

# Structures and Stabilities of the Dimer Dications of First- and Second-Row Hydrides

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**Abstract:** Ab initio molecular orbital theory has been used in a systematic study of the first- and second-row dimer dications  $\text{He}_2^{2+}$ ,  $\text{H}_3\text{NNH}_3^{2+}$ ,  $\text{H}_2\text{OOH}_2^{2+}$ ,  $\text{HFFH}^{2+}$ ,  $\text{Ne}_2^{2+}$ ,  $\text{H}_3\text{PPH}_3^{2+}$ ,  $\text{H}_2\text{SSH}_2^{2+}$ ,  $\text{HClClH}^{2+}$ , and  $\text{Ar}_2^{2+}$ . Although all nine systems are thermodynamically unstable with respect to symmetric fragmentation into two monocations, potential energy barriers inhibiting such fragmentations are predicted to exist for all of the dimers except  $\text{HFFH}^{2+}$ ,  $\text{Ne}_2^{2+}$ , and  $\text{Ar}_2^{2+}$ . In particular, the hydrazinium and diphosphonium dications are found to be very stable kinetically with respect to both symmetric fragmentation and deprotonation. The equilibrium A-A bond lengths in the dimer dications ( $\text{A}_2^{2+}$ ) are all significantly shorter than in the corresponding (hemibonded) monocations ( $\text{A}_2^{+}$ ), but the fragmentation barriers are usually smaller. The equilibrium structures of the dimer dications are found to be very similar to those of their isoelectronic, isostructural, neutral counterparts. The usefulness of the recently introduced  $\Delta$  parameter in understanding the stabilities and fragmentation processes of all nine dications is emphasized.

The chemistry of gas-phase dications is progressing rapidly on both theoretical and experimental fronts.<sup>1</sup> Because the total nuclear (positive) charge in such ions exceeds the total electronic (negative) charge by two electronic units, there is a very strong tendency, in almost all of these systems, for a "coulomb explosion" to occur, leading to the formation of two monocations. Despite this, many dications are metastable species whose lifetimes are sufficiently great that they may be studied experimentally. Indeed, some are even thermodynamically stable; that is, they are lower in energy than any of their possible fragmentation products and are therefore indefinitely stable in isolation.

In a previous study,<sup>2</sup> we have investigated the family of three-electron hemibonded  $\text{A}_2^{+}$  dimers where A is one of the normal-valent hydrides He,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , HF, Ne,  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ , HCl, or Ar and in which the monomeric units are bonded through the heavy atoms. We have found that the hemibond strengths in such species are remarkably strong ( $>100 \text{ kJ mol}^{-1}$ ). The formation of stable monocations of this type is not unexpected because, in ionizing a neutral  $\text{A}_2$  dimer, an electron is removed from an antibonding orbital, leading to the formation of a three-electron bond (Figure 1). For example, ionization in the  $\text{He}_2$  system changes a repulsive four-electron interaction in neutral  $\text{He}_2$  to a bonding three-electron interaction (with a formal bond order of  $1/2$ ) in  $\text{He}_2^+$ . It is natural then to inquire whether the removal of a second antibonding electron, leading to the formation of a dicationic  $\text{A}_2^{2+}$  dimer, will lead to an even stronger A-A bond (with, a formal bond order of unity, Figure 1). Although it is likely that, in some of the dications, the enhanced covalent binding may be partially offset by the substantial coulombic repulsion, which will be present in such species, the counterintuitive theoretical finding that a bond may be strengthened by effective charges on the adjacent nuclei,<sup>3</sup> and the fact that both the  $\text{He}_2^{2+}$  dication<sup>4</sup> and the  $\text{N}_2\text{H}_6^{2+}$  dication<sup>5</sup> have already been observed experimentally, encouraged us to undertake a detailed study of the complete family of  $\text{A}_2^{2+}$  dimers (where A is one of the normal-valent first- or second-row hydrides, as above).

Some of the main properties of the  $\text{A}_2^{2+}$  dimer dications, e.g. their equilibrium structures, would be expected to be well described by conventional theoretical procedures. On the other hand, it is well-known<sup>6,7</sup> that the theoretical study of the fragmentation of

Table I. Basis Set Dependence of the Calculated Equilibrium Bond Length ( $r_{\text{eq}}$ , Å), Transition Structure Bond Length ( $r_{\text{TS}}$ , Å), Dissociation Barrier ( $D_e^*$ ,  $\text{kJ mol}^{-1}$ ), and  $\Delta$  Value ( $\text{kJ mol}^{-1}$ ) for the  $\text{He}_2^{2+}$  Dication<sup>a</sup>

basis set	$r_{\text{eq}}$	$r_{\text{TS}}$	$D_e^*$	$\Delta^b$
STO-3G	c	c	c	2772
3-21G	0.719	0.999	33	2888
6-31G	0.712	1.049	75	2933
6-311G	0.736	1.071	69	2940
(10s) <sup>d</sup>	0.729	1.065	66	2943
6-311G(d,p) <sup>e</sup>	0.739	1.134	98	2903
6-311G(MC)(d,p) <sup>f</sup>	0.714	1.144	133	2895
6-311G(MC)(d,2p) <sup>f</sup>	0.706	1.142	132	2885
6-311G(MC)(d,3p) <sup>f</sup>	0.708	1.144	134	2884
6-311G(MC)(d,3pd) <sup>f,g</sup>	0.705	1.149	141	2880
6-311G(MC)(d,3p2d) <sup>f,g</sup>	0.704	1.148	141	2879
6-311G(MC)(d,3p2d1f) <sup>f,h</sup>	0.704	1.149	142	2878
exact <sup>i</sup>	0.703	1.151	145	2878

<sup>a</sup>All values calculated at the full-CI level. <sup>b</sup>Defined by eq 2; see text. <sup>c</sup>The potential surface is dissociative at this level of theory. <sup>d</sup>A large uncontracted basis<sup>24</sup> without polarization functions. <sup>e</sup>Based on a p exponent of 0.750; see ref 14. <sup>f</sup>Based on a p exponent of 1.366; see ref 21. <sup>g</sup>Based on a d exponent of 2.000; see ref 19. <sup>h</sup>Based on an f exponent of 2.000. <sup>i</sup>See ref 20.

dications poses a number of additional difficulties, which we have discussed in detail in a series of recent papers.<sup>8-13</sup> We have suggested a number of novel modifications<sup>9,11,12</sup> of contemporary procedures, and we employ these throughout the present paper.

## Method and Results

Standard ab initio molecular orbital calculations<sup>14</sup> were carried out using modified versions<sup>15-17</sup> of the GAUSSIAN 82<sup>18</sup> and GAUSSIAN 86<sup>19</sup>

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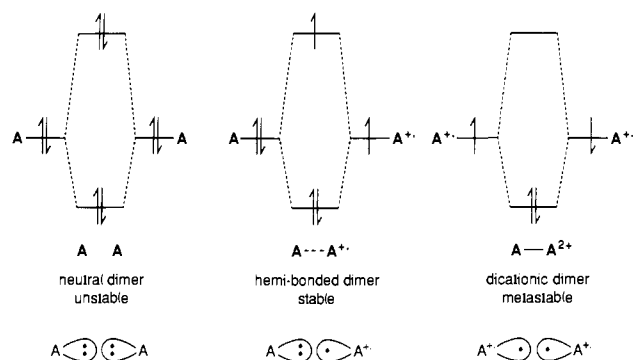


Figure 1. Molecular orbital schemes for bonding in  $A_2^{n+}$  dimers ( $n = 0-2$ ).

Table II. Correlation Dependence of the Calculated Equilibrium Bond Length ( $r_{eq}$ , Å), Transition Structure Bond Length ( $r_{TS}$ , Å), Dissociation Barrier ( $D_e^*$ , kJ mol $^{-1}$ ), and  $\Delta$  Value (kJ mol $^{-1}$ ) for the  $He_2^{2+}$  Dication<sup>a</sup>

correlation level	$r_{eq}$	$r_{TS}$	$D_e^*$	$\Delta^b$
RHF	0.677	2.186	794	<i>c</i>
RMP2	0.696	1.362	337	<i>c</i>
RMP3	0.707	1.196	199	<i>c</i>
RMP4	0.713	1.131	147	<i>c</i>
UHF	0.677	0.959	164	2972
UMP2	0.696	1.018	237	2905
UMP3	0.707	1.038	256	2891
UMP4	0.713	1.052	257	2888
TCSCF	0.719	1.127	116	2972
CISD <sup>d</sup>	0.717	1.142	130	2888

<sup>a</sup> 6-31G(d,p) basis set used. <sup>b</sup> Defined by eq 2; see text. <sup>c</sup> RMP undefined for open-shell systems. <sup>d</sup> Corresponds to full-CI for  $He_2^{2+}$ .

systems of programs. Initial calculations were performed on the prototypical  $He_2^{2+}$  and  $N_2H_6^{2+}$  dications at a variety of levels of theory in order to establish suitable levels for the treatment of the remaining systems. In particular, our results for  $He_2^{2+}$  may be compared with the essentially exact calculations of Yagisawa et al.<sup>20</sup>

Calculations were carried out on  $He_2^{2+}$  at the full-CI level with a sequence of basis sets (STO-3G, 3-21G, 6-31G, and 6-311G, the last of these augmented additionally with several choices of polarization functions). In this way, basis set effects may be examined independently of correlation effects. Moreover, the presence of only two electrons in  $He_2^{2+}$  means that only single and double excitations are possible and therefore that the normally difficult full-CI calculations are achieved by straightforward RCISD. The results are summarized in Table I.

The descriptions of dication dissociation behavior, afforded by various correlation treatments (RHF, RMP2, RMP3, RMP4, UHF, UMP2, UMP3, UMP4, TCSCF, and CISD) were then examined using both  $He_2^{2+}$  and  $N_2H_6^{2+}$  as test cases. When the same basis set is employed at all correlation levels, the effects of correlation can be assessed independently of basis set effects. The results for  $He_2^{2+}$  and  $N_2H_6^{2+}$  are summarized in Tables II and III, respectively. In Table IV, we compare the predictions by four correlation treatments (UHF, UMP2, TCSCF, and RMP4) of the length of the cleaving bond in the transition structures for the symmetric fragmentations of all of the dimer dications.

