

Theoretical search for small linear doubly charged anions

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The electronic stabilities of linear diatomic C_2^{2-} , BN^{2-} , BP^{2-} , BeO^{2-} , BeS^{2-} , MgO^{2-} , MgS^{2-} , O_2^{2-} , SO^{2-} , and S_2^{2-} ; triatomic NCN^{2-} , SBN^{2-} , $OBeO^{2-}$, $SBeC^{2-}$, $SBeO^{2-}$, $OMgO^{2-}$, $SMgS^{2-}$, PCP^{2-} , and SCC^{2-} ; tetratomic $OCOCO^{2-}$ and $SCCS^{2-}$; and pentatomic $Be_2O_3^{2-}$, $Be_2S_3^{2-}$, $Mg_2O_3^{2-}$, and $Mg_2S_3^{2-}$ dianions were studied at the Hartree-Fock level with Gaussian basis sets including diffuse and polarization functions, as well as at the second-order Møller-Plesset level. Vertical first detachment energies of several dianions were also calculated at the fourth-order Møller-Plesset level. All diatomic, triatomic, and tetratomic dianions were found to be *unstable* to electron loss. The pentatomic $Mg_2S_3^{2-}$ dianion is predicted to be stable to electron loss with an electron detachment energy of 0.2 eV. This species is likely to be the *smallest* electronically stable linear dianion.

I. INTRODUCTION

A. Experimental situation for molecular dianions

Doubly charged organic negative ions of fairly large molecules have been observed in the gas phase. Dougherty¹ observed the double negative ion of benz[*cd*]-pyrene-6-one or its dimer; Maas and Nibbering² reported doubly charged anions of the type ${}^{-2}OC-(CH_2)_n-CO_2^{-}$ (with $n=2-7$) and ${}^{-2}OC-CH_2-C(CH_3)_2-CH_2-CO_2^{-}$. Recently, two groups^{3,4} reported the observation of long-lived ($t > 10^{-3}$ sec) C_{60}^{2-} and C_{70}^{2-} in the gas phase, and Compton and co-workers⁵ observed doubly charged carbon clusters C_n^{2-} ($n=7-28$).

Multicharged anions such as O^{2-} , N^{3-} , SO_4^{4-} , and MgF_6^{4-} are common in crystals and in solutions, but the corresponding isolated gas-phase anions are unstable with respect to loss of one or more electrons. Several observations of small multicharged inorganic gas-phase anions including SO_4^{2-} , FeF_6^{3-} , $HFeF_5^{2-}$, $RbBr_2^{2-}$,⁶ SF_6^{2-} , and SF_5^{2-} ,⁷ and even the diatomic species CN^{2-} ,⁸ have been reported. However, several other experimental studies⁹⁻¹⁹ were not able to detect SO_4^{2-} in the gas phase. Therefore, it remains quite uncertain how small a molecular framework can support electronically and geometrically stable dianions. In this paper, we attempt to address this issue for *linear* dianions.

B. Theoretical work on molecular dianions

The electronic stabilities as well as the geometric stabilities with respect to F^- loss of doubly BeF_4^{2-} (Ref. 20), CO_3^{2-} , SO_4^{2-} , MgF_4^{2-} , and SiF_6^{2-} (Ref. 21), and triply MgF_3^{3-} and AlF_6^{3-} , (Ref. 21) charged anions were studied theoretically at the Hartree-Fock and correlated [singles and doubles configuration interaction (CISD) and Green function] levels with DZP+diff. (*s,p*) Gaussian basis sets. CO_3^{2-} , SO_4^{2-} , MgF_3^{3-} , and AlF_6^{3-} were found to be *not* stable to loss of extra electrons. However, BeF_4^{2-} , MgF_4^{2-} , and SiF_6^{2-} were found to be electronically stable and to have local geometrical minima relative to F^- loss. The latter dianions should therefore be metastable and might be detected experimentally.

Recently, Ewig and van Waser²² predicted CF_6^{2-} to be stable to loss of extra electrons and to have a local minimum on its potential energy surface. Miyoshi *et al.*²³ calculated the second electron affinities of MoF_6 , CrF_6 , and WF_6 using a model potential method with configuration interaction. They found a negative second electron affinity (EA) for WF_6 , but positive second EA's for MoF_6 (1.76 eV) and CrF_6 (4.85 eV). However these results were questioned in Ref. 24, and in Refs. 25 and 26 it was argued that, among the MF_6 series, ($M=Cr-Mn-Fe-Ni$; $Mo-Tc-Ru-Rh-Pd$ or $W-Re-Os-Ir-Pt$), the second electron affinities should increase to the end of each period. According to density functional (DVM- X_α) calculations, PtF_6 has a positive second EA (0.7 eV) in the gas phase.²⁴ This result agrees qualitatively with the estimate of the EA of PtF_6^- (3.9 ± 0.6 eV) based on the crystal lattice energy of K_2PtF_6 and the experimental EA of PtF_6 by Korobov *et al.*²⁷

Many small multiply charged anions (C_2^{2-} , BP^{2-} , BeN^{3-} , NBN^{3-} , NCN^{2-} , BO_3^{3-} , CO_4^{4-} , and others) have been studied by Pyykko *et al.*²⁸⁻³⁹ However, the electronic stabilities of these multiply charged species were not considered.

