11\pi^1)$, $^4\Sigma^ (1\sigma^11\pi^2)$, and $^2\Delta$ $(1\sigma^11\pi^2)$ electronic states. Calculations were carried out using the CASSCF-MRCISD(Q) method and the

and

$$(17s12\,p5d4f/7s7p5d4f)_{Si}$$

basis sets. The CASSCF expansion included 64 $(^{2}\Sigma^{+})$, 60 $(^{2}\Pi)$, 22 $(^{4}\Pi)$, 16 $(^{4}\Sigma^{-})$, and 56 $(^{2}\Delta)$ configurations, which represent all possible distributions of all three valence electrons among (4, 2, 2, 1) active orbitals of a_{1} , b_{1} , b_{2} , and $a_{2}C_{2v}$ symmetry. All single and double excitations from these CASSCF configurations were then included in the MRCISD calculations, giving 26,079 ($^{2}\Sigma^{+}$), 24,580 ($^{2}\Pi$), 12,074 ($^{4}\Pi$), 12,639 ($^{4}\Sigma^{-}$), and 23,101 ($^{2}\Delta$) MRCISD configurations. Davidson's corrections were added to the MRCISD energies. Potential energy curves of the $^{2}\Sigma^{+}$, $^{2}\Pi$, $^{4}\Pi$, $^{4}\Sigma^{-}$, and $^{2}\Delta$ states shown are in Figure 3. (See also Tables IV and V.)

For the $X^2\Sigma^+$ ground electronic state, we obtained very similar results to KFC: $R_{\min} = 1.74$ Å, $R_{\max} = 5.75$ Å, and $E^{\#} = 28.8$ kcal/mol. The MRCISD wave function of the $X^2\Sigma^+$ electronic state is well represented by the Hartree-Fock function $(C_{\text{HF}} = 0.98)$ in the region R = 1.0-10.0 Å. Moreover, the fragmentation energy of SiH²⁺ ($X^2\Sigma^+$) to Si⁺ (²P) + H⁺ is -33.1 kcal/mol (-1.43 eV), and our Si⁺ + H⁺ \rightarrow SiH²⁺ ($X^2\Sigma^+$) reverse activation energy is 61.9 kcal/mol, which should be compared to the experimental kinetic energy (T_h) release observed for SiH²⁺ fragmenting into Si⁺ + H⁺: $T_h = 55.8$ kcal/mol [9c].

The first ² Π excited state has very shallow local minimum at R = 1.84 Å and a barrier at R = 2.18 Å with the barrier height 0.6 kcal/mol. Our bond length at the minimum is in good agreement with KFC's value of 1.85 Å and is larger than the PS 1.72 Å bond length. Our deprotonation barrier 0.6 kcal/mol is lower than the 1.15 kcal/mol barrier obtained by PS. Our adiabatic excitation energy is 3.8 eV (87.8 kcal/mol), which is close to the 3.9 eV by KFC and is somewhat lower than the 4.08 ev by PS.

The MRCISD wave function of this state is also well represented by the Hartree–Fock wave function ($C_{\rm HF} = 0.97$) in the region R = 1.0-10.0 Å. We were not able to find any quasi-bound vibrational levels located behind the small barrier of this case. Therefore, we believe that the experimentally observed [9c] excited state of SiH²⁺ may not be the $a^2\Pi$ state, especially because the experimentally observed kinetic energy release switch $T_h = 8.39$ eV for the SiH²⁺ \rightarrow Si⁺ + H⁺ reaction does not agree with our theoretical $\Delta E = 5.27$ eV or with the value $\Delta E = 5.6$ eV obtained by Ps. The $B^2\Sigma^+$ excited state, which has a purely repulsive potential energy curve according to PS, was not studied in this work.

The $a^4\Pi$ excited state with the Si⁺ (⁴P) + H⁺ dissociation limit has a local minimum at $R_{\min} =$ 2.12 Å and a deprotonation barrier at $R_{\max} = 3.65$ Å with a barrier height $E^{\#} = 18.0$ kcal/mol. These results are in a reasonable agreement with the PS data: $R_{\min} = 2.15$ Å and $E^{\#} = 14.8$ kcal/mol. The $X^2\Sigma^+ \rightarrow a^4\Pi$ vertical and adiabatic excitation energies are 6.7 and 6.3 eV, respectively.



FIGURE 3. Total energies (au) for lowest five states of SiH²⁺.

The MRCISD wave function is well represented by the Hartree-Fock wave function ($C_{\rm HF} = 0.99$) in the region R = 1.0-10.0 Å. We found nine quasi-bound vibrational levels inside the local minimum for this state. The four lowest levels have long lifetimes; therefore, we believe that KFSMS probably observed this excited state of SiH²⁺. Indeed, our calculated reverse activation energy for Si⁺ + H⁺ \rightarrow SiH²⁺ ($a^4\Pi$) of 8.49 eV is in excellent agreement with the experimental value $T_h =$ 8.39 eV [9c].

The ${}^{4}\Sigma^{-}$ state of SiH²⁺ has a very shallow minimum at $R_{\min} = 3.607$ Å, and this minimum is located below the Si²⁺(${}^{3}P$) + H(${}^{2}s$) dissociation limit. As a result, the potential energy curve has an attractive character. Its MRCISD wave function is well represented by Hartree–Fock wave function ($C_{\rm HF} = 0.98$). Finally, the ${}^{2}\Delta$ state of SiH²⁺ with the Si⁺ (${}^{2}D$) + H⁺ dissociation limit has a repulsive potential energy curve.