On the basis of these results and more extensive results reported previously,<sup>12</sup> geometry optimizations for the remaining systems were performed with the split-valence plus polarization 6-31G(d) basis set (the 6-31G(p) basis set with *p* exponent of 1.366 was used for  $He_2^{2+}$ )<sup>21</sup> and with electron correlation incorporated via second-order Møller-Plesset

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Table III. Correlation Dependence of the Calculated Equilibrium Bond Length ( $r_{eq}$ , Å), Transition Structure Bond Length ( $r_{TS}$ , Å), Dissociation Barrier ( $D_e^*$ , kJ mol $^{-1}$ ), and  $\Delta$  Value (kJ mol $^{-1}$ ) for the Symmetric Fragmentation of the  $N_2H_6^{2+}$  Dication<sup>a</sup>

correlation level	$r_{eq}$	$r_{TS}$	$D_e^*$	$\Delta^b$
RHF	1.442	4.779	672	<i>c</i>
RMP2	1.465	2.795	288	<i>c</i>
RMP3 <sup>d</sup>	1.464	2.713	283	<i>c</i>
RMP4 <sup>d</sup>	1.473	2.531	209	<i>c</i>
UHF	1.442	1.988	138	1376
UMP2	1.465	2.239	265	1319
UMP3 <sup>d</sup>	1.464	2.215	239	1324
UMP4 <sup>d</sup>	1.473	2.260	242	1319
TCSCF	1.488	2.497	150	1350
RCISD <sup>d</sup>	1.459	3.433	382	
UCISD <sup>d</sup>	1.459	2.247	215	

<sup>a</sup> 6-31G(d) basis set used. <sup>b</sup> Defined by eq 1; see text. <sup>c</sup> RMP undefined for open-shell systems. <sup>d</sup> Frozen-core approximation used.

Table IV. Comparison of Transition Structure A-A Bond Lengths (Å) and  $\Delta$  Values (kJ mol $^{-1}$ ) for the Symmetric Fragmentations of the  $A_2^{2+}$  Dications<sup>a</sup>

	transition structure bond length				$\Delta^{b,c}$
	UHF	UMP2	TCSCF	RMP4	
He-He <sup>2+</sup>	0.960	1.019	1.127	1.129	2904
H <sub>3</sub> N-NH <sub>3</sub> <sup>2+</sup>	1.988	2.239	2.497	2.531	1318
H <sub>2</sub> O-OH <sub>2</sub> <sup>2+</sup>	1.538	1.732	1.832	2.086	1446
HF-FH <sup>2+</sup>	<i>d</i>	1.460	<i>d</i>	1.722	<i>d</i>
Ne-Ne <sup>2+</sup>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	2204
H <sub>3</sub> P-PH <sub>3</sub> <sup>2+</sup>	3.193	3.378	3.690	<i>e</i>	840
H <sub>2</sub> S-SH <sub>2</sub> <sup>2+</sup>	2.502	2.738	2.997	3.138	1076
HCl-ClH <sup>2+</sup>	2.208	2.422	<i>d</i>	2.739	1131
Ar-Ar <sup>2+</sup>	<i>d</i>	2.159	<i>d</i>	<i>d</i>	1307

<sup>a</sup> 6-31G(d) basis set used (6-31G(p) for  $He_2^{2+}$ ; see text). <sup>b</sup> Defined by eq 1; see text. <sup>c</sup> MP2/6-31G(d) values (MP2/6-31G(p) for  $He_2^{2+}$ ; see text). <sup>d</sup> The potential surface is dissociative at this level of theory. <sup>e</sup> The convergence of the RMP4 series is not sufficiently rapid at large P-P separations to give rise to a transition structure.

(MP2) perturbation theory. Improved relative energies were obtained for these MP2/6-31G(d)-optimized (MP2/6-31G(p) for  $He_2^{2+}$ ) structures with the triple- $\zeta$  valence plus *d,p*-polarization 6-311G(MC)(d,p) basis set<sup>21</sup> and by employing full fourth-order Møller-Plesset (MP4) theory.

Harmonic vibrational frequencies were calculated at the HF/6-31G(d) level (HF/6-31G(p) for  $He_2^{2+}$ ) in order to characterize stationary points as minima (representing equilibrium structures) or saddle points (representing transition structures) and to evaluate zero-point vibrational energies. The zero-point energies were scaled by 0.9 to account for their overestimation by ~10% at this level of theory. The spin-unrestricted formalism (UHF, UMP) was used for all odd-electron species and for the geometry optimizations of transition structures linking odd- and even-electron species. It was also employed in the study of proton loss from certain of the dications. However, the degree of spin contamination in the UHF wave functions, as measured by the expectation value ( $\langle S^2 \rangle$ ) of the spin-squared operator, was found to be large (>0.6) for all of the UMP2 transition structures for symmetric cleavage of the dications, indicating thereby that spin-unrestricted (UMP) perturbation theory would display unsatisfactory convergence behavior.<sup>11-13,22</sup> For this reason, as we have previously discussed,<sup>12</sup> the MP4 single-point energies were computed within the spin-restricted (RMP) framework. The total energies of the fragment and dimer species are available as supplementary material. The resulting relative energies are given in Table V. The optimized geometries (bond lengths in angstroms and bond angles in degrees) of the equilibrium structures of the dimer dications, the transition structures for their symmetric fragmentations, the equilibrium structures of their deprotonated forms, the transition structures for their deprotonation, and the equilibrium structures of their hydrogen-abstracted forms are depicted in Figures 1-5, respectively.

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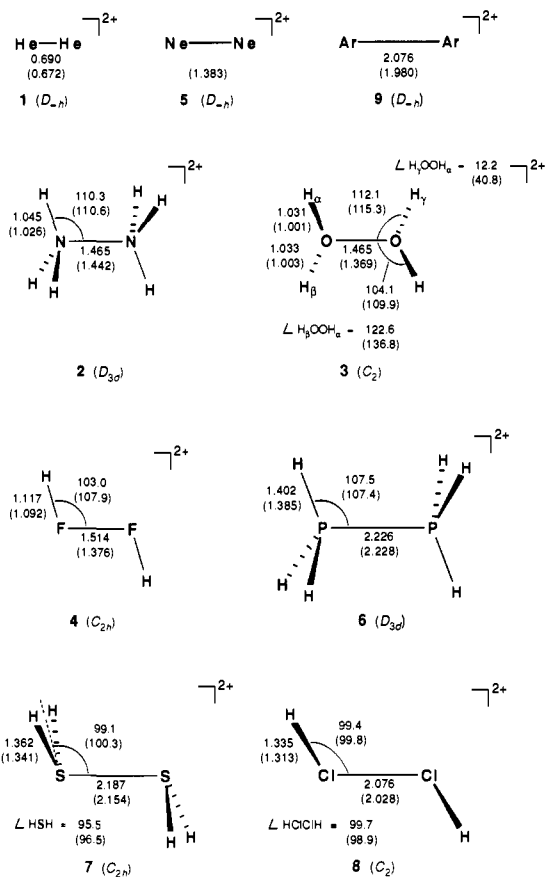


Figure 2. Optimized structures (RMP2/6-31G(d) [RMP2/6-31G(p) for  $\text{He}_2^{2+}$ ], with RHF/6-31G(d) [RHF/6-31G(p) for  $\text{He}_2^{2+}$ ] values in parentheses) for singlet dimer dications.

## Discussion

**Fragmentations of Dications.** It is sometimes believed that, because even the ground-state potential surfaces of most dications are strongly coupled to energetically low-lying excited states of the same multiplicity, such surfaces should be studied theoretically using multiconfiguration self-consistent-field (MCSCF) techniques. Unfortunately, MCSCF procedures rapidly become very demanding computationally as the system size increases. In particular, if a uniform treatment of the entire potential surface of a polyatomic dication is required, the simplest satisfactory level of MCSCF theory is full-valence CAS (complete-active-space) SCF, which if subsequently augmented by configuration interaction (to include the effects of dynamical electron correlation), is prohibitively expensive for all but very small dications. On the other hand, although MCSCF is certainly desirable for systems that contain dissociating *multiple bonds*,<sup>7</sup> we believe that the fragmentations of dicationic systems in which only a *single bond* is broken may profitably be studied by the application of carefully chosen methods based on a single-configuration starting point. Provided that they are size-consistent and offer an adequately uniform treatment of most of a potential surface, such approaches can lead (as we describe below) to satisfactory results at a reasonable computational cost.

In previous papers,<sup>8-10</sup> we have discussed a very useful model for bonding in a dication  $\text{AB}^{2+}$  in which we picture the potential curve along a reaction coordinate for fragmentation into  $\text{A}^+$  and  $\text{B}^+$  as arising from an avoided crossing between the repulsive  $\text{A}^+ + \text{B}^+$  and attractive  $\text{A}^{2+} + \text{B}$  diabatic states. When the fragment monocations are infinitely separated, the attractive diabatic state is higher in energy than the repulsive one by a quantity  $\Delta$  defined<sup>8</sup> by

$$\Delta = E(\text{A}^{2+}) + E(\text{B}) - E(\text{A}^+) - E(\text{B}^+) = \text{IE}_a(\text{A}^+) - \text{IE}_a(\text{B}) \quad (1)$$

where  $\text{IE}_a$  refers to the adiabatic ionization energy of a fragment.