In spite of all of these findings, the question remains. What is the *smallest linear dianion* that is stable to loss of extra electrons and is a local minimum on its potential surface? Our plan is to examine linear molecules with highly electronegative groups at the termini to concentrate the extra electron density at the ends to reduce the Coulomb repulsion. In this work, we present results of our quantum chemical investigations of the stability of linear diatomic, triatomic, tetratomic, and pentatomic dianions, and we conclude that specific members of the latter family are likely to be the sought-after species.

II. COMPUTATIONAL DETAILS

Full geometry optimizations (to locate minima on the potential energy surfaces) were carried out at the Hartree-Fock self-consistent field (SCF) level and at the correlated second-order Møller-Plesset (MP2) perturbation theory level using analytical energy gradient methods⁴⁰ with polarized split-valence basis sets augmented by diffuse *s* and *p*

functions (this basis is denoted SCF/6-31+G^{*}).^{41,42} The fundamental vibrational frequencies and normal coordinates were calculated by standard force constant matrix methods. The MP2(full)/6-31+G^{*} equilibrium geometries for the smaller and SCF/6-31+G^{*} geometries for the larger systems were then used to evaluate electron correlation energies at the full fourth-order frozen-core approximation (MP4) by Møller–Plesset perturbation theory⁴³ using the 6-311+G^{*}(2df) basis set for small and 6-31+G^{*} basis set for large dianions. The unrestricted SCF (USCF) wave functions for open-shell systems were spin projected to generate pure spectroscopic states for use

in the subsequent energy calculations and the corresponding results are denoted PUSCF, PMP2, PMP3, and PMP4.⁴⁴ The GAUSSIAN 90 program suite⁴⁵ was used to perform all of these calculations. For several smaller dianions, larger bases of QZP+diff.(s,p) quality were used for the SCF calculations. In the latter case, the (10s6p/5s4p) bases for B, C, N, and O were taken from Ref. 46; 3d polarization functions (with exponents α of 0.7 for B, 0.75 for C, 0.8 for N, and 0.85 for O) were taken from Ref. 47. The diffuse p functions for B, C, N, and O were taken from Ref. 47 and diffuse s functions for B ($\alpha=0.0297$), C ($\alpha=0.0505$), N ($\alpha=0.0680$), and O ($\alpha=0.0914$) were op-

TABLE I. Calculated and experimental (crystal) properties of AB²⁻ species.

Species	Method	Bond length (Å)	Total energy (a.u.)	Frequencies (cm ⁻¹)	HOMO symmetry	IP (Koopmans, eV)	IP (ΔSCF, eV)	Coulomb Energy (eV)	Refs.
C ₂ ²⁻	SCF/4-31G	1.271	-75.123 99		1π _u	-6.80			56,57
D _{∞h}	SCF/6-31G [*]	1.263		1998					28,35
¹ Σ _g ⁺	MP2/6-31G [*]	1.299		1716					28,35
	SCF/6-31+G [*]	1.271	-75.389 83	1900	1π _u	-2.88	-4.83	11.33	^a
	MP2(full)/6-31+G [*]	1.293	-75.676 94	1737	1π _u	-2.96			^a
	SCF/QZP+diff(s,p)	1.266	-75.407 57		1π _u	-2.83		11.38	^a
	Expt.	1.19–1.35		1847 1831					28,54,55
BN ²⁻	SCF/4-31G	1.304	-78.591 41		3σ	-7.07			56
C _{∞v}	SCF/6-31G [*]	1.291		1781					28
¹ Σ _g ⁺	SCF/6-31+G [*]	1.281	-78.866 14	1769	3σ	-3.02	-4.95	11.23	^a
	MP2(full)/6-31+G [*]	1.325	-79.160 30	1528	3σ	-2.93			^a
	SCF/QZP+diff(s,p)	1.288	-78.888 91		3σ	-2.85		11.18	^a
BP ²⁻	SCF/6-31G [*]	1.781		952					33
C _{∞v}	MP2/6-31G [*]	1.782		923					33
¹ Σ _g ⁺	SCF/6-31+G [*]	1.764	-365.171 33	947	3σ	-2.40	-4.44	8.16	^a
	MP2(full)/6-31+G [*]	1.745	-365.392 06	952	3σ	-2.44		8.25	^a
BeO ²⁻	SCF/6-31G [*]	1.394		1337					28
C _{∞v}	SCF/6-31+G [*]	1.360	-89.330 94	1441	3σ	-3.56	-4.39	10.59	^a
¹ Σ _g ⁺	MP2(full)/6-31+G [*]	1.410	-89.597 23	1250	3σ	-3.50		10.21	^a
	SCF/QZP+diff(s,p)	1.361	-89.357 76		3σ	-3.54	-4.33	10.89	^a
BeS ²⁻	SCF/6-31+G [*]	1.863	-412.042 08	810	3σ	-3.06	-4.24	7.73	^a
C _{∞v}	MP2(full)/6-31+G [*]	1.843	-412.231 01	839	3σ	-3.08		7.81	^a
¹ Σ _g ⁺	SCF/QZP+diff(s,p)	1.865	-412.064 79		3σ	-3.09	-4.06	7.72	^a
MgO ²⁻	SCF/6-31+G [*]	1.778	-274.275 81	808	3σ	-2.70	-3.39	8.10	^a
C _{∞v}	MP2(full)/6-31+G [*]	1.868	-274.558 80	652	3σ	-2.65		7.71	^a
¹ Σ _g ⁺	SCF/QZP+diff(s,p)	1.773	-247.308 66		3σ	-2.89	-3.52	8.12	^a
MgS ²⁻	SCF/6-31+G [*]	2.272	-597.042 89	452	3σ	-2.43	-3.18	6.34	^a
C _{∞v}	MP2(full)/6-31+G [*]	2.269	-597.226 23	451	3σ	-2.43		6.35	^a
¹ Σ _g ⁺	SCF/QZP+diff(s,p)	2.276	-597.074 45		3σ	-2.57	-3.25	6.33	^a
O ₂ ²⁻	SCF/6-31+G [*]	1.498	-149.276 69	867	1π _g	-5.37		9.61	^a
D _{∞h}	MP2(full)/6-31+G [*]	1.606	-149.712 86	637	1π _g	-4.72		8.96	^a
¹ Σ _g ⁺	SCF/QZP+diff(s,p)	1.480	-149.334 68		1π _g	-5.10		9.71	^a
	Expt	1.50							51,52
SO ²⁻	SCF/6-31+G [*]	1.662	-472.118 55	704	2π	-4.19		8.66	^a
C _{∞v}	MP2(full)/6-31+G [*]	1.693	-472.470 17	652	2π	-4.10		8.50	^a
¹ Σ _g ⁺	SCF/QZP+diff(s,p)	1.668	-472.168 23		2π	-4.13		8.63	^a
S ₂ ²⁻	SCF/6-31+G [*]	2.166	-794.888 39	453	1π _g	-3.12		6.65	^a
D _{∞h}	MP2(full)/6-31+G [*]	2.179	-795.158 24	411	1π _g	-3.09		6.61	^a
¹ Σ _g ⁺	SCF/QZP+diff(s,p)	2.183	794.936 47		1π _g	-3.14		6.60	^a
	Expt	2.10–2.15							53