PH²⁺

This dication was previously studied theoretically [10]. In the most extensive ab initio study by Senekowitsch et al. [10d], three quasi-bound states, $X^{1}\Sigma$, $A^{1}\Pi$, and $a^{3}\Pi$, have been found at the CASSCF-MRCISD level of theory using

 $(14s10p4d1f/10s7p4d1f)_{P}$

and

$$(8s3p1d/5s3p1d)_{\rm H}$$

basis sets (Tables VI–VIII). At this level, the $X^{1}\Sigma^{+}$ ground electronic state has a minimum at $R_{\min} =$ 1.472 Å and barrier at $R_{\max} = 3.387$ Å with a deprotonation barrier height of $E^{\#} = 63.6$ kcal/mol. The excited $a^{3}\Pi$ state has a minimum at $R_{\min} = 1.770$ Å and a barrier at $R_{\max} = 2.857$ Å with a deprotonation barrier height $E^{\#} = 10.2$ kcal/mol. The $A^{1}\Pi$ second excited state has minimum at $R_{\min} = 1.988$ Å and a barrier at $R_{\max} =$ 3.204 Å with a deprotonation barrier height of $E^{\#} = 11.2$ kcal/mol. The authors of [10d] also found 15, 5, and 4 quasi-bound vibrational levels inside the $X^{1}\Sigma^{+}$, $A^{1}\Pi$, and $a^{3}\Pi$ barriers, respectively.

We repeated such ab initio calculations for the lowest $X^{1}\Sigma^{+}$ $(1\sigma^{2}2\sigma^{2})$, ${}^{3}\Pi$, $(1\sigma^{2}1\pi^{1}2\sigma^{1})$, ${}^{3}\Sigma^{-}$ $(1\sigma^{2}1\pi^{2})$, ${}^{1}\Delta$ $(1\sigma^{2}1\pi^{2})$, and ${}^{1}\Pi$ $(1\sigma^{2}1\pi^{1}2\sigma^{1})$ electronic states. Our calculations were carried out using the CASSCF-MRCISD(Q) method and $(17s12p5d4f/7s7p5d4f)_{\rm P}$ and $(8s4p3d/6s4p3d)_{\rm H}$ basis sets. The CASSCF expansion included 152 $({}^{1}\Sigma^{+})$, 152 $({}^{3}\Pi_{r})$, 146 $({}^{3}\Sigma^{-})$, 128 $({}^{1}\Delta)$, and $({}^{1}\Pi)$ configurations, which represent all possible distributions of all four valence electrons among (4, 2, 2, 1) active orbitals of a_{1} , b_{1} , b_{2} , and $a_{2}C_{2v}$ symmetry, respectively. All single and doubleexcitations from these CASSCF configurations were

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TABLE IV	S. Stern					
Quasi-bound	levels	of the	² Σ ⁺	state	of the	SiH ²⁺ .

Levels	E (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)
$v = 0, J = 0^{-1}$	- 470.8	œ	0
$\nu = 0, J = 1$	481.8	0	0
$\nu = 0, J = 2$	503.9	∞	0
$\nu = 1, J = 0$	1353:0	00	0
$\nu = 1, J = 1$	1363.2	00	0
$\nu = 1, J = 2$	1383.8	8	0
v = 2, J = 0	2188.7	∞	0
v = 2, J = 1	2198.4	∞	0
v = 2, J = 2	2217.7	8	.0
v = 3, J = 0	2987.3	8	0
v = 3, J = 1	2996.4	∞	0
v = 3, J = 2	3014.7	∞	0
v = 4, J = 0	3751.1	∞	0
v = 4, J = 1	3759.8	00	0
v = 4, J = 2	3777.1	80	0 -
v = 5, J = 0	4480.5	8	0
v = 5, J = 1	4488.7	œ	0
v = 5, J = 2	4505.2	•	0
v = 6, J = 0	5174.7	8	0
v = 6, J = 1	5182.5	∞	Ō
v = 6, J = 2	5198.1	∞	Ō
v = 0, v = 2 v = 7, l = 0	5832.1	∞	Ō
v = 7, 0 = 0 v = 7, l = 1	5839.5	œ ⁻	õ
v = 7, 0 = 1	5854.2	00	0
v = 1, 0 = 2	6450.9	80	Ő
v = 0, J = 0	6457.8	~ ~	ő
$\nu = 0, J = 1$	6471 7	0	Ő
v = 0, J = 2	7029.0	~	ŏ
v = 9, J = 0	7020.9	~	õ
$\nu = 9, J = 1$	7035.5	~	õ
v = 9, J = 2	7562 7	~	0
$\nu = 10, J = 0$	7560.7	~	• •
$\nu = 10, J = 1$	7509.7	~ ~	ŏ
v = 10, J = 2	2051.0	0.17 - 10+10	0 30 × 10 - 20
$\nu = 11, J = 0$	8051.0	0.16 × 10+10	0.30×10^{-20}
$\nu = 11, J = 1$	0007.2	0.10×10	0.35×10^{-20}
$\nu = 11, J = 2$	0000.4	$0.13 \times 10^{+5}$	0.40×10^{-15}
$\nu = 12, J = 0$	0409.3	$0.52 \times 10^{+5}$	0.10 × 10
$\nu = 12, J = 1$	0494.4	$0.47 \times 10^{+5}$	0.11 × 10
$\nu = 12, J = 2$	8504.0	0.40×10^{-1}	0.13 × 10
$\nu = 13, J = 0$	8872.1	$0.30 \times 10^{+1}$	0.18 × 10
$\nu = 13, J = 1$	8876.7	0.27×10^{-1}	0.19 × 10
$\nu = 13, J = 2$	8885.8	0.23×10^{-3}	0.23 × 10
$\nu = 14, J = 0$	9194.3	0.40×10^{-3}	0.13×10^{-7}
$\nu = 14, J = 1$	9198.3	0.37×10^{-3}	0.14×10^{-7}
$\nu = 14, J = 2$	9206.3	0.32×10^{-3}	0.17×10^{-4}
$\nu = 15, J = 0$	9448.3	0.22 × 10 -5	0.24 × 10 4
$\nu = 15, J = 1$	9451.6	0.21 × 10 ⁻⁶	0.26 × 10 4
$\nu = 15, J = 2$	9458.2	0.18 × 10 ⁻⁰	0.29 × 10 ⁻⁴
$\nu = 16, J = 0$	9645.4	0.10 × 10 ⁻⁸	0.52 × 10 ⁻²
$\nu = 16, J = 1$	9648.3	0.98×10^{-9}	0.54×10^{-2}
$\nu = 16, J = 2$	9654.2	0.88×10^{-9}	0.60 × 10 ⁻²
$\nu = 17, J = 0$	9834.0	0.29 × 10 ⁻¹¹	1.8363
$\nu = 17, J = 1$	9837.6	0.27×10^{-11}	1.9879
$\nu = 17, J = 2$	9843.0	0.23 × 10 ***	2.3411