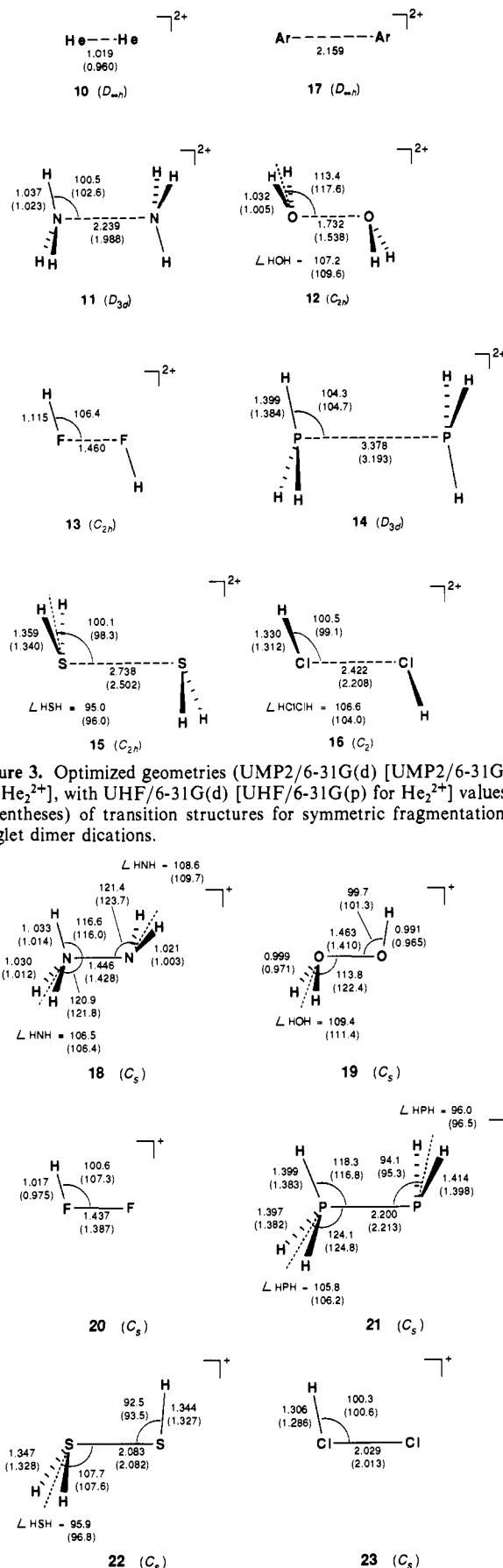
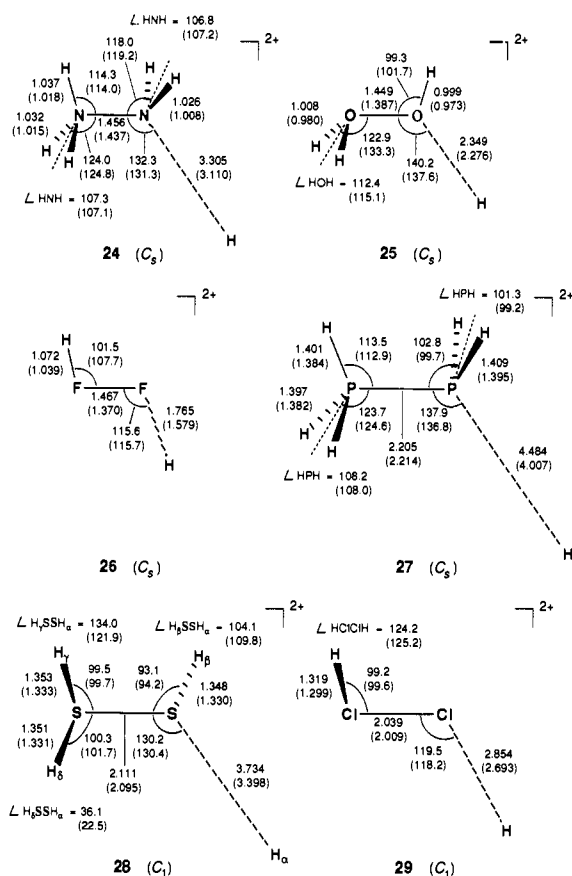


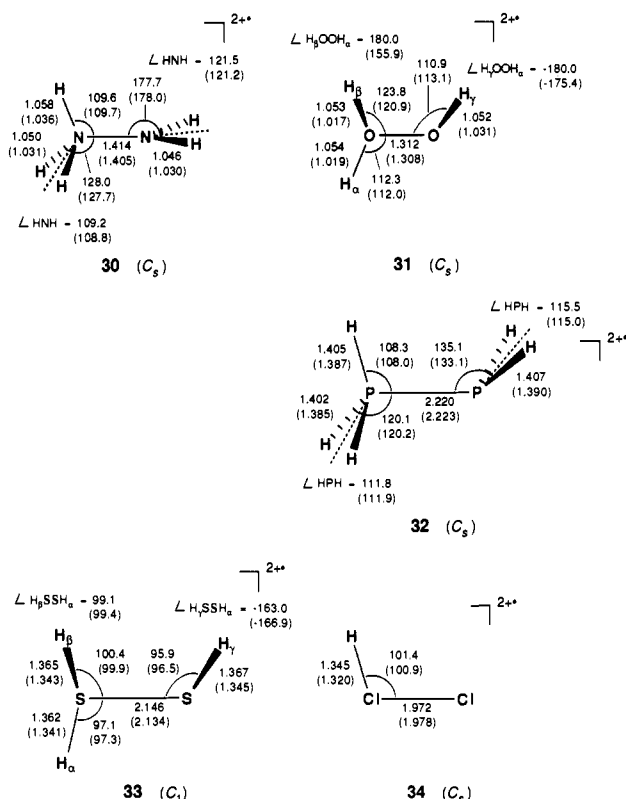
Figure 3. Optimized geometries (UMP2/6-31G(d) [UMP2/6-31G(p) for  $\text{He}_2^{2+}$ ], with UHF/6-31G(d) [UHF/6-31G(p) for  $\text{He}_2^{2+}$ ] values in parentheses) of transition structures for symmetric fragmentation of singlet dimer dications.

Figure 4. Optimized structures (RMP2/6-31G(d), with RHF/6-31G(d) values in parentheses) for deprotonated singlet dimer dications.

Normally,  $\Delta$  is positive. However, if it is negative, it indicates not only that the fragmentation into  $\text{A}^{2+}$  and  $\text{B}$  is less costly



**Figure 5.** Optimized geometries (RMP2/6-31G(d), with RHF/6-31G(d) values in parentheses) of transition structures for deprotonation of singlet dimer dications.



**Figure 6.** Optimized structures (UMP2/6-31G(d), with UHF/6-31G(d) values in parentheses) for species that result from the loss of a hydrogen atom from singlet dimer dications.

energetically than that into  $A^+$  and  $B^+$  but also that both fragmentations are thermodynamically unfavorable and that  $AB^{2+}$

is therefore thermodynamically stable.

The ground-state potential energy curve for  $AB^{2+}$  along the fragmentation reaction coordinate results from coupling between these diabatic curves,<sup>10</sup> and, consequently, the ground-state wave function at any fragment separation is a mixture of the  $A^+ + B^+$  and  $A^{2+} + B$  wave functions. If  $AB^{2+}$  is a singlet, one of the diabatic states (either  $A^{+} + B^{+}$  or  $A^{2+} + B^{\bullet}$ ) will be diradicaloid in nature, and the UHF wave function for this state, particularly when the fragment separation is large, will therefore be significantly contaminated by the corresponding triplet state.<sup>13</sup> Because spin contamination adversely affects the convergence behavior of the unrestricted Møller–Plesset (UMP) perturbation expansion,<sup>11–13,22</sup> UMP theory is not useful at points along the fragmentation pathway where the diradicaloid diabatic state contributes substantially to the ground-state wave function. As a result, the energies of transition structures for homolytic fragmentation of dications are not well-described by UMP theory,<sup>11</sup> and, in cases where the restricted Møller–Plesset (RMP) series converges well, it is preferable to employ moderately high levels of RMP theory.<sup>12</sup> Note, however, that the transition structure geometries are much less sensitive to choice of theoretical level, and we have found<sup>12</sup> that use of either UMP2 or RMP2 structures is generally satisfactory. In a number of cases where suitable comparisons are possible, we have demonstrated<sup>12</sup> that application of RMP4 theory leads to results in substantial agreement with full-CI or CISDTQ calculations. Moreover, using a simple formula,<sup>12</sup> it is possible to estimate the radius of convergence ( $\Delta$ ) of the Møller–Plesset  $\lambda$  parameter in a given RMP calculation and, consequently, to assess the likely reliability of the associated RMP4 energy. Thus, on each occasion in the present study where we have used RMP theory to calculate the energy of the transition structure for the homolytic fragmentation of a dication, we have also calculated the associated  $\Delta$  value (see *f* in Table V).

On the other hand, where a singlet  $AH^{2+}$  dication has a small  $\Delta$  for proton loss (i.e. the second ionization energy of A is only a little more than 13.6 eV), we have found<sup>9</sup> that the deprotonation ought to be studied using UHF (not RHF) theory because, for moderate extensions of the A–H bond, the system resembles the diradicaloid  $A^{*2+} \cdots H^{\bullet}$  rather than the eventual products  $A^+ + H^+$ . Of course, although UHF theory can account satisfactorily for the energetics of such a bond extension, the underlying UHF wave function becomes grossly spin-contaminated and is an unsuitable starting point for a higher level treatment using perturbation theory. As a result, neither UMP nor RMP theory is found to be appropriate. In such cases we have argued<sup>9</sup> that it is preferable to treat the system at the transition structure as if the nascent radicaloid fragments were noninteracting; i.e., instead of the MP energy of  $A^{*2+} \cdots H^{\bullet}$ , we use the *sum* of the MP energies of  $A^{*2+}$  and  $H^{\bullet}$ .

The presence of a local minimum on the otherwise repulsive potential surface of a dication can be traced to a combination of two effects:<sup>10</sup> first, that the  $A^{2+} + B$  diabatic surface is attractive (because of polarization effects) and, second, that coupling between the  $A^+ + B^+$  and  $A^{2+} + B$  diabatic surfaces can become sufficiently strong when the fragments approach one another that a local minimum is formed. These effects can be modeled semi-quantitatively by assuming reasonable forms for the diabatic curves and for the coupling between them and then solving the resulting  $2 \times 2$  CI problem. We have found that this procedure, which we have termed the ACDPC (avoided crossing with diabatic coupling and polarization) model, leads to remarkably accurate estimates of the transition-structure bond length and the kinetic energy released in the fragmentation of a diatomic dication.<sup>10</sup>

If the perspective of the ACDPC model is adopted in a qualitative assessment of the symmetric fragmentations of the  $A_2^{2+}$  dimer dications, it is possible to make predictions of the trends in dissociation behavior that should be observed. In general, any  $A_2^{2+}$  system for which A has a comparatively low second ionization energy (leading to a small  $\Delta$  value for the symmetric fragmentation) will have a rather late transition structure<sup>8</sup> and, therefore, the covalent bonding will have largely disappeared before the transition structure is reached.<sup>9</sup> Moreover, because the well in