^aPresent work.

timized by us. The (12s9p/6s5p) bases for S and Mg were taken from Ref. 48 (the 3p functions with $\alpha=0.4821$ and $\alpha=0.1651$ were optimized by us). The 3d polarization functions ($\alpha=0.2$ for Mg and $\alpha=0.5$ for S) were taken from Ref. 49; diffuse p functions were taken from Ref. 47 and diffuse s functions ($\alpha=0.02133$ for Mg and $\alpha=0.0723$ for S) were optimized by us. Calculations with these large basis sets were performed using our Utah MESSKIT modular electronic structure codes.⁵⁰

III. RESULTS AND DISCUSSION

All of our equilibrium geometries, frequencies, total energies, first vertical ionization potential (IP) or electron detachment energies (DE's) at the Koopmans' theorem, and Δ SCF approximations and the Coulomb repulsion energies within a simple point charge approximation are summarized in Tables I-IV. In Table V, vertical DE's calculated at the Δ PUSCF, Δ PMP2, Δ PMP3 and Δ PMP4 levels

TABLE II. Calculated and experimental (crystal) properties of ABC^{2-} species.

Species	Method	Bond	Bond length (Å)	Total energy (a.u.)	Symmetry of vibrations	Frequencies (cm ⁻¹)	HOMO symmetry	IP (Koopmans, eV)	IP (Δ SCF, eV)	Coulomb energy (eV)	Refs.	
NCN ²⁻ $D_{\infty h}$ $^1\Sigma_g^+$	SCF/4-31G	C-N	1.240								56,57	
	SCF/6-31G*	C-N	1.231		$\nu_1(\sigma_g)$	1998					29	
					$\nu_2(\pi_u)$	770						
					$\nu_3(1\sigma_u)$	2114						
	MP2/6-31G* SCF/6-31+G*	C-N C-N	1.267 1.232	-146.520 24	$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\nu_3(\sigma_u)$	1347 682 1946	$1\pi_g$	-4.02	-6.19	5.84	a	
MP2(full)/6-31+G*	C-N	1.270	-147.018 37	$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\nu_3(\sigma_u)$	1151 515 1816	$1\pi_g$	-3.92		5.67	a		
	SCF/QZP+diff(s,p) Expt	C-N C-N	1.227 1.230	-146.560 75	$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\nu_3(\sigma_u)$	1234 620-690 2000-2120	$1\pi_g$	-3.90	-5.47	5.87	a 61	
SBN ²⁻ $C_{\infty v}$ $^1\Sigma^+$	SCF/6-31G*	B-N B-S	1.262 1.837		$\nu_1(\sigma)$ $\nu_2(\pi)$ $\nu_3(\sigma)$	610 470 1955					32	
	SCF/6-31+G*	B-N B-S	1.273 1.823	-476.530 77	$\nu_1(\sigma)$ $\nu_2(\pi)$ $\nu_3(\sigma)$	617 448 1862	2π	-2.10	-4.05	4.65	a	
	OBcO ²⁻ $D_{\infty h}$ $^1\Sigma_g^+$	SCF/6-31G*	Be-O	1.426		$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\nu_3(\sigma_u)$	802 487 1521	2π	-2.10		4.65	29
		SCF/6-31+G*	Be-O	1.441	-164.228 03	$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\nu_3(\sigma_u)$	769 565 1436	$1\pi_g$	-1.80	-4.60	5.00	a
MP2(full)/6-31+G*	Be-O	1.479	-164.711 76	$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\theta_3(\sigma_u)$	680 487 1261	$1\pi_g$	-1.73	-3.50	4.87	a		
	SCF/QZP+diff(s,p)	Be-O	1.439	-164.281 37	$\nu_1(\sigma)$ $\nu_2(\pi)$ $\nu_3(\sigma)$	484 403 1466	$1\pi_g$	-1.73		5.00	a	
SBeO ²⁻ $C_{\infty v}$ $^1\Sigma^+$	SCF/6-31G*	Be-O Be-S	1.377 1.975		$\nu_1(\sigma)$ $\nu_2(\pi)$ $\nu_3(\sigma)$	484 403 1466					32	
	SCF/6-31+G*	Be-O Be-S	1.392 1.976	-486.976 83	$\nu_1(\sigma)$ $\nu_2(\pi)$ $\nu_3(\sigma)$	478 423 1391	2π	-1.44	-3.00	4.27	a	
SBeS ²⁻ $D_{\infty h}$ $^1\Sigma_g^+$	SCF/6-31+G*	Be-S	1.910	-809.702 82	$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\nu_3(\sigma_u)$	386 326 981	$1\pi_g$	-0.91	-2.12	3.77	a	
	MP2(full)/6-31+G*	Be-S	1.892	-810.017 68	$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\nu_3(\sigma_u)$	387 272 996	$1\pi_g$	-0.94		3.80	a	
	SCF/QZP+diff(s,p)	Be-S	1.910	-809.749 20			$1\pi_g$	-0.94	-1.73	3.77	a	
	OMgO ²⁻ $D_{\infty h}$ $^1\Sigma_g^+$	SCF/6-31+G*	Mg-O	1.827	-349.100 81	$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\nu_3(\sigma_u)$	595 253 849	$1\pi_g$	-1.39	-5.02	3.94	a
MP2(full)/6-31+G*		Mg-O	1.900	-349.614 73	$\nu_1(\sigma_g)$ $\nu_2(\pi_u)$ $\nu_3(\sigma_u)$	497 187 707	$1\pi_g$	-1.33		3.79	a	
SCF/QZP+diff(s,p)		Mg-O	1.816	-349.168 21			$1\pi_g$	-1.28	-2.58	3.96	a	