Levels	E (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)
$\nu=0, \ J=0$	445.8	œ	0
v = 0, J = 1	453.5	00	0
v = 0, J = 2	468.8	00	0
$\nu 1, J = 0$	1313.4	8	0
v = 1, J = 1	1320.8	80	0
$\nu = 1, J = 2$	1335.6	8	0
v = 2, J = 0	2141.3	$0.35 \times 10^{+8}$	0.15×10^{-18}
$\nu = 2, J = 1$	2148.5	$0.32 \times 10^{+8}$	0.16×10^{-18}
v = 2, J = 2	2162.7	$0.29 \times 10^{+8}$	0.19×10^{-18}
$\nu = 3, J = 0$	2928.7	$0.49 \times 10^{+3}$	0.11×10^{-13}
$\nu = 3, J = 1$	2935.5	$0.46 \times 10^{+3}$	0.11×10^{-13}
$\nu = 3, J = 2$	2949.1	$0.42 \times 10^{+3}$	0.13×10^{-13}
v = 4, J = 0	3672.8	0.26×10^{-1}	0.21×10^{-9}
v = 4, J = 1	3679.3	0.25×10^{-1}	0.22×10^{-9}
v = 4, J = 2	3692.2	0.22×10^{-1}	0.24×10^{-9}
v = 5, J = 0	4372.0	0.45×10^{-5}	0.12×10^{-5}
$\nu = 5, J = 1$	4378.1	0.43×10^{-5}	0.12×10^{-5}
$\nu = 5, J = 2$	4390.3	0.40×10^{-5}	0.13×10^{-5}
$\nu = 6, J = 0$	5016.7	0.28×10^{-8}	0.19×10^{-2}
$\nu = 6, J = 1$	5022.4	0.27×10^{-8}	0.20×10^{-2}
$\nu = 6, J = 2$	5033.7	0.25×10^{-8}	0.21×10^{-2}
$\nu = 7, J = 0$	5604.4	0.69×10^{-11}	0.76516
$\nu = 7, J = 1$	5610.0	0.67×10^{-11}	0.78725
$\nu = 7, J = 2$	5620.3	0.64×10^{-11}	0.83297
$\nu = 8, J = 0$	6174.9	0.12×10^{-12}	44.597
$\nu = 8, J = 1$	6180.1	0.12×10^{-12}	45.074
v = 8, J = 2	6190.4	0.12×10^{-12}	46.041

then included in the MRCISD calculations, giving 109,999 (${}^{1}\Sigma^{+}$), 109,999 (${}^{3}\Pi_{r}$), 155,661 (${}^{3}\Sigma^{-}$), 105,235 (${}^{1}\Delta$), and (${}^{1}\Pi$) MRCISD configurations, respectively. Davidson's corrections were added to the MRCISD energies, giving the potential energy curves presented in Figure 4.

In accordance with the previous ab initio calculations, we found ${}^{1}\Sigma^{+}(1\sigma^{2}2\sigma^{2})$, ${}^{3}\Pi(1\sigma^{2}2\sigma^{1}1\pi^{1})$ and ${}^{1}\Pi$ $(1\sigma^{2}2\sigma^{1}1\pi^{1})$ low-lying quasi-bound potential energy curves and determined that the ${}^{3}\Sigma^{+}$ $(1\sigma^{2}2\sigma^{1}3\sigma^{1})$ state has an attractive potential energy curve. The ${}^{1}\Delta$ state has a purely repulsive potential energy curve.

The lowest $X^{1}\Sigma^{+}$ state has a minimum at $R_{\min} = 1.470$ Å and a barrier at $R_{\max} = 3.373$ Å with a barrier height of $E^{\#} = 64.2$ kcal/mol. The MRCISD wave function of this state is well represented by the Hartree-Fock wave function ($C_{\text{HF}} = 0.96-0.95$) in the minimum region R = 1.0-2.0 Å. At the barrier region, a second configuration $C(1\sigma^{2}3\sigma^{2}) = -(0.15-0.21)$ begins to contribute to

TABLE VI	and the second	i siyas	- service products described and services	
Quasi-bound levels	of the	¹ Σ ⁺	state of PH2+.	

Levels	E (cm ⁻¹)	Lifetime (s)	Width (cm $^{-1}$)
$\nu = 0, J = 0$	989.7	8	0
$\nu = 0, J = 1$	1,005.6	00	0
$\nu = 0, J = 2$	1,037.5	∞	0
$\nu = 1, J = 0$	3,051.6	8	0
$\nu = 1, J = 1$	3,067.0	∞	0
$\nu = 1, J = 2$	3,097.7	∞	0
$\nu = 2, J = 0$	5,020.7	∞	0
v = 2, J = 1	5,035.6	8	0
v = 2, J = 2	5,065.2	œ	0
v = 3, J = 0	6,900.5	00	0
v = 3, J = 1	6,914.8	∞	0
$\nu = 3, J = 2$	6,943.2	∞	0
v = 4, J = 0	8,695.8	00	0
v = 4, J = 1	8,709.5	8	0
$\nu = 4, J = 2$	8.736.7	00	0
$\nu = 5, J = 0$	10,409.7	00	0
v = 5, J = 1	10,422.7	œ	0
v = 5, J = 2	10.448.7	00	0
v = 6, J = 0	12.041.7	∞	0
v = 6, J = 1	12.054.0	∞ .	0
v = 6, J = 2	12.078.7	00	0
v = 7, J = 0	13.592.1	8	Ō
v = 7, J = 1	13.603.8	8	Ō
v = 7, J = 2	13.627.1	8	0
v = 8, J = 0	15.059.1	. co	ō
v = 8, J = 1	15.070.1	8	Ō
v = 8, J = 2	15.092.1	∞	0
v = 9, J = 0	16,440.5	00	0
v = 9, J = 1	16,450.8		0
v = 9, l = 2	16 471.5	∞	Ő
$v = 10 \ J = 0$	17 733 5	$0.31 \times 10^{+8}$	0.17×10^{-18}
v = 10, J = 1	17 743 3	$0.29 \times 10^{+8}$	0.18×10^{-18}
v = 10, J = 2	17 762 7	$0.24 \times 10^{+8}$	0.22×10^{-18}
v = 10, v = 2 v = 11, J = 0	18 934 8	$0.31 \times 10^{+2}$	0.17×10^{-12}
v = 11, J = 1	18 943 9	$0.29 \times 10^{+2}$	0.18×10^{-12}
v = 11, J = 2	18 962 1	$0.25 \times 10^{+2}$	0.21×10^{-12}
v = 12, J = 0	20.038.5	0.24×10^{-3}	0.22×10^{-7}
v = 12, v = 0 v = 12, J = 1	20,000.0	0.23×10^{-3}	0.23×10^{-7}
v = 12, l = 2	20.063.9	0.20×10^{-3}	0.26×10^{-7}
v = 13, J = 0	21 033 5	0.12 × 10 ⁻⁷	043 × 10-3
v = 13, J = 1	21 041 3	0.12 × 10 ⁻⁷	0.45 × 10-3
y = 13, l = 2	21 056 8	0.11 × 10-7	0.49 × 10-3
v = 10, 0 = 2	21,000.0	0.45 × 10-11	1 1864
v = 14, 0 = 0 v = 14, 1 = 1	21,091.9	0.43 × 10-11	1 2264
v = 14, J = 2	21 912 5	0.41 × 10 ⁻¹¹	1 3107
- 17, 0 - 2	21,012.0	0.41 ~ 10	1.0107