Table V. Calculated Relative Energies (kJ mol<sup>-1</sup>)<sup>a</sup>

		HF/6-31G(d) <sup>b</sup>	MP2/6-31G(d)	MP4/6-31G(d,p)	MP4/WGNR <sup>d</sup>	MP4/WGNR <sup>d,e</sup>
HeHe <sup>2+</sup>	1	0	0	0	0	0
He <sup>+</sup> ...He <sup>+</sup>	10	172	247	125	127 <sup>f</sup>	105
He <sup>++</sup> + He <sup>++</sup>		-1023	-906	-871	-868	-890
He <sup>2+</sup> + He		1949	1998	2018	2028	2005
H <sub>3</sub> NNH <sub>3</sub> <sup>2+</sup>	2	0	0	0	0	0
H <sub>3</sub> N <sup>+</sup> ...NH <sub>3</sub> <sup>+</sup>	11	138	265	184	189 <sup>f</sup>	168
H <sub>3</sub> N <sup>++</sup> + NH <sub>3</sub> <sup>++</sup>		-350	-173	-200	-193	-234
H <sub>3</sub> N <sup>2+</sup> + NH <sub>3</sub>		1027	1145	1116	1109	1062
H <sub>3</sub> NNH <sub>2</sub> <sup>+</sup> + H <sup>+</sup>	18	249	253	266	260	228
H <sub>3</sub> NNH <sub>2</sub> <sup>+</sup> ...H <sup>+</sup>	24	509	504	520	514	485
H <sub>3</sub> NNH <sub>2</sub> <sup>2+</sup> + H <sup>+</sup>	30	432	535	552	552	508
H <sub>2</sub> OOH <sub>2</sub> <sup>2+</sup>	3	0	0	0	0	0
H <sub>2</sub> O <sup>+</sup> ...OH <sub>2</sub> <sup>+</sup>	12	31	137	26	29 <sup>f</sup>	22
H <sub>2</sub> O <sup>++</sup> + OH <sub>2</sub> <sup>++</sup>		-591	-365	-397	-399	-428
H <sub>2</sub> O <sup>2+</sup> + OH <sub>2</sub>		894	1081			
H <sub>2</sub> OOH <sup>+</sup> + H <sup>+</sup>	19	-72	-64	-45	-46	-68
H <sub>2</sub> OOH <sup>+</sup> ...H <sup>+</sup>	25	260	261	285	283	262
H <sub>2</sub> OOH <sup>2+</sup> + H <sup>+</sup>	31	476	571	584	580	543
HFFH <sup>2+</sup>	4	0	0	0	0	0
HF <sup>+</sup> ...FH <sup>+</sup>	13	<i>g</i>	140	6	7 <sup>f</sup>	5
HF <sup>++</sup> + FH <sup>++</sup>		-863	-530	-558	-588	-597
HFF <sup>+</sup> + H <sup>+</sup>	20	-442	-376	-368	-374	-386
HFF <sup>+</sup> ...H <sup>+</sup>	26	30	52	66	64	53
NeNe <sup>2+</sup>	5	0	<i>g</i>	<i>g</i>	<i>g</i>	<i>g</i>
Ne <sup>+</sup> ...Ne <sup>+</sup>		<i>g</i>	<i>g</i>	<i>g</i>	<i>g</i>	<i>g</i>
Ne <sup>++</sup> + Ne <sup>++</sup>		-1376	<i>g</i>	<i>g</i>	<i>g</i>	<i>g</i>
Ne <sup>2+</sup> + Ne		877	<i>g</i>	<i>g</i>	<i>g</i>	<i>g</i>
H <sub>3</sub> PPH <sub>3</sub> <sup>2+</sup>	6	0	0	0	0	0
H <sub>3</sub> P <sup>+</sup> ...PH <sub>3</sub> <sup>+</sup>	14	147	203	182	184 <sup>f</sup>	171
H <sub>3</sub> P <sup>++</sup> + PH <sub>3</sub> <sup>++</sup>		-195	-118	-124	-117	-137
H <sub>3</sub> P <sup>2+</sup> + PH <sub>3</sub>		683	722	712	709	686
H <sub>3</sub> PPH <sub>2</sub> <sup>+</sup> + H <sup>+</sup>	21	291	273	287	284	259
H <sub>3</sub> PPH <sub>2</sub> <sup>+</sup> ...H <sup>+</sup>	27	510	483	485	480	457
H <sub>3</sub> PPH <sub>2</sub> <sup>2+</sup> + H <sup>+</sup>	32	351	398	427	429	401
H <sub>2</sub> SSH <sub>2</sub> <sup>2+</sup>	7	0	0	0	0	0
H <sub>2</sub> S <sup>+</sup> ...SH <sub>2</sub> <sup>+</sup>	15	30	94	50	60 <sup>f</sup>	52
H <sub>2</sub> S <sup>++</sup> + SH <sub>2</sub> <sup>++</sup>		-398	-291	-300	-281	-303
H <sub>2</sub> S <sup>2+</sup> + SH <sub>2</sub>		720	720	776	786	759
H <sub>2</sub> SSH <sup>+</sup> + H <sup>+</sup>	22	135	137	166	174	149
H <sub>2</sub> SSH <sup>+</sup> ...H <sup>+</sup>	28	395	385	409	414	392
H <sub>2</sub> SSH <sup>2+</sup> + H <sup>+</sup>	33	314	373	401	405	377
HCiClH <sup>2+</sup>	8	0	0	0	0	0
HCl <sup>+</sup> ...ClH <sup>+</sup>	16	13	82	20	30 <sup>f</sup>	26
HCl <sup>++</sup> + ClH <sup>++</sup>		-519	-387	-393	-364	-378
HCl <sup>2+</sup> + ClH		644	744			
HCiCl <sup>+</sup> + H <sup>+</sup>	23	-104	-88	-50	-39	-60
HCiCl <sup>+</sup> ...H <sup>+</sup>	29	219	222	259	271	252
HCiCl <sup>2+</sup> + H <sup>+</sup>	34	362	422	453	462	439
ArAr <sup>2+</sup>	9	0	0	0	0	0
Ar <sup>+</sup> ...Ar <sup>+</sup>	17	<i>g</i>	65	-4	0 <sup>f</sup>	-3
Ar <sup>++</sup> + Ar <sup>++</sup>		-726	-565	-554	-523	-526
Ar <sup>2+</sup> + Ar		616	742			

<sup>a</sup> MP2/6-31G(d)-optimized structures (MP2/6-31G(p) for He<sub>2</sub><sup>2+</sup>; see text), unless otherwise noted. Energies correspond to RHF/RMP values for closed-shell systems and UHF/UMP for open-shell systems except for the transition structures for homolytic fragmentation where the results are UHF, UMP2, and RMP4. <sup>b</sup> HF/6-31G(d)-optimized structures (HF/6-31G(p) for He<sub>2</sub><sup>2+</sup>). <sup>c</sup> 6-31G(p) basis set for He. <sup>d</sup> 6-311G(MC)(d,p) basis set used. <sup>e</sup> Including zero-point vibrational contribution. <sup>f</sup> The  $\Delta$  values (see text) for the transition structures for homolytic cleavage are 1.590 (He<sub>2</sub><sup>2+</sup>, 10), 1.388 (N<sub>2</sub>H<sub>6</sub><sup>2+</sup>, 11), 1.491 (O<sub>2</sub>H<sub>4</sub><sup>2+</sup>, 12), 1.610 (F<sub>2</sub>H<sub>2</sub><sup>2+</sup>, 13), 1.369 (P<sub>2</sub>H<sub>6</sub><sup>2+</sup>, 14), 1.489 (S<sub>2</sub>H<sub>4</sub><sup>2+</sup>, 15), 1.452 (Cl<sub>2</sub>H<sub>2</sub><sup>2+</sup>, 16), and 1.669 (Ar<sub>2</sub><sup>2+</sup>, 17). <sup>g</sup> The potential surface is dissociative at this level of theory.

which a dication resides is due to polarization and diabatic coupling effects,<sup>10</sup> the deepest wells are likely to occur in dimer dications in which A is rather polarizable and in which A has a comparatively diffuse lone pair. All three of these considerations lead to the prediction that, of the dimer dications considered in the present study, the dimer dications of the group V hydrides will be the most stable.

**Performance of ab Initio Methods in Describing Dicationic Fragmentation.** In Table I, we summarize the performance of a variety of different basis sets at the full-CI level (i.e. with complete electron correlation within the basis set) when applied to the prototypical He<sub>2</sub><sup>2+</sup> dication 1. For each basis set, we have tabulated the bond lengths of the equilibrium and transition

structures ( $r_{\text{eq}}$  and  $r_{\text{TS}}$ , respectively), together with the dissociation barrier ( $D_e^*$ , uncorrected for zero-point vibrational effects) and the value of the  $\Delta$  parameter,<sup>8</sup> whose definition reduces, for He<sub>2</sub><sup>2+</sup>, to

$$\Delta = E(\text{He}) - 2E(\text{He}^{++}) \quad (2)$$

At the full-CI/STO-3G level of theory, the bond length in the neutral H<sub>2</sub> molecule is calculated to be 0.735 Å and the dissociation energy (without a correction for zero-point vibration) is 536 kJ mol<sup>-1</sup>. By comparison, the "exact" values<sup>23</sup> are 0.741 Å and 458 kJ mol<sup>-1</sup>, respectively, indicating that, for the neutral H<sub>2</sub>