TABLE II. (Continued.)

Species	Method	Bond	Bond length (Å)	Total energy (a.u.)	Symmetry of vibrations	Frequencies (cm ⁻¹)	HOMO symmetry	IP (Koopmans eV)	IP (ΔSCF, eV)	Coulomb energy (eV)	Refs.
SMgS ²⁻ <i>D_{∞h}</i> <i>1Σ_g⁺</i>	SCF/6-31+G*	Mg-S	2.286	-994.655 87	<i>ν</i> ₁ (σ _g)	314	1π _g	-0.46	-1.70	3.15	^a
	MP2(full)/6-31+G*	Mg-S	2.280	-994.969 08	<i>ν</i> ₂ (π _u) <i>ν</i> ₃ (σ _u)	175 556					
PCP ²⁻ <i>D_{∞h}</i> <i>1Σ_g⁺</i>	SCF/QZP+diff(<i>s,p</i>)	Mg-S	2.279	-994.715 51	<i>ν</i> ₁ (σ _g)	310	1π _g	-0.46	-1.26	3.16	^a
	SCF/6-31G*	C-P	1.657		<i>ν</i> ₂ (π _u) <i>ν</i> ₃ (σ _u)	164 555					33
	MP2/6-31G*	C-P	1.673		<i>ν</i> ₁ (σ _g) <i>ν</i> ₂ (π _u) <i>ν</i> ₃ (σ _u)	570 387 1328					33
	SCF/6-31+G*	C-P	1.653	-719.126 85	<i>ν</i> ₁ (σ _g) <i>ν</i> ₂ (π _u) <i>ν</i> ₃ (σ _u)	604 403 1212	1π _g	-3.03	-4.40	4.36	^a
	MP2(full)/6-31+G*	C-P	1.668	-719.524 65	<i>ν</i> ₁ (σ _g) <i>ν</i> ₂ (π _u) <i>ν</i> ₃ (σ _u)	567 336 1286	1π _g	-3.00		4.32	^a
	EXPT	C-P	1.63								
SCC ²⁻ <i>C_{∞v}</i> <i>1Σ_g⁺</i>	SCF/6-31G*	S-C	1.764		<i>ν</i> ₁ (σ)	671					32
		C-C	1.235		<i>ν</i> ₂ (π) <i>ν</i> ₃ (σ)	421 2156					
	SCF/6-31+G*	S-C	1.742	-473.022 04	<i>ν</i> ₁ (σ) <i>ν</i> ₂ (π) <i>ν</i> ₃ (σ)	2083 396 681	2π	-2.49	-3.79	4.83	^a
		C-C	1.240		<i>ν</i> ₁ (σ) <i>ν</i> ₂ (π) <i>ν</i> ₃ (σ)	1826 294 645	2π	-2.60		4.79	^a
	MP2(full)/6-31+G*	S-C	1.731	-473.430 48	<i>ν</i> ₁ (σ) <i>ν</i> ₂ (π) <i>ν</i> ₃ (σ)						
		C-C	1.276								

^aPresent work.

are presented. In what follows, we examine our results for diatomic, triatomic, and larger linear dianions.