the MRCISD wave function, while $C_{\rm HF} = 0.95-0.86$. Finally, when R > 3.0 Å, in the region past the barrier, the contribution from the second configuration decreases and two other configurations $C(1\sigma^21\pi_x^2) = C(1\sigma^21\pi_y^2) = -(0.15-0.38)$ con-

TABLE VII _____ Quasi-bound levels of the ³II state of PH²⁺.

Levels	E (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)
v = 0, J = 0	462.9	0.2 × 10 ⁺¹	0.2 × 10 ⁻¹¹
v = 0, J = 1	473.9	$0.2 \times 10^{+1}$	0.2×10^{-11}
v = 0, J = 2	495.7	$0.2 \times 10^{+1}$	0.3×10^{-11}
v = 1, J = 0	1384.7	0.6×10^{-4}	0.9×10^{-7}
$\nu = 1, J = 1$	1395.0	0.5×10^{-4}	0.9×10^{-7}
$\nu = 1, J = 2$	1415.5	0.5×10^{-4}	0.1×10^{-6}
$\nu = 2, J = 0$	2237.4	0.8×10^{-8}	0.7×10^{-3}
v = 2, J = 1	2246.9	0.8×10^{-8}	0.7×10^{-3}
v = 2, J = 2	2265.9	0.7×10^{-8}	0.8×10^{-3}
v = 3, J = 0	2995.1	0.5×10^{-11}	1.0
$\nu = 3, J = 1$	3003.7	0.5×10^{-11}	1.1
$\nu = 3, J = 2$	3020.8	0.5×10^{-11}	1.1

tribute to the MRCISD wave function. The behavior of the wave function along the dissociation coordinate reflects the avoided crossing between two ${}^{1}\Sigma^{+}$ states. Because of the high barrier, this state has 15 quasi-bound vibrational levels. Senekowitsch et al. [10d] also found 15 quasi-bound vibrational states for this state. The first 10 states have very large lifetimes. Between $\nu = 10$ and $\nu = 11$, a crossing between the ground ${}^{1}\Sigma^{+}$ and the first excited ${}^{3}\Pi$ potential energy curves occurs. Nonadiabatic coupling in this region could further decrease the lifetimes of the quasi-bound levels in this energy region. However, because of the long lifetimes of the lowest vibrational levels of the

TABLE VIII

Quasi-bound	levels of the	'II state	of PH ²⁺ .

Levels	E (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)
v = 0, J = 0	415.4	0.8 × 10 ⁺⁰³	0.7 × 10 ⁻¹⁴
v = 0, J = 1	424.2	$0.8 \times 10^{+03}$	0.7×10^{-14}
v = 0, J = 2	441.7	$0.7 \times 10^{+03}$	0.8×10^{-14}
v = 1, J = 0	1235.5	0.2×10^{-01}	0.3×10^{-09}
v = 1, J = 1	1243.8	0.2×10^{-01}	0.3×10^{-09}
$\nu = 1, J = 2$	1260.6	0.2×10^{-01}	0.3×10^{-09}
v = 2, J = 0	2017.4	0.2×10^{-05}	0.2×10^{-05}
$\nu = 2, J = 1$	2025.3	0.2×10^{-05}	0.2×10^{-05}
v = 2, J = 2	2041.1	0.2×10^{-05}	0.3×10^{-05}
v = 3, J = 0	2750.2	0.8×10^{-09}	0.6×10^{-02}
v = 3, J = 1	2757.5	0.8×10^{-09}	0.7×10^{-02}
v = 3, J = 2	2772.0	0.8×10^{-09}	0.7×10^{-02}
v = 4, J = 0	3400.2	0.1×10^{-11}	4.1
v = 4, J = 1	3406.6	0.1 × 10 ⁻¹¹	4.2
v = 4, J = 2	3419.4	0.1×10^{-11}	4.5



FIGURE 4. Total energies (au) for lowest five states of PH²⁺.

ground electronic state, it should be amenable to experimental study.

The excited ${}^{3}\Pi$ state has a minimum at $R_{\min} =$ 1.763 Å and the barrier at $R_{\text{max}} = 2.835$ Å with a barrier height of $E^{\#} = 10.0$ kcal/mol. We found four quasi-bound levels inside the local minimum of the ³ Π state, with the $\nu = 0$ level having a 2 s tunneling lifetime. Senekowtsch et al. [10d] also found four quasi-bound vibrational levels for this state with vibrational frequencies somewhat higher than ours and with lifetimes somewhat longer than ours. Because the vibrational levels for this state are located below the top of the barrier of the ground electronic state, the results for lifetimes should be viewed as preliminary. Nonadiabatic interactions between the vibrational-rotational levels of the ${}^{1}\Sigma^{+}$ and ${}^{3}\Pi$, states may cause perturbations.