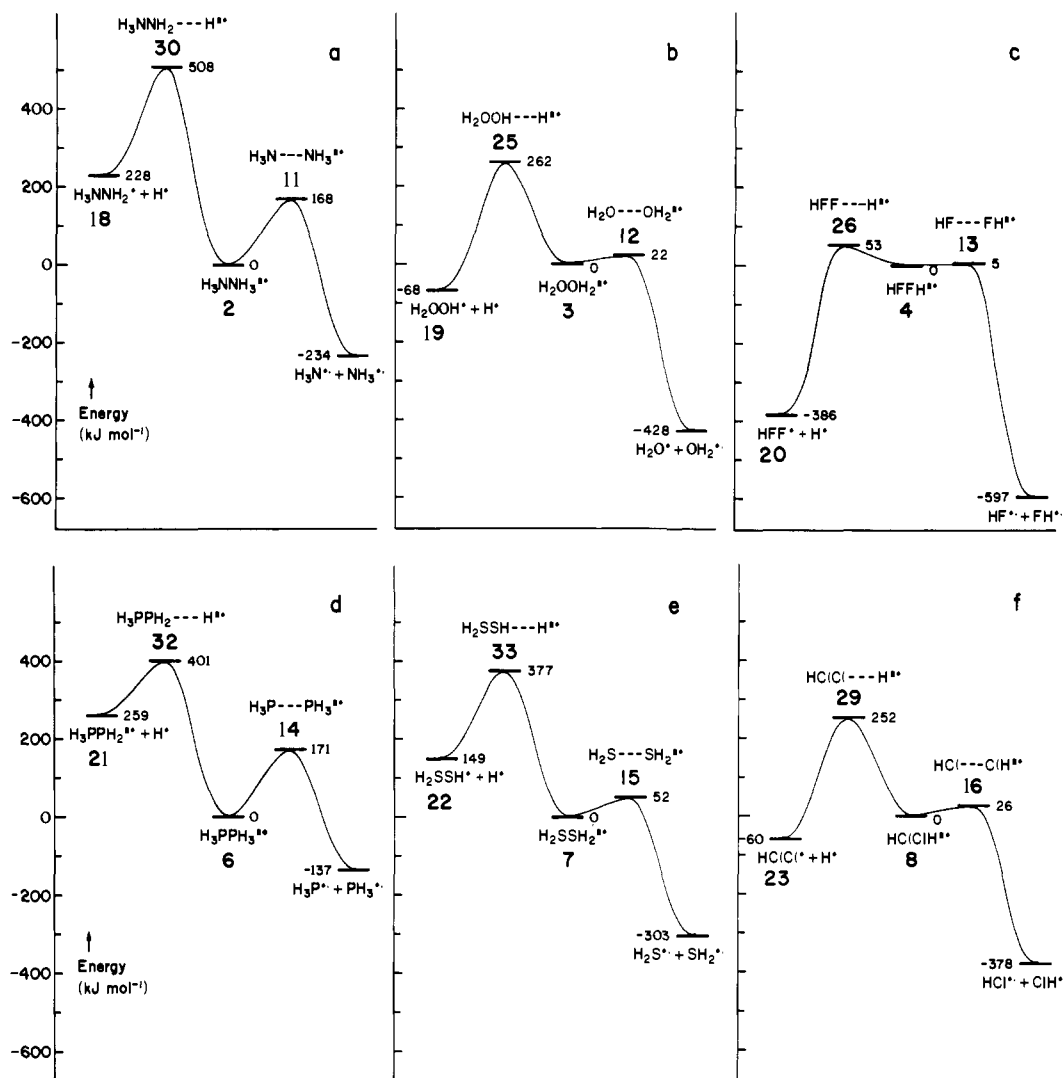


Figure 7. Schematic potential energy surfaces showing symmetric fragmentation and deprotonation processes for dimer dications: (a)  $\text{H}_3\text{NNH}_2^{2+}$ ; (b)  $\text{H}_2\text{OOH}_2^{2+}$ ; (c)  $\text{HFFH}^{2+}$ ; (d)  $\text{H}_3\text{PPH}_2^{2+}$ ; (e)  $\text{H}_2\text{SSH}_2^{2+}$ ; (f)  $\text{HCIClH}^{2+}$ .

molecule, even this modest basis set leads to predictions in reasonable agreement with experiment. In stark contrast, the isoelectronic  $\text{He}_2^{2+}$  dication is predicted by the same level of theory to have no barrier whatsoever preventing its spontaneous dissociation, a result which accords very poorly indeed with the very accurate calculations of Yagisawa et al.<sup>20</sup> who found  $\text{He}_2^{2+}$  to be a metastable species with an extremely short bond (0.703 Å) whose fragmentation is inhibited by a substantial barrier of 145  $\text{kJ mol}^{-1}$ .

The first five basis sets in Table I range from the single- $\zeta$  STO-3G basis to the decuple- $\zeta$  (10s) basis of van Duijneveldt,<sup>24</sup> but none of these includes polarization functions. The sequences of  $r_{\text{eq}}$  and  $r_{\text{TS}}$  values show that, while the equilibrium bond length is not particularly sensitive to the basis set quality, the transition structure bond length is significantly more so. However, the basis set dependence of the bond lengths is dwarfed by that of the dissociation barrier  $D_e^*$ , which varies dramatically from 0 (STO-3G) through 33 (3-21G) to 66  $\text{kJ mol}^{-1}$  (10s). Furthermore, comparison of the bond length and barrier height values for the (10s) basis set with the exact values reveals that the absence of polarization functions in the basis set has a small effect on the equilibrium bond length, a larger effect on the transition structure bond length, and a very large effect indeed on the barrier height. It was pointed out above that the barrier height depends on both polarization and diabatic coupling effects.<sup>10</sup> If we assume that most of the coupling is adequately treated by the (10s) basis set, then it follows that, of the 145  $\text{kJ mol}^{-1}$  barrier in  $\text{He}_2^{2+}$ , ap-

proximately 66  $\text{kJ mol}^{-1}$  is due to diabatic coupling and the remainder (roughly 79  $\text{kJ mol}^{-1}$ ) to polarization effects.

The simplest way to introduce polarization effects into our treatment of  $\text{He}_2^{2+}$  is to add one or more sets of p functions to the helium basis. Using the 6-311G s basis, we have investigated two possible helium p exponents. The exponent used in the 6-311G(d,p) basis set<sup>14</sup> is 0.75 but, although this leads to a substantial improvement over the 6-311G barrier (69  $\text{kJ mol}^{-1}$  becomes 98  $\text{kJ mol}^{-1}$ ), it is still in poor agreement with the exact result (145  $\text{kJ mol}^{-1}$ ). In our recently developed 6-311G(MC)(d,p) basis set,<sup>21</sup> the helium p exponent is 1.366 and the use of this value leads to a much more satisfactory barrier of 133  $\text{kJ mol}^{-1}$ . Likewise, the bond lengths of the equilibrium and transition structures, using the 6-311G(MC)(d,p) basis, are also in good agreement with the exact values.

Finally, we note that the full-CI estimates of the equilibrium and transition structure bond lengths and of the barrier, using our largest basis set 6-311G(MC)(d,3p2d1f), are in good agreement with the very accurate calculations of Yagisawa et al.<sup>20</sup>

In summary, rather modest basis sets are sufficient to give satisfactory estimates of the equilibrium bond length in  $\text{He}_2^{2+}$ , while to obtain a reasonable transition-structure bond length, larger basis sets with polarization functions are necessary. To achieve a satisfactory estimate of the dissociation barrier, the valence part of the basis set should ideally be of at least triple- $\zeta$  quality and must be augmented by polarization functions with well-chosen exponents.

In Table II, we list the  $r_{\text{eq}}$ ,  $r_{\text{TS}}$ , and  $D_e^*$  values afforded by a number of different levels of electron correlation in order to gauge

(24) Van Duijneveldt, F. B. *IBM J. Res. Dev.* 1971, 945.

the performance of these various levels of theory when applied to the two-electron  $\text{He}_2^{2+}$  dication with the 6-31G(d,p) basis set. Because all of the dimer dications considered in this paper are singlets, they may be treated by either restricted or unrestricted Møller–Plesset (RMP or UMP) perturbation theory. These perturbation theories are equivalent in the vicinity of the equilibrium structures, but for larger bond lengths, they become distinct. As we found in an earlier study,<sup>11</sup> UMP theory does not provide good estimates of barrier heights for homolytic dissociations because of the poor convergence properties of Møller–Plesset perturbation series based on spin-contaminated Hartree–Fock wave functions.<sup>13,22</sup> On the other hand, we have proposed<sup>12</sup> that, for moderate extensions of the cleaving bond, fourth-order *restricted* Møller–Plesset (RMP4) theory can lead to satisfactory results, and, indeed, it is clear from Table II that, of the eight levels of Møller–Plesset theory, RMP4 gives the best agreement with the exact (within the basis set) bond length and dissociation barrier for the  $\text{He}_2^{2+}$  dication, as given by the CISD values. We will use RMP4 single-point transition-structure energies throughout this paper to estimate the dissociation barriers of other dications. We have recently introduced<sup>12,13</sup> the  $\Lambda$  parameter as an estimator of the radius of convergence of the  $\lambda$  parameter in the Møller–Plesset series. The value of  $\Lambda$  provides an indication of the rate of convergence of the Møller–Plesset expansion and hence of the reliability of MP4 energies. Relevant values for systems examined in the present paper are in the range from 1.369 ( $\text{P}_2\text{H}_6^{2+}$ ) to 1.669 ( $\text{Ar}_2^{2+}$ ) (Table V, f). That they are all significantly greater than unity indicates<sup>12</sup> that the convergence of the RMP series is satisfactory at the transition structures of all of these systems.

Although we will not be generally using an MCSCF approach in this paper, it is interesting to note that a two-configuration (TCSCF) treatment ( $1\sigma_g^2$  and  $1\sigma_u^2$ ) leads to good agreement with the exact CISD results. This is not surprising when we recall that the potential curve for  $\text{He}_2^{2+}$  may be derived, at least to a first approximation, by mixing the  $\text{He}^{+} + \text{He}^{+}$  and  $\text{He}^{2+} + \text{He}$  diabatic states, which, it is easy to show, span the same space as the  $1\sigma_g^2$  and  $1\sigma_u^2$  configurations. Indeed, the ADCDP model that we have introduced<sup>10</sup> is essentially an approximate TCSCF treatment of the fragmenting bond in a dication.

Table III, which is analogous to Table II, shows the effects of different levels of electron correlation on the equilibrium and transition-structure N–N bond lengths and on the dissociation barrier in the  $\text{N}_2\text{H}_6^{2+}$  (hydrazinium) dication **2** using the 6-31G(d) basis set. Because of the size of the system, we were unable to calculate exact results, but, in a previous study,<sup>12</sup> we have examined this dication in considerable detail and many of the conclusions regarding  $\text{He}_2^{2+}$  appear to apply to  $\text{N}_2\text{H}_6^{2+}$  as well. UMP theory underestimates  $r_{\text{TS}}$  and seriously overestimates  $D_e^*$ . On the other hand, RMP4 and TCSCF agree that the N–N separation at the transition structure is roughly 2.5 Å. The full-CI dissociation barrier is probably close to the RMP4 value, and we note (as pointed out previously<sup>12</sup>) that, because of its lack of size consistency, the RCISD dissociation barrier is much too large.

In Table IV, we compare the predictions at the UHF, UMP2, TCSCF, and RMP4 levels of theory of the heavy atom–heavy atom bond length in the transition structures for symmetric fragmentation of the complete set of  $\text{A}_2^{2+}$  dimers. Calculations at the RMP4 level lead to shallow wells for  $\text{HFFH}^{2+}$  and  $\text{HCIClH}^{2+}$  while TCSCF predicts that both potential surfaces are purely repulsive. However, apart from these minor discrepancies and the fact<sup>12</sup> that, because  $\Delta$  for the fragmentation of  $\text{H}_3\text{PPH}_3^{2+}$  is comparatively small, RMP4 fails to find the correspondingly late transition structure, the agreement between the TCSCF and RMP4 bond lengths is reasonably good. The RMP4 estimates are always slightly larger than the TCSCF values, which are, themselves, somewhat greater than the UMP2 values. The UHF bond lengths are even shorter still. We have noted before<sup>11</sup> that, as a consequence of the slow convergence<sup>11–13,22</sup> of a UMP series based on a heavily spin-contaminated Hartree–Fock wave function, UMP2 and (especially) UHF underestimate transition-structure bond lengths for homolytic cleavages. Nonetheless, we have demonstrated<sup>12</sup> that UMP2 structures are often satisfactory for

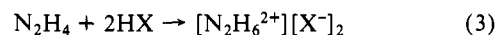
use in RMP4 single-point calculations.