A. Diatomic dianions

Dianions with 14 valence electrons such as O₂²⁻, SO₂²⁻, S₂²⁻, etc., and with 10 valence electrons such as C₂²⁻, BN₂²⁻, BeO₂²⁻, etc., are thought to be the best candidates to form electronically stable diatomic dianions for the following reasons: (i) Dianions from both of these groups are known in crystals [e.g., O₂²⁻ in Li₂O₂, Na₂O₂, K₂O₂, and Rb₂O₂, (Refs. 51 and 52), and S₂²⁻ in Li₂S₂ and K₂S₂ (Ref. 53), and C₂²⁻ (Refs. 54 and 55); (ii) the O, S, and C atoms have positive high atomic electron affinities; and (iii) species with 14 and 10 valence electrons have closed-shell F₂ and N₂ type electronic configurations, respectively.

Previously, the equilibrium bond lengths of several diatomic dianions [C₂²⁻ (Refs. 28, 56, and 57), BN₂²⁻ (Refs. 28 and 56), BP²⁻ (Ref. 33), and BeO₂²⁻ (Ref. 28)] were calculated at the SCF level using 4-31G and 6-31G* basis sets and at the MP2/6-31G* level. The equilibrium bond lengths of the isolated dianions were found to be quite close to the corresponding values in crystal salts.

Summers and Tyrrell⁵⁶ published orbital energies for BN₂²⁻ and C₂²⁻. Their highest occupied molecular orbital (HOMO) orbital energies (with the 4-31G basis set) are

positive (+7.1 eV for BN₂²⁻ and +6.8 eV for C₂²⁻), which suggests that both of these dianions should *not* be stable to loss of an extra electron. However, the calculations of Ref. 56 employed basis sets without diffuse functions, which are known to be very important for anions (see, e.g., Refs. 58–60).

In the present study, we carried out *ab initio* calculations to optimize the bond lengths and electronic energies of BeO₂²⁻, BeS₂²⁻, MgO₂²⁻, MgS₂²⁻, C₂²⁻, Si₂²⁻, BN₂²⁻, BP₂²⁻, O₂²⁻, SO₂²⁻, and S₂²⁻ at the SCF level with 6-31+G* and QZP+diff(*s,p*) bases and at the MP2(full)/6-31+G* level. Our results, together with the available crystal data and previous *ab initio* results are presented in Table I. As this data shows, all of the diatomic dianions we studied are *not* stable to loss of an extra electron. In all cases, the HOMO orbital energies are very positive, and hence the Koopmans' theorem DE's are negative. Electron relaxation corrections calculated at the ΔSCF level move these DE's to even more negative values. Calculated correlation corrections at the PMP2, PMP3, and PMP4 levels with the large 6-311+G(2*df*) basis set reduce the instabilities (Table V), but the DE's remain very negative and, hence, the species unstable.

In our perturbation theory calculations, we used the orbital eigenvalue spectrum of the free dianions. This is

TABLE III. Calculated and experimental (crystal) molecular properties of $ABCD^{2-}$ species.

Species	Method	Bond	Bond length (Å)	Total energy (a.u.)	Symmetry of vibrations	Frequencies (cm ⁻¹)	HOMO symmetry	IP (Koopmans, eV)	Coulomb energy (eV)	Refs.	
OCCO ²⁻ $D_{\infty h}$ ${}^1\Sigma_g^+$	SCF/4-31G	C-O	1.337							57	
		C-C	1.216								
${}^1\Sigma_g^+$	SCF/6-31+G*	C-O	1.305	-225.186 62	$\nu_1(\sigma_g)$	2281	$1\pi_u$	-3.98	3.75	a	
		C-C	1.225		$\nu_2(\sigma_g)$	867					
					$\nu_3(\sigma_u)$	1284					
					$\nu_4(\pi_g)$	401					
					$\nu_5(\pi_u)$	301					
	C_{2h} 1A_g	MP2(full)/6-31+G*	C-O	1.328	-225.847 92	$\nu_1(a_g)$	1953	$2a_u$	-3.88	3.69	a
			C-C	1.276		$\nu_2(a_g)$	804				
			<CCO	164.7		$\nu_3(a_g)$	266				
						$\nu_4(a_u)$	229				
						$\nu_5(b_u)$	1225				
				$\nu_6(b_u)$		245					
Expt		C-O	1.28						65		
		C-C	1.21								
${}^1\Sigma_g^+$	SCF/6-31G*	C-S	1.734		$\nu_1(\sigma_g)$	2363				39	
		C-C	1.206		$\nu_2(\sigma_g)$	456					
					$\nu_3(\sigma_u)$	903					
					$\nu_4(\pi_g)$	514					
					$\nu_5(\pi_u)$	207					
	SCF/6-31+G*	C-S	1.727	-870.641 35	$\nu_1(\sigma_g)$	2317	$1\pi_u$	-1.80	3.08	a	
		C-C	1.210		$\nu_2(\sigma_g)$	453					
					$\nu_3(\sigma_u)$	906					
					$\nu_4(\pi_g)$	505					
					$\nu_5(\pi_u)$	189					
	MP2(full)/6-31+G*	C-S	1.706	-871.177 35			$1\pi_u$	1.98	3.09	a	
		C-C	1.248								
	${}^1\Sigma_g^+$	SCF/6-31G*	B-N	1.256		$\nu_1(\sigma_g)$	2086				
			B-B	1.692		$\nu_2(\sigma_g)$	606				
						$\nu_3(\sigma_u)$	1947				
				$\nu_4(\pi_g)$		560					
				$\nu_5(\pi_u)$		262					
SCF/6-31+G*		B-N	1.263	-158.111 47	$\nu_1(\sigma_g)$	2036	$1\pi_g$	-0.83	3.42		
		B-B	1.689		$\nu_2(\sigma_g)$	608					
					$\nu_3(\sigma_u)$	1875					
					$\nu_4(\pi_g)$	545					
					$\nu_5(\pi_u)$	258					
MP2(full)/6-31+G*		B-N	1.305	-158.656 09	$\nu_1(\sigma_g)$	1767	$1\pi_g$	-0.96	3.37		
		B-B	1.661		$\nu_2(\sigma_g)$	591					
					$\nu_3(\sigma_u)$	1619					
					$\nu_4(\pi_g)$	482					
					$\nu_5(\pi_u)$	224					