The excited ¹II state has a minimum at $R_{min} =$ 1.984 Å and a barrier at $R_{max} = 3.181$ Å with a barrier height $E^{\#} = 10.6$ kcal/mol. In our calculations, we found that this state supports five quasibound vibrational states. Senekowtsch et al. [10d] found six quasi-bound vibrational levels for this state with vibrational frequencies somewhat higher than ours and with lifetimes somewhat longer than ours. However, in both calculations, the ground vibrational state has a substantial lifetime and, thus, could be experimentally observed.

The experimental ion fragmentation signal corresponding to the reaction $PH^{2+} \rightarrow P^+ + H^+$ reaction is expected to have a composite nature with three distinct peaks corresponding to kinetic en-

ergy releases of $T_h = 4.1$ eV, $T_h = 3.8$ eV, and $T_{h} = 3.6$ eV. The first peak can be considered in terms of two reverse reactions: P^+ (³P) + $H^+ \rightarrow$ PH^{2+} ($^{1}\Sigma^{+}$) and P^{+} (^{3}P) + $H^{+} \rightarrow PH^{2+}$ ($^{3}\Pi$), the first reaction occurring through the nonadiabatic coupling of ${}^{1}\Sigma^{+}$ and ${}^{3}\Pi$ potential energy curves at R = 2.6 Å, while the second reaction is adiabatic. Both have essentially the same kinetic energy release (4.1 eV) because the crossing between the two curves occurs near the top of the barrier of the ${}^{3}\Pi$ potential energy curve. The second and third peaks with kinetic energy releases of 3.8 and 3.6 eV are adaibatic in nature and correspond to $^{1}\Pi$ and ${}^{1}\Sigma$ PH²⁺ fragmenting to P⁺ (${}^{1}D$) + H⁺, respectively. Experimental vertification of our predicitions would be welcomed.

SH2+

This dication was studied both experimentally [11a] and theoretically, [11b, c] in high-quality CASSCF and CASSCF-MRCISD calculations with

and

$$(14s11p4d1f/10s9p4d1f)_{s}$$

$$(8s3p1d/6s3p1d)_{H}$$

basis sets, Miller et al. [11c] found only one $X^2\Pi$ metastable state with $R_{min} = 1.466$ Å, $R_{max} = 2.656$ Å, a dissociation barrier of 35.1 kcal/mol (1.52 eV), and a dissociation energy of $D_e = -3.11$ eV. No other metastable states for energies up to 10 eV above the ground state were found at the

CASSCF-MRCISD level. However, at the CASSCF level, three ${}^{2}\Pi$, ${}^{2}\Sigma^{-}$, and ${}^{4}\Sigma^{-}$ states were found to be metastable. Miller et al. [11c] also calculated metastable vibrational levels inside the $X^{2}\Pi$ local minimum using a CASSCF-MRCISD potential energy curve. They found seven vibrational levels below the barrier. The four lowest vibrational levels below the barrier. The four lowest vibrational levels have very long tunneling lifetimes. However, the $X^{2}\Pi$, electronic state is crossed by a ${}^{4}\Sigma^{-}$ state in the region of its n = 2-7 vibrational levels, which should lead to shorter lifetimes for these levels.

We repeated ab initio calculations on the lowest $X^2 \Pi_r$ $(1\sigma^2 2\sigma^2 1\pi^1)$, ${}^4\Sigma^ (1\sigma^2 1\pi^2 2\sigma^1)$, ${}^2\Sigma^ (1\sigma^2 1\pi_x^2 2\sigma^1 - 1\sigma^2 1\pi_y^2 2\sigma^1)$, and ${}^2\Pi_i$ $(1\sigma^2 1\pi^3)$ electronic states using the CASSCF-MRCISD(Q) method and

$$(17s12p5d4f/7s7p5d4f)_{s}$$

and

$$(8s4p3d/6s4p3d)_{H}$$

basis sets. The CASSCF expansion included 470 (${}^{2}\Pi_{r}$), 484 (${}^{2}\Sigma^{-}$), 264 (${}^{4}\Sigma^{-}$), and 470 (${}^{2}\Pi_{i}$) configurations, which represent all possible distributions of all five valence electrons among (4, 2, 2, 1) active orbitals, respectively, of a_{1} , b_{1} , b_{2} , and $a_{2}C_{2v}$ symmetry. All single and double excitations from these

CASSCF configurations were than included in the MRCISD calculations, giving 733,618 (${}^{2}\Pi_{r}$), 735,826 (${}^{2}\Sigma^{-}$), 528,504 (${}^{4}\Sigma^{-}$), and 733,618 (${}^{2}\Pi_{i}$) MRCISD configurations. Davidson's corrections were added to the MRCISD energies, yielding the potential energy curves shown in Figure 5.

In accordance with the results of Miller et al. [11c], we found only one $X^2 \Pi_i$ quasi-bound potential energy curve with the S^+ (2D) + H^+ dissociation limit (Table IX). Our parameters ($R_{\min} = 1.442$ Å, $R_{\max} = 2.658$ Å, $E^{\#} = 34.2$ kcal/mol, $D_e = 3.05$ eV) are very close to results obtained at the CASSCF-MRCISD level by Miller et al. [11c] (see above).

In our calculations of the metastable vibrational levels inside the local minimum of the $X^2\Pi$, electronic state, we found eight levels, as did [13c]. Our energies are 0.1–0.6% lower than those of Miller et al [11c]. However, as a result of the somewhat lower deprotonation barriers, our lifetimes of the quasi-bound states are one order of magnitude smaller than those of [13c]. We also found that the $X^2\Pi$ electronic state is crossed by a ${}^{4}\Sigma^{-}$ state near the $\nu = 3-7$ vibrational levels, as a result of which nonadiabatic interaction between these two states should lead to reduction of the lifetimes of these levels.





NEFEDOVA, BOLDYREV, AND SIMONS

TABLE IX _				S. Standing
Quasi-bound	levels o	f the $^{2}\Pi$	state of	SH2+.