**$\text{He}_2^{2+}$  Dication.** As the  $\text{H}_2$  molecule is generally regarded as the archetypal neutral molecule, so likewise, the isoelectronic  $\text{He}_2^{2+}$  dication **1** is the prototype of dications. The shape of the potential curve for its fragmentation typifies those for positive- $\Delta$  dicationic fragmentations in general—a (meta)stable species protected from its dissociation into two monocations by a barrier that arises because the potential curve results from an avoided crossing.

Pauling<sup>25</sup> was the first worker to examine this system theoretically, more than 50 years before its recent experimental discovery.<sup>3</sup> His two-configuration SCF calculations, using an exponent-optimized single- $\zeta$  Slater-type basis set, led to the predictions that the bond lengths of the equilibrium and transition structures are  $r_{\text{eq}} = 0.75$  Å and  $r_{\text{TS}} = 1.05$  Å and that the dissociation barrier (without a zero-point energy correction) is  $D_e^* = 1.4$  eV (135 kJ mol<sup>-1</sup>). Subsequent calculations<sup>26–28</sup> led to improved theoretical estimates of these quantities and culminated in the work of Yagisawa et al.<sup>20</sup> who used the very accurate James–Coolidge method<sup>29</sup> to determine that the exact parameters are  $r_{\text{eq}} = 0.703$  Å,  $r_{\text{TS}} = 1.151$  Å, and  $D_e^* = 145$  kJ mol<sup>-1</sup>, values which are remarkably similar to the Pauling estimates. We note additionally that the equilibrium bond lengths in  $\text{H}_2$  and  $\text{He}_2^{2+}$  are also similar, with that in the dication being a little shorter. The  $\text{He}_2^{2+}$  bond length is, in fact, the shortest known, despite the fact that fragmentation to two  $\text{He}^{+}$  monocations is exothermic by nearly 900 kJ mol<sup>-1</sup>. It is also pertinent to note that, as might have been anticipated from Figure 1, the  $\text{He}_2^{2+}$  dication is much more tightly bound than the hemibonded  $\text{He}_2^{+}$  monocation,<sup>2</sup> their optimized bond lengths being 0.690 and 1.077 Å, respectively.

At the UHF/6-31G(p) level (Table V), the dissociation barrier is found to be  $D_e^* = 172$  kJ mol<sup>-1</sup>, an overestimate that becomes 127 kJ mol<sup>-1</sup> at the higher RMP4/6-311G(MC)(d,p)//UMP2/6-31G(p) level (Table V). The observation that the improved estimate is in satisfactory agreement with the exact barrier (145 kJ mol<sup>-1</sup>) lends confidence to our RMP4/6-311G(MC)(d,p)//UMP2/6-31G(d) estimates for other, larger, dications. At the full-CI/6-311G(MC)(d,3p2d1f) level (Table I), the estimates of  $r_{\text{eq}}$ ,  $r_{\text{TS}}$ , and  $D_e^*$  are in excellent agreement with the exact values. The effect of the zero-point vibrational energy of the equilibrium structure is to decrease the estimated dissociation barrier by 23 kJ mol<sup>-1</sup>. After combining this with our best value of the uncorrected dissociation barrier ( $D_e^* = 142$  kJ mol<sup>-1</sup>, Table I), we conclude that our best estimate of the dissociation barrier (corrected for zero-point vibration) is  $D_0^* = 119$  kJ mol<sup>-1</sup>. Zero-point vibrational effects do not affect the kinetic energy release in diatomic dications, and our best estimate of this quantity for  $\text{He}_2^{2+}$  is 10.3 eV. Because  $\Delta$  is so large (29.8 eV) for this fragmentation, the kinetic energy release for  $\text{He}_2^{2+}$  is very possibly greater than that for the fragmentation of any other stable dication.

**$\text{N}_2\text{H}_6^{2+}$  Dication.** The hydrazinium dication **2** is a well-known species, which may be prepared experimentally<sup>5</sup> as a crystalline salt formed in the neutralization of hydrazine by appropriate acids in aqueous solution:



It is isoelectronic and isostructural with the neutral ethane ( $\text{C}_2\text{H}_6$ ) molecule, and its calculated ( $D_{3d}$ ) equilibrium structure ( $r_{\text{NN}} = 1.465$  Å,  $r_{\text{NH}} = 1.045$  Å; Figure 2), is similar to that of the alkane ( $r_{\text{CC}} = 1.527$  Å,  $r_{\text{CH}} = 1.094$  Å).<sup>14</sup> The calculated N–N bond length in **2** compares favorably with the experimental crystal structure value<sup>5</sup> of 1.43 Å, and, as was found for the corresponding helium dimers, the N–N bond in the hydrazinium dication is much shorter than that in the hemibonded hydrazinium monocation<sup>2</sup>  $\text{H}_3\text{N}^+ - \text{NH}_3^{+}$  (2.151 Å). Indeed, the N–N bond lengths in neutral, singly and doubly protonated hydrazine (1.439, 1.446, and 1.465

(25) Pauling, L. *J. Chem. Phys.* **1933**, *1*, 56.

(26) Kolos, W.; Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 219.

(27) Schwart, M. E.; Schaad, L. J. *J. Chem. Phys.* **1967**, *46*, 4112.

(28) Mackrodt, W. C. *J. Chem. Phys.* **1971**, *54*, 2952.

(29) James, H. M.; Coolidge, A. S. *J. Chem. Phys.* **1933**, *1*, 825.

Å, respectively, see ref 14 and Figures 2 and 4) are all remarkably similar.

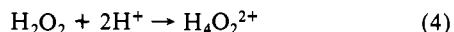
The hydrazinium dication has previously been examined theoretically by Bouma and Radom<sup>30</sup> whose calculations led them to predict that the barriers to cleavage of the N–N and N–H bonds are 194 and 495 kJ mol<sup>-1</sup>, respectively. They pointed out that the dication **2** is a prototype for the doubly ionized bicyclo bridgehead diamines (such as the 1,6-diazabicyclo[4.4.4]tetradecane dication), which have recently been prepared and studied in detail by Alder and co-workers,<sup>31</sup> and concluded that, because the dissociation of **2** into two NH<sub>3</sub><sup>+</sup> units is inhibited by a substantial barrier, the bicyclo dications may exhibit bond-stretch isomerism:<sup>32</sup> i.e., two kinetically stable isomers, differing primarily in the length of the N–N bond, should exist.

Our calculations are at a more reliable level of theory than those of Bouma and Radom for the following reasons: (1) Our largest basis set, 6-311G(MC)(d,p) is of triple- $\zeta$  valence plus-polarization quality whereas they employed the double- $\zeta$  valence plus-polarization 6-31G(d,p) set, (2) we have calculated the relative energy of the transition structure for homolytic fission<sup>12</sup> of the N–N bond using RMP4, rather than UMP3, theory; and (3) we have recognized the fact<sup>9</sup> that the UHF description of the proton loss from N<sub>2</sub>H<sub>6</sub><sup>2+</sup> is to be preferred over the RHF description.

The barrier to the symmetric fragmentation of the hydrazinium dication into two NH<sub>3</sub><sup>+</sup> ions is estimated to be  $D_0^\ddagger = 168$  kJ mol<sup>-1</sup>. Because RMP4 theory probably recovers a little less of the correlation energy<sup>12</sup> at the transition structure **11** than at the equilibrium structure **2**, this estimate of  $D_0^\ddagger$  may be a slight overestimate of the full-CI value with this basis set. On the other hand, the fact that the UMP2/6-31G(d) transition structure **11** underestimates the RMP4/6-31G(d) N–N bond length (Table III) will tend to compensate for this overestimation. The calculated kinetic energy release for this fragmentation is 4.2 eV.

The deprotonation of the hydrazinium dication is endothermic and has a  $\Delta$  value of only 280 kJ mol<sup>-1</sup> (2.9 eV), which indicates<sup>9</sup> that the fragmentation will resemble a hydrogen atom loss until the N–H bond is very extended (at which point an electron transfer will take place leading to N<sub>2</sub>H<sub>5</sub><sup>+</sup> and H<sup>+</sup>) and that the kinetic energy release for deprotonation will be nearly equal to  $\Delta$  (2.9 eV). The RMP2 structure **24** is therefore a poor approximation to the true transition structure for proton loss from **2**. The deprotonation barrier cannot be greater than that for hydrogen atom loss<sup>9</sup> (508 kJ mol<sup>-1</sup>, Table V) and is calculated to be 485 kJ mol<sup>-1</sup> at the straightforward RMP4/6-311G(MC)(d,p)//RMP2/6-31G(d) level of theory. That these two estimates are similar suggests that the true barrier is probably of this magnitude, i.e. approximately 500 kJ mol<sup>-1</sup>.