*Present work.

physically not correct because several occupied orbitals have positive orbital energies and thus lie in the continuum. We therefore carried out PMP4SDTQ/6-31+G(2df) calculations of vertical DE's for a model system consisting of MgS^{2-} plus two point positive charges located on the axis 2.0 Å to the left and right of the dianion. This models the external field that may occur in a crystal structure. All of the occupied orbitals of this model system had negative orbital energies, and this model's $\Delta PMP2$ (0.35 eV), $\Delta PMP3$ (0.47 eV), and $\Delta PMP4$ (0.47 eV) corrections to DE's (at the PUSCF level) are not very different from the $\Delta PMP2$ (0.54 eV), $\Delta PMP3$ (0.63 eV), and $\Delta PMP4$ (0.70 eV) corrections obtained for the isolated MgS^{2-} dianion. Therefore, we think that our electron correlation corrections are reasonable even for dianions

with positive-energy occupied molecular orbitals.

The instability of all diatomic dianions to loss of an extra electron is a result of the very high Coulomb repulsion energy (see Table I). The bond lengths of these diatomic species do not exceed 2.3 Å, so even if the two excess charges were localized at the termini, the Coulomb repulsion would be (6.3 eV). In diatomics with heavier atoms, the interatomic distances may be larger, but even at 4 Å the Coulomb repulsion is (3.6 eV). Our *conclusion*, therefore, is that all isolated diatomic dianions are not stable to loss of an extra electron.

B. Triatomic dianions

The 22 valence electron dianions NCN^{2-} , $OBeO^{2-}$ are the best candidates to form stable triatomic doubly nega-

TABLE IV. Calculated properties of $ABCDE^{2-}$ species.

Species	Method	Bond length/angle	Bond length (Å)/ angle (deg)	Total energy (a.u.)	Symmetry of vibrations	Frequencies (cm ⁻¹)	HOMO symmetry	IP (Koopmans, eV)	Coulomb energy (eV)
$Be_2O_3^{2-}$ $D_{\infty h}$ $1\Sigma_g^+$	SCF/6-31+G*	Be-O _b	1.458	-253.948 57	$\nu_1(\sigma_g)$	1535	$2\pi_u$	0.62	2.53
			Be-O _t		1.394	$\nu_2(\sigma_g)$			
		$\nu_3(\sigma_u)$	1574						
		$\nu_4(\sigma_u)$	958						
		$\nu_5(\pi_g)$	479						
		$\nu_6(\pi_u)$	654						
		$\nu_7(\pi_u)$	140						
$Be_2S_3^{2-}$ C_{2v} $1A_1$	SCF/6-31+G*	Be-S _b	1.961	-1222.020 32	$\nu_1(a_1)$	1043	$2b_1$	0.88	2.18
			Be-S _t		1.846	$\nu_2(a_1)$			
		<BeS _b Be	113.8		$\nu_3(a_1)$	282			
		<S _b BeS _t	173.4		$\nu_4(a_1)$	52			
		$\nu_5(a_2)$	293						
		$\nu_6(b_1)$	289						
		$\nu_7(b_2)$	1017						
		$\nu_8(b_2)$	424						
$\nu_8(b_2)$	278								
$Mg_2O_3^{2-}$ $D_{\infty h}$ $1\Sigma_g^+$	SCF/6-31+G*	Mg-O _b	1.834	-623.697 72	$\nu_1(\sigma_g)$	886	$2\pi_u$	0.40	1.98
			Mg-O _t		1.791	$\nu_2(\sigma_g)$			
		$\nu_3(\sigma_u)$	962						
		$\nu_4(\sigma_u)$	717						
		$\nu_5(\pi_g)$	200						
		$\nu_6(\pi_u)$	268						
		$\nu_7(\pi_u)$	49						
$Mg_2S_3^{2-}$ C_{2v} $1A_1$	SCF/6-31+G*	Mg-S _b	2.329	-1591.925 64	$\nu_1(a_1)$	571	$2b_1$	1.07	1.75
			Mg-S _t		2.228	$\nu_2(a_1)$			
		<MgS _b Mg	124.9		$\nu_3(a_1)$	158			
		<S _b MgS _t	175.3		$\nu_4(a_1)$	32			
		$\nu_5(a_2)$	146						
		$\nu_6(b_1)$	162						
		$\nu_7(b_2)$	581						
		$\nu_8(b_2)$	356						
		$\nu_9(b_2)$	140						

*Present work.

tive ions because (i) NCN^{2-} is known in crystals, [e.g., Li_2NCN (Ref. 61)] and (ii) these dianions have closed-shell electronic configurations like CO_2 . Moreover, OBO (which is isoelectronic with $OBeO^-$) and $OAlO$ (isoelec-

TABLE V. Calculated vertical IP's (eV) of doubly charged anions at correlated levels with 6-311+G(2df) basis set.