Levels	E (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)
$\nu = 0, J = 0$	993.0		0
$\nu = 0, J = 1$	1,009.4		0
$\nu = 0, J = 2$	1,042.2		0
$\nu = 1, J = 0$	2,912.6		0
$\nu = 1, J = 1$	2,928.2		0
$\nu = 1, J = 2$	2,959.4		0
v = 2, J = 0	4,723.2	$1.0 \times 10^{+13}$	0.5×10^{-24}
$\nu = 2, J = 1$	4,738.0	$0.9 \times 10^{+13}$	0.6×10^{-24}
$\nu = 2, J = 2$	4,767.5	$0.7 \times 10^{+13}$	0.7×10^{-24}
$\nu = 3, J = 0$	6,411.8	$1.0 \times 10^{+6}$	0.6×10^{-17}
$\nu = 3, J = 1$	6,425.7	$0.9 \times 10^{+6}$	0.6×10^{-17}
$\nu = 3, J = 2$	6,453.7	$0.8 \times 10^{+6}$	0.7×10^{-17}
$\nu = 4, J = 0$	7,970.5	1.0	0.5×10^{-11}
$\nu = 4, J = 1$	7,983.6	1.0	0.5×10^{-11}
v = 4, J = 2	8,009.8	0.9	0.6×10^{-11}
v = 5, J = 0	9,392.4	0.9×10^{-5}	0.6×10^{-6}
$\nu = 5, J = 1$	9,404.5	0.9×10^{-5}	0.6×10^{-6}
$\nu = 5, J = 2$	9,428.7	0.8×10^{-5}	0.7×10^{-6}
v = 6, J = 0	10,654.8	0.5×10^{-9}	0.1×10^{-1}
$\nu = 6, J = 1$	10,665.8	0.5×10^{-9}	0.1×10^{-1}
$\nu = 6, J = 2$	10,687.7	0.5×10^{-9}	0.1×10^{-1}
$\nu = 7, J = 0$	11,686.5	0.3×10^{-12}	16.0
$\nu = 7, J = 1$	11,695.8	0.3×10^{-12}	16.5
$\nu = 7, J = 2$	11,714.2	0.3×10^{-12}	17.4

The experimental fragmentation kinetic energy signal corresponding to the reaction $SH^{2+} \rightarrow S^+ +$ H⁺ should have a composite nature with two distinct peaks having kinetic energy releases of $T_h = 4.5$ and 5.5 eV, corresponding, respectively, to reverse activation energies for: $S^+(^2D) + H^+ \rightarrow$ $SH^{2+}(^{2}\Pi)$ and $S^{+}(^{4}S) + H^{+} \rightarrow SH^{2+}(^{2}\Pi)$, respectively. The second reaction involves coupling of the ${}^{4}\Sigma^{-}$ and ${}^{2}\Pi$ potential energy curves at the R = 1.8 Å and, therefore, the kinetic energy release is calculated as the energy difference between SH^{2+} at the crossing of ${}^{4}\Sigma^{-}$ and ${}^{2}\Pi$ potential energy curves and the energy of the dissociation limit $[S^+({}^4S) + H^+]$. However, the intensities of these peaks may be different due to the different nature (adiabatic and nonadiabatic) of these reactions.

CIH²⁺

This dication was extensively studied experimentally [12a-f] and theoretically [12f-h]. Curtis and Eland [12e] experimentally observed ClH²⁺ and found kinetic energy released for the process

 $ClH^{2+} \rightarrow Cl^+ + H^+$ to be 6.4 \pm 1.1 eV. Olsson and Larsson [12g] performed CASSCF-CI calculations using $(14s10p5d/7s5p3d)_{CI}$ and $(9s4p1d/4s3p1d)_{H}$ basis sets for the ${}^{3}\Sigma^{-}$, ${}^{1}\Delta$, and ${}^{3}\Pi$ states. The ${}^{3}\Sigma^{-}$ and Δ states were found to process local minima above the thermodynamic limit for dissociation; the 'II state was found to be purely repulsive. Banichevich et al. [12h] performed extensive MRDCI calculations on low-lying electronic states using $(/8s6p4d1f)_{CI} + (/5s2p)_{H}$ basis sets. They found three low-lying quais-bound potential energy curves corresponding to $X^{3}\Sigma^{-}$, $^{1}\Delta$, and $^{1}\Sigma^{+}$ electronic states, and they found a ${}^5\Sigma^-$ state that possesses a minimum below its dissociation limit. The low-lying ${}^{1}\Pi$ and ${}^{3}\Pi$ states were found to be repulsive. Banichevich et al. [12h] found three quasi-bound vibrational levels for both the $X^{3}\Sigma^{-}$ and $^{1}\Delta$ states and two quasi-bound vibrational levels for the ${}^{1}\Sigma^{+}$ state.

We repeated ab initio calculations for the lowest $X^{3}\Sigma^{-}$ $(1\sigma^{2}2\sigma^{2}\pi^{2}), \ ^{3}\Pi_{i}$ $(1\sigma^{2}1\pi^{3}2\sigma^{1}), \ ^{1}\Sigma^{+}$ $(1\sigma^2 1\pi^4)$, ${}^{1}\Delta (1\sigma^2 2\sigma^2 1\pi^2)$, and ${}^{1}\Pi (1\sigma^2 1\pi^3 2\sigma^1)$ electronic states using the CASSCF-MRCISD(Q) method and $(17s12p5d4f/7s7p5d4f)_{CI}$ and (8s4p3d/6s4p3d)_H basis sets. The CASSCF expansion included 378 $(^{3}\Sigma^{-})$, $(^{3}\Pi_{1})$, 318 $(^{1}\Sigma^{+})$, $(^{1}\Delta)$, and 288 ($^{1}\Pi$) configurations, which represent all possible distributions of all six valence electrons among (3, 2, 2, 1) active orbitals, of a_1 , b_1 , b_2 , and $a_2 C_{2n}$ symmetry. All single and double excitations from these CASSCF configurations were then included in the MRCISD calculations, giving 1,517,112 (${}^{3}\Sigma^{-}$), $({}^{3}\Pi_{i})$, 9337,842 $({}^{1}\Sigma^{+})$, $({}^{1}\Delta)$, and 935,340 $({}^{1}\Pi)$ MRCISD configurations, respectively. Davidson's corrections were added to the MRCISD energies.