**H<sub>4</sub>O<sub>2</sub><sup>2+</sup> Dication.** The water dimer dication **3** is formally produced by the protonation of hydrogen peroxide:



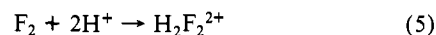
However, unlike hydrazinium salts (presumably because hydrogen peroxide is a much weaker base than hydrazine), salts of **3** seem to be unknown. The dication is isoelectronic and isostructural with the neutral hydrazine (N<sub>2</sub>H<sub>4</sub>) molecule, and the equilibrium structures of both species are of C<sub>2</sub> symmetry. As was also found for N<sub>2</sub>H<sub>6</sub><sup>2+</sup>, the bond lengths in H<sub>4</sub>O<sub>2</sub><sup>2+</sup> are similar to those in its isoelectronic neutral counterpart ( $r_{\text{NN}} = 1.439$  Å in N<sub>2</sub>H<sub>4</sub>,  $r_{\text{OO}} = 1.465$  Å in **3**), and the O–O bond length is much shorter than in the hemibonded H<sub>2</sub>O–OH<sub>2</sub><sup>+</sup> system<sup>2</sup> where  $r_{\text{OO}} = 2.023$  Å. However, unlike the N–N bond in the hydrazinium dication, the O–O bond in H<sub>4</sub>O<sub>2</sub><sup>2+</sup> is found to fragment very easily. The calculated barrier to symmetric fragmentation (which, as discussed for the N<sub>2</sub>H<sub>6</sub><sup>2+</sup> system, is possibly an overestimate) is only 22 kJ mol<sup>-1</sup> (Table V) and, since the O–O bond length (1.732 Å) in the

transition structure **12** is shorter than the O–O hemibond length (2.023 Å)<sup>2</sup> in the dimer radical cation H<sub>2</sub>O–OH<sub>2</sub><sup>•+</sup>, the dication formed by the vertical ionization of the equilibrium structure of the radical cation is expected to dissociate immediately. Nonetheless, in view of the ease with which substituted derivatives of the analogous H<sub>4</sub>S<sub>2</sub><sup>2+</sup> dication **7** are formed in aqueous solution (vide infra), it is entirely possible that comparable derivatives of H<sub>4</sub>O<sub>2</sub><sup>2+</sup> (e.g. the dications of cyclic diethers) may also be experimentally observable.

The barrier to deprotonation of **3** (262 kJ mol<sup>-1</sup>) is much larger than that for the symmetric dissociation. The kinetic energy releases for the symmetric and proton-loss fragmentations are calculated to be 4.7 and 3.4 eV, respectively.

Both of the fragmentations considered involve transition structures (**12** and **25**) whose point groups (C<sub>2h</sub> and C<sub>s</sub>, respectively) are different from that (C<sub>2</sub>) of the equilibrium structure **3**. Consequently, the minimum energy paths for these fragmentations must each pass through various branching points on the H<sub>4</sub>O<sub>2</sub><sup>2+</sup> potential surface. We have located some of these branching points using the algorithm of Baker and Gill<sup>33</sup> and have found that, along the symmetric dissociation pathway, the system assumes C<sub>2h</sub> symmetry in the very early stages of the fragmentation and that, along the deprotonation pathway, C<sub>s</sub> symmetry is achieved similarly quickly (in fact, before the cleaving O–H bond length has even stretched to 1.1 Å).

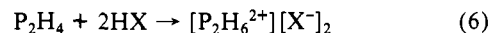
**H<sub>2</sub>F<sub>2</sub><sup>2+</sup> Dication.** Because the neutral fluorine molecule F<sub>2</sub> is an even weaker base than hydrogen peroxide, the preparation of the H<sub>2</sub>F<sub>2</sub><sup>2+</sup> dication **4** by the reaction



is unlikely to be viable. The neutral, isoelectronic, isostructural analogue of **4** is hydrogen peroxide, but whereas the equilibrium structure of H<sub>2</sub>O<sub>2</sub> has C<sub>2</sub> symmetry, species **4** is calculated to have a planar (C<sub>2h</sub>) structure. The calculated F–F bond length in **4** (1.514 Å) is significantly less than that in the hemibonded monocation HFFH<sup>+</sup> (1.843 Å).<sup>2</sup> Although **4** is predicted to exist in a shallow potential well by some (comparatively low) levels of theory, it appears likely that, at sufficiently high levels of theory, the H<sub>2</sub>F<sub>2</sub><sup>2+</sup> potential surface is purely repulsive. For example, the barrier to fluorine–fluorine cleavage at the RMP4/6-31G(d) level is only 0.5 kJ mol<sup>-1</sup>, and this disappears altogether when zero-point vibrational corrections are made.

**Ne<sub>2</sub><sup>2+</sup> Dication.** The neon dimer dication **5** is predicted to be even less stable (than **4**), and its experimental observation has never been reported. Its potential curve is predicted to be purely repulsive by all levels of theory beyond restricted Hartree–Fock. Moreover, the recently developed ACDCP model<sup>10</sup> predicts that the bond length of the transition structure for dissociation into two neon cations is only 1.34 Å (which is less than the RHF equilibrium bond length), providing further confirmation that the species is highly unlikely to exist.

**P<sub>2</sub>H<sub>6</sub><sup>2+</sup> Dication.** The phosphorus analogue of hydrazine is diphosphine P<sub>2</sub>H<sub>4</sub>, a reactive liquid with essentially no basic properties. Consequently, salts of the hitherto unknown diphosphinium dication **6** probably cannot be prepared by the reaction



However, our calculations indicate that, once formed, the diphosphinium dication **6** should exhibit comparable stability to the related hydrazinium dication **2**. Like **2**, the equilibrium diphosphinium dication **6** structurally resembles its isoelectronic, isostructural, neutral counterpart Si<sub>2</sub>H<sub>6</sub> ( $r_{\text{SiSi}} = 2.338$  Å,  $r_{\text{PP}} = 2.226$  Å). It has a much shorter P–P bond than that (2.700 Å) which we have recently calculated for the hemibonded diphosphinium monocation.<sup>2</sup> Because both the symmetric and proton-loss fragmentations have comparatively small  $\Delta$  values, the corresponding transition structures are late and the kinetic energy releases are small.<sup>8,9</sup> Indeed, the P–P bond length at the transition

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(31) (a) Alder, R. W.; Sessions, R. B.; Mellor, J. M.; Rawlins, M. F. *J. Am. Chem. Soc.* **1977**, *99*, 747. (b) Alder, R. W.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3651. (c) Alder, R. W.; Sessions, R. B.; Bennet, A. J.; Moss, R. E. *J. Chem. Soc., Perkin Trans 1* **1982**, 603. (d) Alder, R. W.; Orpen, A. G.; White, J. M. *J. Chem. Soc., Chem. Commun.* **1985**, 949.

(32) Stohrer, W. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661.

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Table VI. Best Calculated Data for Singlet Dimer Dications  $H_nXXH_n^{2+}$ 

		$r_{eq}^c$	$r_{eq}^d$	symmetric fragmentation <sup>a</sup>				deprotonation <sup>b</sup>				
				$r_{TS}^e$	$D_0^{*f}$	$T^g$	$\Delta^h$	$r_{TS}^e$	$D_0^{*f}$	$T^g$	$\Delta^h$	
HeHe <sup>2+</sup>	1	0.704 <sup>i</sup>	1.151	1.149 <sup>i</sup>	119 <sup>i</sup>	10.3 <sup>i</sup>	29.8 <sup>i</sup>					
H <sub>3</sub> NNH <sub>3</sub> <sup>2+</sup>	2	1.465	2.151	2.239	168	4.2	13.7	<i>j</i>	508	2.9 <sup>k</sup>	2.9	
H <sub>2</sub> OOH <sub>2</sub> <sup>2+</sup>	3	1.465	2.023	1.732	22	4.7	15.0	2.349	262	3.4	6.6	
HFFH <sup>2+</sup>	4	1.514	1.843									
NeNe <sup>2+</sup>	5											
H <sub>3</sub> PPH <sub>3</sub> <sup>2+</sup>	6	2.226	2.700	3.378	171	3.2	8.7	<i>j</i>	401	1.3 <sup>k</sup>	1.3	
H <sub>2</sub> SSH <sub>2</sub> <sup>2+</sup>	7	2.187	2.835	2.738	52	3.7	11.2	<i>j</i>	377	2.4 <sup>k</sup>	2.4	
HClClH <sup>2+</sup>	8	2.076	2.642	2.422	26	4.2	11.7	2.854	252	3.2	5.3	
ArAr <sup>2+</sup>	9	2.076	2.519									

<sup>a</sup>  $H_nXXH_n^{2+} \rightarrow H_nX^{+} + XH_n^{+}$ . <sup>b</sup>  $H_nXXH_n^{2+} \rightarrow H_nXXH_{n-1}^{+} + H^{+}$ . <sup>c</sup> Equilibrium length of the X-X bond in  $H_nXXH_n^{2+}$  (Å, RMP2/6-31G(d), unless otherwise noted). <sup>d</sup> Equilibrium length of the X-X bond in  $H_nXXH_n^{+}$  (Å, UMP2/6-31G(d)), <sup>e</sup> Transition structure length of the cleaving bond (Å, UMP2/6-31G(d), unless otherwise noted). <sup>f</sup> Barrier to fragmentation with zero-point vibrational correction (kJ mol<sup>-1</sup>, MP4/6-311G-(MC)(d,p)//MP2/6-31G(d), unless otherwise noted). <sup>g</sup> Kinetic energy release in fragmentation with zero-point vibrational correction (eV, MP4/6-311G-(MC)(d,p)//MP2/6-31G(d), unless otherwise noted). <sup>h</sup> Value of the  $\Delta$  parameter for the fragmentation (eV, MP2/6-31G(d), unless otherwise noted), see eq 1 and text. <sup>i</sup> Calculated at the full-CI/6-311G(MC)(d,3p2d1f) level; see Table I. <sup>j</sup> Electron transfer occurs very late along the dissociation pathway; see text. <sup>k</sup> Assumed equal to  $\Delta$ ; see text.

structure **14** for the symmetric fragmentation, which (because UMP2 theory generally underestimates such quantities for homolytic fissions<sup>11</sup>) is probably even greater than the value (3.378 Å) shown in Figure 3, is significantly greater than the P-P hemibond length (2.700 Å)<sup>2</sup> in the dimer radical cation  $H_3PPH_3^{+}$ , indicating that it may be possible to form the dication **6** by the mass spectrometric charge stripping of the hemibonded species. Because the deprotonation of **6** (which, like that in **2**, is endothermic) has a very small  $\Delta$  value (1.3 eV), it is best viewed<sup>9</sup> as a hydrogen atom loss followed, when the cleaving P-H bond is extremely elongated, by an electron transfer. The RMP2 structure **27** is therefore a poor approximation to the true transition structure for proton loss from **6**. Moreover, the barrier to deprotonation will be essentially equal to that for loss of a hydrogen atom, i.e. 401 kJ mol<sup>-1</sup>.