Species	DE (Koop.)	DE (DPUSCF)	DE (DPMP2)	DE (DPMP3)	DE (DPMP4)
BP^{2-}	-2.51	-4.94	-3.30	-3.47	-3.25
Si_2^{2-}	-2.65	-3.38	-2.71	-2.76	-2.72
S_2^{2-}	-3.14	-4.53	-3.85	-3.88	-3.88
MgO^{2-}	-2.61	-4.40	-1.77	-2.97	-1.46
MgS^{2-}	-2.42	-3.22	-2.68	-2.59	-2.52
$OMgO^{2-}$	-1.33	-5.60	-0.66	-2.73	-0.72
$SMgS^{2-}$	-0.50	-2.06	-0.99	-1.12	-1.17
$NBBN^{2-}$	-0.96 ^a	-3.86 ^a	-0.96 ^a	-1.94 ^a	-1.37 ^a
$SCCS^{2-}$	-1.98 ^a	-3.13 ^a	-2.64 ^a	-2.73 ^a	-2.73 ^a
$Be_2O_3^{2-}$	0.62 ^a	-2.03 ^a	-0.05 ^a	-0.63 ^a	-0.39 ^a
$Mg_2O_3^{2-}$	0.40 ^a	-3.03 ^a	+1.25 ^a	-0.59 ^a	+1.39 ^a
$Be_2S_3^{2-}$	0.88 ^a	-0.20 ^a	+0.06 ^a	+0.03 ^a	-0.03 ^a
$Mg_2S_3^{2-}$	1.07 ^a	-0.67 ^a	+0.23 ^a	+0.12 ^a	+0.20 ^a

^a6-31+G* basis set.

tronic with $OMgO^-$) possess very high electron affinities [4.2 eV (Ref. 62) and 4.1 eV (Ref. 63) respectively].

Previously, Radom⁵⁷ optimized the geometry of NCN^{2-} at the SCF/4-31G level and Pyykko^{29,31-33} calculated equilibrium geometries and harmonic frequencies of NCN^{2-} , NNC^{2-} , OBN^{2-} , FCB^{2-} , $FBeN^{2-}$, OCC^{2-} , SCC^{2-} , $OBeO^{2-}$, $SBeO^{2-}$, POB^{2-} , PNC^{2-} , PCN^{2-} , and PBO^{2-} at the SCF/6-31G* level and for some of these species at the MP2/6-31G* level. All of these dianions were found to have minima with no imaginary frequencies on the potential energy surfaces if electron detachment were restricted by using a finite basis set. The calculated frequencies and bond lengths of NCN^{2-} are in agreement with the corresponding crystal data (see Table II).

Because these previous calculations were made without diffuse basis functions, we repeated the calculations on NCN^{2-} , SBN^{2-} , $OBeO^{2-}$, $SBeO^{2-}$, PCP^{2-} , and SCC^{2-} and we carried out geometry optimizations for these species as well as for $SBeS^{2-}$, $OMgO^{2-}$, and $SMgS^{2-}$ using 6-31+G* and QZP+diff.(s,p) basis sets at the SCF level and with the 6-31+G* basis set at the MP2(full) level. We

found all these dianions to have linear structures at both SCF/6-31+G* and MP2(full)/6-31+G* levels.

Although the maximum distances between the negative charges in these triatomic species are larger than in the diatomic dianions, even these dianions are predicted to be not stable to loss of an extra electron because of the large Coulombic repulsion. Their HOMO orbital energies are still positive, and including electron relaxation (at the Δ SCF approximation) makes the instabilities even worse (see Table II). However, electron correlation corrections decrease the instabilities, but their vertical DE's calculated at the PMP2, PMP3, and PMP4 levels with the large 6-311+G(2df) basis set are still negative (see Table V). We therefore predict that isolated linear triatomic dianions are not viable species.

C. Tetraatomic dianions

Previously, several linear tetraatomic dianions have been studied; they include OCCO²⁻,^{36,57} SCCS²⁻,³⁹ CCCC²⁻,³⁶ NBBN²⁻,³⁶ and NNNN²⁻.³⁶ Geometries and frequencies were calculated at the SCF/6-31G* level and several of these species were studied also at the MP2(full)/6-31G* level. For all of these dianions local minima have been found, but for N₄²⁻ a D_{4h} planar dianion was found to have lower energy. The electronic stability was considered in only one case OCCO²⁻,^{36b} and a positive energy HOMO was found.

We studied three tetraatomic dianions OCCO²⁻, NBBN²⁻, and SCCS²⁻ because we expected they would be good candidates to form stable dianions. In these species, the electronegative atoms (O or S) are placed at the termini and therefore minimize the Coulomb repulsion. Moreover, the corresponding terminal atoms -O and -S have unsaturated valences and quite high EAs. Moreover, the OCCO²⁻ dianion is known as a structural unit in the crystal salts.