In agreement with the results of Banichevich et al. [12h], we found quasi-bound potential energy curves for the $X^{3}\Sigma^{-}$, ${}^{1}\Delta$, and ${}^{1}\Sigma^{+}$ states (see Fig. 6 and Tables X–XII); the ${}^{1}\Pi$ and ${}^{3}\Pi$ states have purely repulsive potential energy curves.

The $X^{3}\Sigma^{-}$ ground electronic state has a local minimum at $R_{\min} = 1.458$ Å, a barrier at $R_{\max} =$ 2.231 Å, and a barrier height of $E^{*} = 13.0$ kcal/mol. Three quasi-bound vibrational levels were found for this state. The lifetime is 0.05 s for the ground vibrational state and a one-tenth of microsecond for the first vibrational state. Our calculated kinetic energy release for

$ClH^{2+} \rightarrow Cl^+(^{3}P) + H^+$

is 5.0 eV, which is substantially less than the experimentally observed value 6.4 ± 1.1 eV by

Curtis and Eland [12e], but these experimental results using the PIPICO [12a] method are difficult to interpret due to large uncertainties in the measurement of the energy release obtained by detection of the ionic fragments $Cl^+ + H^+$ in coincidence.

The ${}^{1}\Delta$ excited state has a local minimum at $R_{\min} = 1.455$ Å, a barrier at $R_{\max} = 2.204$ Å, and a barrier height of $E^{\#} = 12.4$ kcal/mol. Three quasi-bound vibrational levels have also been found for this state and the lifetime is 0.007 s for the ground vibrational state.

The ${}^{1}\Sigma^{+}$ excited state has a local minimum at $R_{\min} = 1.470$ Å, a barrier at $R_{\max} = 2.057$ Å, and a barrier height of $E^{\#} = 7.8$ kcal/mol. Only two quasi-bound vibrational levels have been found for this state; the lifetime is 0.01 μ s for the ground vibrational state. Fournier et al. [12f] proposed that the ${}^{1}\Sigma^{+}$ state with its Cl⁺ (${}^{1}D$) + H⁺ dissociation limit and 6.3 eV kinetic-energy release during fragmentation may explain the PIPICO [12a] findings mentioned earlier in this section.

ArH2+

We were not able to find experimental or theoretical data on this dication in the literature.

We studied two electronic states ${}^{2}\Sigma^{+}(1\sigma^{2}1\pi^{4}2\sigma^{1})$ and ${}^{2}\Pi(1\sigma^{2}1\pi^{4}2\sigma^{1})$ (Fig. 7) which have the same dissociation limit Ar⁺ (${}^{2}P$) + H⁺, because the 2σ and 1π -MOs become degenerate at large internuclear distances. These calculations were carried out using the CASSCF-MRCISD(Q) method and

$$(17s12 p5d4f/7s7p5d4f)_{\rm Ar}$$

and

$$(8s4p3d/6s4p3d)_{\rm H}$$

basis sets. The CASSCF expansion included 57 (${}^{2}\Sigma^{+}$) and 51 (${}^{2}\Pi$) configurations, which represent all possible distributions of all seven valence electrons among (3, 1, 1, 1) active orbitals of a_1 , b_1 , b_2 , and a_2C_{2v} symmetry. All single and double excitations from these CASSCF configurations were then included in MRCISD calculations, giving the 679,996 (${}^{2}\Sigma^{+}$) and 655,916 (${}^{2}\Pi$) MRCISD configurations. Davidson's corrections were added to the MRCISD energies.

The ${}^{2}\Sigma^{+}$ state with the σ -orientation of the hole in Ar atom has a purely repulsive potential energy curve. The ${}^{2}\Pi$ state with π -orientation of the hole has a very shallow minimum at $R_{\min} = 1.54$ Å and a barrier at $R_{\max} = 1.61$ Å with a height of $E^{\#} =$





Quasi-bound levels of the ${}^{3}\Sigma^{-}$ state of CIH ²⁺ .				
Levels	<i>E</i> (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)	
$\nu = 0, J = 0$	778.0	0.5×10^{-1}	0.1 × 10 ⁻⁹	
$\nu = 0, J = 1$	793.7	0.5×10^{-1}	0.1×10^{-9}	
$\nu = 0, J = 2$	825.1	0.4×10^{-1}	0.1×10^{-9}	
$\nu = 1, J = 0$	2369.0	0.1×10^{-6}	0.4×10^{-4}	
$\nu = 1, J = 1$	2383.2	0.1×10^{-6}	0.4×10^{-4}	
$\nu = 1, J = 2$	2411.7	0.1×10^{-6}	0.5×10^{-4}	
$\nu = 2, J = 0$	3729.4	0.6×10^{-11}	0.9	
$\nu = 2, J = 1$	3741.9	0.6×10^{-11}	0.9	
$\nu=2,\;J=2$	3766.6	0.5 × 10 ⁻¹¹	1.0	

TABLE X

0.6 kcal/mol. However, we are not able to find any quasi-bound vibrational levels inside this minimum. The MRCISD wave functions for both states are well represented by Hartree-Fock wave functions: $C_{\rm HF} = 0.97 (^2 \Sigma^+ \text{ and } ^2 \Pi)$ in the region R =1.0-10.0 Å.

Overview

In previous publications [21] we showed that the isoelectronic principle [22], which is widely used in chemistry, does not work well for certain diatomic molecules. However, in the case of AH, AH⁺, and AH²⁺, this principle works rather well. Starting from the conventional valence MO $1\sigma <$ $2\sigma < 1\pi$ ordering for the AH diatomic molecules, one predicts the following ground electronic states for 1–8 valence electrons: ${}^{2}\Sigma^{+}$ (1 σ^{1}), ${}^{1}\Sigma^{+}$ (1 σ^{1}), $^{2}\Sigma^{+}$ $(1\sigma^{2}2\sigma^{1}), ^{1}\Sigma^{+}$ $(1\sigma^{2}2\sigma^{2}), ^{2}\Pi, (1\sigma^{2}2\sigma^{2}1\pi^{1}),$ ${}^{3}\Sigma^{-}$ $(1\sigma^{2}2\sigma^{2}1\pi^{2})$, ${}^{2}\Pi_{i}$ $(1\sigma^{2}2\sigma^{2}1\pi^{3})$, and ${}^{1}\Sigma^{+}$ $(1\sigma^2 2\sigma^2 1\pi^4)$. Indeed, we find that all AH, AH⁺ (the ground electronic states and configurations for

TABLE XI				
Quasi-bound levels	of the	1Δ	state of CIH2+.	