In summary, our calculations indicate that the barriers inhibiting the symmetric and proton-loss fragmentations of the diposphonium dication **6** are large (171 and 401 kJ mol<sup>-1</sup>, respectively) and the associated kinetic energy releases for these processes are small (3.2 and 1.3 eV, respectively). Presumably, because of the sizable barrier to P-P cleavage, bond-stretch isomerism (analogous to that predicted<sup>30</sup> for the doubly ionized bicyclo bridgehead diamines, vide supra) may also be exhibited by doubly ionized bicyclo bridgehead diposphines. *It appears that both **6** and its derivatives are ideal candidates for future experimental investigation.*

**H<sub>4</sub>S<sub>2</sub><sup>2+</sup> Dication.** The existence and stability in solution of dicationic dithioethers [R<sub>2</sub>S<sup>+</sup>-SR<sub>2</sub>] containing a sulfur-sulfur bond have been known for many years, having first been reported<sup>34</sup> by Musker and Roush more than a decade ago. Such species have continued to attract interest,<sup>35</sup> and it has been proposed<sup>34c</sup> that the ease with which the S-S bond is oxidized may be utilized in certain biochemical systems. Nonetheless, the preparation of the prototype **7** has never been reported. The H<sub>4</sub>S<sub>2</sub><sup>2+</sup> dication is structurally similar to its isoelectronic, isostructural, neutral counterpart P<sub>2</sub>H<sub>4</sub> ( $r_{pp} = 2.210$  Å,  $r_{ss} = 2.187$  Å) and has a much shorter equilibrium S-S bond length than that (2.835 Å)<sup>2</sup> in the hemibonded H<sub>2</sub>S-SH<sub>2</sub><sup>+</sup> monocation.

Our calculations indicate that the  $\Delta$  values for the symmetric fragmentation and the deprotonation of **7** are both significantly greater than the corresponding values for the diposphonium dication **6**. As a result, the S-S bond length (2.738 Å) in the transition structure **15** for the symmetric fragmentation is much

shorter than the corresponding P-P bond length in **14** (3.378 Å). Nevertheless, because the barrier to S-S cleavage is found to be significant (52 kJ mol<sup>-1</sup>), the dication **7** may be experimentally observable under appropriate conditions. The kinetic energy release for the symmetric fragmentation is calculated to be 3.7 eV.

As was also found for the deprotonation of the diposphonium dication **6**, the transition structure for proton loss from **7** is predicted to occur very late along the fragmentation coordinate, and, until the late electron transfer, the process is better described as a hydrogen atom loss than as a proton loss.<sup>9</sup> The RMP2 structure **28** is therefore a poor approximation to the true transition structure for proton loss from **7**. Moreover, the barrier to deprotonation will be essentially equal to that for loss of a hydrogen atom, i.e. 377 kJ mol<sup>-1</sup>. The associated kinetic energy release is calculated to be 2.4 eV.

Experimental observation of the hydrogen sulfide dimer dication **7** is likely to be difficult except, perhaps, at low temperatures or under conditions in which thermal equilibrium is not rapidly achieved. Nevertheless, the facile oxidation<sup>35</sup> of species such as 1,5-dithiacyclooctane is most easily interpreted as arising from the formation of a substituted derivative of **7** with a transannular S-S bond.

**H<sub>2</sub>Cl<sub>2</sub><sup>2+</sup> Dication.** The preparation of the hydrogen chloride dimer dication **8** has never been reported, but our calculations indicate that it probably does correspond to a local minimum on the H<sub>2</sub>Cl<sub>2</sub><sup>2+</sup> potential surface. Its calculated structure resembles that of the isoelectronic, isostructural, neutral species H<sub>2</sub>S<sub>2</sub> in which the S-S bond length is 2.069 Å (cf.  $r_{ClCl} = 2.076$  Å in **8**). The Cl-Cl bond in **8** is much shorter than the corresponding bond in the hemibonded HCl-ClH<sup>+</sup> dimer monocation (2.642 Å).<sup>2</sup> The  $\Delta$  values for the fragmentations of its Cl-Cl and H-Cl bonds are 11.7 and 5.3 eV, respectively. Because these are each larger than the corresponding values for the hydrogen sulfide dimer dication **7**, it is not surprising<sup>8,9</sup> that the transition structures for the symmetric fragmentation and for the deprotonation of **8** occur earlier, and the corresponding kinetic energy releases are larger, than in **7**.

The Cl-Cl bond length (2.422 Å) in the transition structure **16** for symmetric fragmentation of **8** is significantly shorter than the hemibond length (2.642 Å)<sup>2</sup> in HCl-ClH<sup>+</sup>, implying that vertical ionization of the equilibrium structure of HClClH<sup>+</sup> will lead to immediate dissociation of the resulting dication. Moreover, even if **8** were to be produced, its lifetime (under normal equilibrium conditions) would be short because of the low barrier (26 kJ mol<sup>-1</sup>) to homolytic chlorine-chlorine cleavage. The kinetic energy release for this fragmentation is calculated to be 4.2 eV.

Although the breaking bond in the transition structure **29** for deprotonation of **8** is very long, it is not as long as those for the deprotonations of **6** and **7** because its  $\Delta$  value (5.3 eV) is substantially larger. The barrier to deprotonation (252 kJ mol<sup>-1</sup>) is

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also not as high and the associated kinetic energy release (3.2 eV) is larger.

**Ar<sub>2</sub><sup>2+</sup> Dication.** The calculated stability of the argon dimer dication **9**, like that of the hydrogen fluoride dimer dication **4**, is sensitive to the introduction of electron correlation into the calculations. At the Hartree-Fock level, **9** is predicted to be unbound, but at the UMP2 level, a barrier of 65 kJ mol<sup>-1</sup> impedes its fragmentation. However, more sophisticated correlation treatments reduce this barrier until, at the level of fourth-order perturbation theory (RMP4), it disappears altogether. However, at this level, it appears that the potential curve is rather flat for 2 < r < 3 Å, and this plateau may be detectable in collision experiments. The simple ACDCP model<sup>10</sup> for the fragmentation of a diatomic dication predicts that the transition-structure bond length in the case of Ar<sub>2</sub><sup>2+</sup> is 2.24 Å, which is similar to that (2.159 Å) of the UMP2/6-31G(d) structure **17**.

### Concluding Remarks

Many of the important results of this paper are summarized in Table VI, and it is useful to note some of the features of dicationic structure and stability that are revealed in this table.

(1) The dimer dications (A<sub>2</sub><sup>2+</sup>) are more tightly bound than corresponding (hemibonded) monocations (A<sub>2</sub><sup>+</sup>) in the sense of exhibiting shorter equilibrium A-A bond lengths, but the dissociation barriers are generally smaller (and in some cases close to zero) for the dications.

(2) Transition-structure bond lengths and the associated barriers for the symmetric fragmentations and deprotonations of the dimer dications H<sub>n</sub>XXH<sub>n</sub><sup>2+</sup> are largest when X is a group V element, and both quantities decrease from left to right across the periodic table. This is in accord with the qualitative predictions of the ACDCP model (vide supra) but contrasts with the pattern of hemibond strengths in the related H<sub>n</sub>XXH<sub>n</sub><sup>+</sup> systems,<sup>2</sup> which are greatest when X is from group VII.

(3) The hydrazinium and diphosphonium dications (**2** and **6**, respectively) should form very stable salts. Three of the remaining dimer dications (H<sub>2</sub>OOH<sub>2</sub><sup>2+</sup>, H<sub>2</sub>SSH<sub>2</sub><sup>2+</sup>, and HClClH<sup>2+</sup>) may be experimentally observable under certain (nonequilibrium, low-temperature, or short-time-scale) conditions. The other dimer dications (HFFH<sup>2+</sup>, Ne<sub>2</sub><sup>2+</sup>, and Ar<sub>2</sub><sup>2+</sup>) appear to be unstable.

(4) The equilibrium structures of the dimer dications are comparable to those in their isoelectronic, isostructural, neutral analogues. For example, the geometries of He<sub>2</sub><sup>2+</sup> (**1**) and H<sub>3</sub>NNH<sub>3</sub><sup>2+</sup> (**2**) are very similar to those of the hydrogen and ethane molecules, respectively.

(5) The value of the Δ parameter for a dicationic fragmentation is a very useful indicator of the dissociation behavior. Thus, (a) a small Δ value (less than ~2-3 eV) indicates that the associated transition structure will be late and, in such cases, Δ constitutes a reliable measure of the consequent kinetic energy release; (b) for fragmentations with larger Δ values, the transition structures occur earlier along the reaction coordinate, and the resulting kinetic energy releases are larger, though bounded above by Δ; and (c) if the Δ value for a fragmentation is large (greater than ~15 eV), the barrier inhibiting the fragmentation is likely to be small or nonexistent. A notable exception is the extraordinary He<sub>2</sub><sup>2+</sup> dication **1**.

**Acknowledgment.** We gratefully acknowledge a generous allocation of time on the Fujitsu FACOM VP-100 of the Australian National University Supercomputer Facility.

**Supplementary Material Available:** Calculated total energies, zero-point vibrational energies, and ⟨S<sup>2</sup>⟩ values of the dimeric dications, their deprotonated and dehydrogenated forms, and relevant transition structures (Table VII) and of fragment neutrals, monocations, and dications (Table VIII) (4 pages). Ordering information is given on any current masthead page.

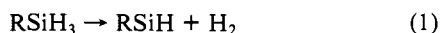
## A Theoretical Investigation of the Primary Dissociation Paths of Ethynylsilane

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Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. Received July 5, 1988

**Abstract:** Various mechanisms leading to the dissociation of ethynylsilane have been investigated by ab initio molecular orbital methods. Geometries corresponding to the reactant, transition states, and products have all been optimized at the HF/3-21G and HF/6-31G\* levels of theory. Heats of reaction and barrier heights have been obtained at the MP4SDTQ/6-31G\* level. Zero-point energy corrections and harmonic vibrational frequencies have been computed at the HF/3-21G level. These results have been used to calculate unimolecular dissociation rate constants by RRKM theory. This information is then used to reexamine the mechanisms of dissociation for ethynylsilane from previous experimental shock-tube and stirred-flow studies.

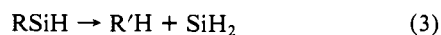
It has become generally accepted that the predominant dissociation process in alkyl-, alkenyl-, and arylsilanes is the formation of hydrogen via



with alkanes (or alkenes) formed from minor channels for primary dissociation pathways



or secondary reaction from the substituted silylene formed in reaction 1.



It is the minor and secondary channels that are responsible for the production of SiH<sub>2</sub>, an intermediate acknowledged to be important in the formation of amorphous silicon thin films. Results from numerous shock-tube and photodissociation studies<sup>1-10</sup> of

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(3) Sawrey, B. A.; O'Neal, H. E.; Ring, M. A.; Coffey, D., Jr. *Int. J. Chem. Kinet.* **1984**, *16*, 801.

(4) Rickburn, S. F.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1984**, *16*, 1371.