At the SCF/6-31+G* level, we found linear structures for these molecules. However, at the MP2(full)/6-31+G* level, the OCCO²⁻ dianion has two imaginary frequencies and the linear structure is thus not a minimum. Actually, the OCCO²⁻ dianion has a C_{2h} minimum at the MP2(full)/6-31+G* level. However, the barrier to reach linearity is very small (0.3 kcal/mol at MP2(full)/6-31+G*) so this dianion is quasilinear with the ground vibrational state lying above the barrier.

We find OCCO²⁻, NBBN²⁻, and SCCS²⁻ to be unstable to the loss of an extra electron. Their HOMO orbital energies are positive, and electron relaxation and electron correlation corrections do not change this conclusion (see Table V). While the HOMO orbital energy decreases by 1.2 eV from OCCO²⁻ to SCCS²⁻, we do not expect that isoelectronic species with heavier atoms will be electronically stable.

D. Pentatomic dianions

Earlier, two nonlinear pentatomic dianions BeF₄²⁻ and MgF₄²⁻ were predicted to be stable to loss of an extra electron and to be kinetically stable to loss of F⁻.^{20,21} The

stability of these dianions arises from the delocalization of the two extra electrons over four electronegative (F) atoms. In the case of the linear species treated here, such delocalization is less effective but localizing the charge on the two terminal atoms will keep the Coulomb repulsion to a minimum.

We investigated the Be₂O₃²⁻, Be₂S₃²⁻, Mg₂O₃²⁻, and Mg₂S₃²⁻ dianions at the SCF/6-31+G* level. We optimized their geometries within both D_{∞h} and C_{2v} symmetry constraints. The Be₂O₃²⁻ and Mg₂O₃²⁻ dianions are predicted to be linear, but Be₂S₃²⁻ and Mg₂S₃²⁻ dianions have two imaginary vibrational frequencies at linear geometries. The barriers to linearity in the latter two species are small 6.8 kcal/mol for Be₂S₃²⁻ and 1.3 kcal/mol for Mg₂S₃²⁻.

All of the above pentatomic dianions are found to have negative HOMO orbital energies and thus to be stable to loss of an extra electron within the Koopmans' approximation. The HOMO energies of Be₂S₃²⁻ and Mg₂S₃²⁻ change by 0.12 and 0.07 eV, respectively, when their structures change from C_{2v} to D_{∞h}. When electronic relaxation is taken into account, all four dianions became unstable to the loss of an extra electron, but when correlation energy is also included, the DE's of Be₂O₃²⁻ and Mg₂O₃²⁻ vary so strongly among the PMP2, PMP3, and PMP4 treatments that we cannot reliably predict the stability of these dianions. Our best calculated electron detachment energies are +0.20 eV for Mg₂S₃²⁻ and about ~0 eV for Be₂S₃²⁻ at the PMP 4SDTQ/6-31+G* level. Mg₂S₃²⁻ is thus our candidate for the smallest stable linear dianion.

The smallest linear doubly charged anion that has been experimentally identified is C₇²⁻;⁵ Compton and co-workers⁵ proposed a simple explanation for why C₆²⁻ is not stable. They assumed that each of the extra electrons is attached to a C₂ moiety (rather than a C atom) at the end of the linear carbon cluster chain. The total electron binding energy, relative to the neutral molecule, is then computed as twice the electron affinity of HC₂ (2.97 eV) minus the repulsion energy between the distant electron pair. This simple picture predicts that C_n²⁻ will become electronically stable for n=7. For our Be₂S₃²⁻, and Mg₂S₃²⁻ species, the electron affinity of the terminal -O or -S groups are higher than that of HC₂, therefore it is not surprising that these species are stable to loss of an extra electron.

One of the important questions that follows from this work is why doubly charged anions like C₂²⁻, O₂²⁻, NCN²⁻, and others that are calculated with incorrect wave functions (e.g., functions in which the dianion has a positive-energy occupied MO), often have bond lengths and frequencies very close to experimental data for dianions in solid state. Moreover, the electronic instability of many multiply charged anions in the gas phase means that these species are stable in the solid state only due to environmental effects. The answer is that in solids, dianions experience external electrostatic fields from surrounding counterpart cations; these fields constrain the electrons from escaping. In the gas phase, multiply charged anions studied using basis sets without diffuse functions have barriers to the loss of an electron due to the restricted form of the basis sets (i.e., no diffuse functions).

IV. CONCLUSIONS

The main conclusions of this study are the following. (1.) Isolated, gas-phase *linear* diatomic, triatomic, and tetraatomic molecular dianions are *not stable* to electron loss. (2.) The pentatomic dianion, $Mg_2S_3^{2-}$, is predicted to be stable to electron loss and thus might be detected in mass-spectrometric experiments. Pentatomic dianions such as $Mg_2S_3^{2-}$ and isoelectronically related species are probably the smallest stable doubly charged quasilinear negative ions. (3.) Electron relaxation and electron correlation corrections are essential to consider when predicting the stability of doubly charged negative ions. The Koopmans' approximation is not adequate.

Note added in proof. Recently, M. K. Scheller and L. S. Cederbaum [J. Phys. B **25**, 2257 (1992)] examined a very small nonlinear dianion LiE_3^{2-} . This may be the smallest stable dianion.

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