Levels	E (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)	
v = 0, J = 0	750.9	0.7×10^{-2}	0.7 × 10 ⁻⁹	
v = 0, J = 1	766.8	0.7×10^{-2}	0.8×10^{-9}	
$\nu = 0, J = 2$	798.6	0.6×10^{-2}	0.9×10^{-9}	
$\nu = 1, J = 0$	2288.0	0.3×10^{-7}	0.2×10^{-3}	
$\nu = 1, J = 1$	2302.7	0.3×10^{-7}	0.2×10^{-3}	
$\nu = 1, J = 2$	2332.0	0.3×10^{-7}	0.2×10^{-3}	
$\nu = 2, J = 0$	3576.7	0.4×10^{-11}	1.5	
$\nu = 2, J = 1$	3589.7	0.3×10^{-11}	1.6	
v = 2, J = 2	3615.7	$0.3 imes 10^{-11}$	1.7	

Juasi-bound	level of the	¹ Σ ⁺	state of CIH2+.
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Levels	E (cm ⁻¹)	Lifetime (s)	Width (cm ⁻¹)
$\nu = 0, J = 0$	733.6	0.1 × 10 ⁻⁷	0.4×10^{-3}
$\nu = 0, J = 1$	749.2	0.1×10^{-7}	0.5×10^{-3}
$\nu = 0, J = 2$	780.2	0.1×10^{-7}	0.5×10^{-3}
$\nu = 1, J = 0$	2081.7	0.1×10^{-11}	3.9
$\nu = 1, J = 1$	2095.4	0.1×10^{-11}	4.0
$\nu = 1, J = 2$	2122.8	0.1×10^{-11}	4.3

AH and AH⁺ were taken from [23]), and AH²⁺ (A = Na - Ar) species have the ground electronic states that are expected based on the above MO ordering:

NaH⁺, MgH²⁺ [$^{2}\Sigma^{+}$ (1 σ^{1})], NaH, MgH⁺, AlH²⁺ [$^{1}\Sigma^{+}$ (1 σ^{2})], MgH, AlH⁺, SiH²⁺ [$^{2}\Sigma^{+}$ (1 $\sigma^{2}2\sigma^{1}$)], AlH, SiH⁺, PH²⁺ [${}^{1}\Sigma^{+}$ (1 $\sigma^{2}2\sigma^{2}$)], SiH, PH⁺, SH²⁺ [$^{2}\Pi$, (1 $\sigma^{2}2\sigma^{2}1\pi^{1}$)], PH, SH⁺, ClH²⁺ $[^{3}\Sigma^{-} (1\sigma^{2}2\sigma^{2}1\pi^{2})]$, SH, ClH⁺, ArH²⁺ [$^{2}\Pi$, (1 $\sigma^{2}2\sigma^{2}1\pi^{3}$)], and ClH, ArH⁺ $[{}^{1}\Sigma^{+} (1\sigma^{2}2\sigma^{2}1\pi^{4})]$.

Hence, the very useful notion of isoelectronic species having the same ground states seems to hold well here. Another aspect of the isoelectronic principle was examined by Senekowitsch and ONeil who have shown that the potential energy curve of F_2^{2+} with the Coulomb repulsion term removed is very similar to the potential energy curve of the neutral isoelectronic O2 molecules [24]. Thus, we were led to speculate that one should be able to obtain the potential energy curve of the doubly charged AH2+ cation by adding the Coulomb repulsion term to the potential energy curve of the corresponding isoelectronic neutral molecule. We tested this model on PH2+ and AlH, and the results of our calculations are shown in Figure 8. As seen, the approximate PH²⁺ potential energy curve obtained as AlH + e^2/R has no local minimum and is quite different from the actual PH²⁺ curve. It is likely that the relatively weaker bonding in our AH²⁺ species, compared to that in F_2^{2+} , combined with the smaller size of H and, hence, the smaller R values involved, make the AlH + e^2/R approximation to PH²⁺ especially poor.

All the doubly charged cations studied here, except MgH2+, have short bond lengths, ranging ENERGIES AND LIFETIMES OF AH2+ (A = Mg-Ar) DIATOMICS



FIGURE 7. Total energies (au) for lowest two states of ArH2+.

from 1.442 Å for SH^{2+} to 1.739 Å for SiH^{2+} . MgH²⁺ has a very long bond length because it has only one bonding electron. Along the

series, only the σ -electrons participate in bonding. The magnitude of the (negative) dissociation energy is smallest for MgH²⁺, it increases (-50.6 kcal/mol) for AlH²⁺, then it drops (-33.1 kcal.mol) for SiH²⁺ and it decreases again (-18.7





kcal/mol) for PH²⁺. Along the rest of the series:

SH²⁺-ClH²⁺-ArH²⁺,

the 1π -MO is filling and these dications have substantially more negative dissociation energies: SH²⁺ (-114.7 kcal/mol), ClH²⁺ (-101.5 kcal/mol), and ArH²⁺ (-136.2 kcal/mol).

The deprotonation barriers have the opposite trend. The first four dications $(MgH^{2+}-PH^{2+})$ have relatively high deprotonation barriers with a maximum (64.2 kcal/mol) at PH^{2+} , while the remaining three dications $(SH^{2+}-ArH^{2+})$ have low deprotonation barriers.

The primary findings of this work in addition to the qualitative trends described above are

- The characterization of the ground- and lowenergy electronic potential energy curves for all seven AH²⁺ species.
- Determination of quasi-bound vibrational/rotational energy levels for electronic states that display barriers (and wells).
- 3. Determination of R_{\min} , $E^{\#}$, and D_e values that can guide experimental study of these dications.

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