

***Ab initio* predictions of atomic properties of element 120 and its lighter group-2 homologues**

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(Received 20 November 2012; published 4 February 2013)

The ionization potentials, excitation energies, and electron affinity of superheavy element 120 and the polarizabilities of its neutral and ionized states are calculated. Relativity is treated within the four-component Dirac-Coulomb formalism; Breit or Gaunt terms are added in some cases. Electron correlation is included via the intermediate Hamiltonian Fock-space coupled cluster method for the spectra and ionization potentials and via the single reference coupled cluster singles and doubles with perturbative triples [CCSD(T)] approach for the electron affinities and polarizabilities. To assess the accuracy of the results, the atomic properties of the lighter homologues, Ba and Ra, are also calculated. Very good agreement with available experimental values is obtained, lending credence to the predictions for element 120. The atomic properties in group 2 are largely determined by the valence ns orbital, which experiences relativistic stabilization and contraction in the heavier group-2 elements. As a result, element 120 is predicted to have a relatively high ionization potential (5.851 eV), similar to that of Sr, and rather low electron affinity (0.021 eV) and polarizability (163 a.u.), comparable to those of Ca. The adsorption enthalpy of element 120 on Teflon, which is important for possible future experiments on this atom, is estimated as 35.4 kJ/mol, the lowest among the elements considered here.

DOI: [10.1103/PhysRevA.87.022502](https://doi.org/10.1103/PhysRevA.87.022502)

PACS number(s): 31.15.bw, 31.15.ag

I. INTRODUCTION

A first attempt at producing element 120 was recently made at the GSI, Darmstadt [1,2]. There are two promising nuclear reactions that should yield this element. The first is $^{50}\text{Ti} + ^{249}\text{Cf}$, giving the $^{295}120$ and $^{296}120$ isotopes in the $4n$ and $3n$ evaporation channels, respectively [3]. The second reaction with a lower expected cross section is $^{54}\text{Cr} + ^{248}\text{Cm}$, yielding the $^{298}120$ and $^{299}120$ isotopes, again in the $4n$ and $3n$ evaporation channels, respectively. All these isotopes are expected to be extremely short-lived, with half-lives between 5 and 50 μs , close to the lowest limit of a half-life (1 μs) for a nucleus to be observable [4].

Theoretical investigations of atomic properties of superheavy elements are important in assigning these atoms their place in the periodic table and in gaining insight into their chemical behavior [5–10]. As the significance of relativistic effects grows dramatically with increasing atomic number, superheavy elements provide a unique opportunity for investigating the influence of relativity on electronic structure. Knowledge of atomic properties can also assist in experimental research; for example, ionization potentials (IPs) and polarizabilities (α) are linked to adsorption properties on various surfaces, used to characterize and separate elements produced in accelerators. To be reliable, theoretical predictions of atomic properties should be based on benchmark quality calculations, which treat relativity and electron correlation at the highest possible level.

Atomic properties of element 120 have been calculated in a number of previous publications. The earliest Dirac-Slater and Dirac-Fock (DF) calculations are reported in Refs. [7,11,12]. More recently, the IP and excitation spectra of neutral and

singly ionized element 120 were studied by Dinh *et al.*, using the relativistic configuration interaction method combined with many-body perturbation theory (CI + MBPT) [13,14]. Another investigation of the IP of element 120 has been published by Thierfelder *et al.*, using the relativistic Fock-space coupled cluster (FSCC) approach, albeit with a rather limited basis set and a minimal model space [15]. Finally, we have recently published a relativistic density functional theory (DFT) study of the properties of M_2 and MAu dimers, where $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Ra}$, and element 120 [16]. There, molecular properties (dissociation energies) were used to make predictions of the sublimation enthalpy (ΔH_{sub}) of element 120 and its adsorption enthalpies (ΔH_{ads}) on gold, silver, and platinum surfaces. In addition to the molecular calculations, we also examined trends in the atomic properties of group-2 elements. It was shown that the studied properties, such as IPs, electron affinities (EAs), polarizabilities, electronegativities, and atomic radii exhibit a trend reversal at Ba, caused by the relativistic effects experienced by the valence ns electrons of the heavier atoms in the group.

Here we present relativistic benchmark calculations of the first and second IPs, EAs, excitation energies (EEs), and static dipole polarizabilities of element 120 and the polarizabilities of its singly and doubly charged ions. Similar calculations for the lighter homologues Ba and Ra, for which experimental atomic properties are available, provide an assessment of the accuracy of our calculations and the reliability of the predictions for the superheavy atom. In addition, we estimate the ΔH_{ads} of element 120 on a Teflon surface. Teflon capillaries are used to transport the newly produced atoms from the target chamber to the chemistry setup. Thus, knowledge of the ΔH_{ads} of the

atom on Teflon is important for predicting its yield at the end of the transport capillary.

II. METHOD AND COMPUTATIONAL DETAILS

A. Ionization potentials and excitation energies

The IPs and EEs were calculated within the framework of the projected four-component (4c) Dirac-Coulomb-Breit Hamiltonian [17],

$$H_{\text{DCB}} = \sum_i h_D(i) + \sum_{i<j} (1/r_{ij} + B_{ij}). \quad (1)$$

Here, h_D is the one-electron Dirac Hamiltonian,

$$h_D(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2\beta_i + V_{\text{nuc}}(i), \quad (2)$$

where $\boldsymbol{\alpha}$ and β are the four-dimensional Dirac matrices. The nuclear potential takes into account the finite size of the nucleus, modeled by a uniformly charged sphere [18]. The two-electron term includes the nonrelativistic electron repulsion and the frequency-independent Breit operator,

$$B_{ij} = -\frac{1}{2r_{ij}} [\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + (\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})/r_{ij}^2], \quad (3)$$

and is correct to second order in the fine structure constant α .

Electron correlation is included by the multireference FSCC, described in detail in Refs. [19,20]. One advantage of the method is the capability of obtaining a large number of energy levels in one calculation; it is therefore well suited for calculating the excitation spectra. A single reference approach is more easily amenable to incorporating triple excitations and is therefore preferable when these are important (see following subsections).

In order to allow the use of large model spaces without encountering convergence difficulties in the coupled cluster iterations, the FSCC calculations are augmented by the extrapolated intermediate Hamiltonian approach (XIH) [21], which has been applied to a large number of atomic systems [21,22], yielding IPs, EAs, and EEs in excellent agreement with experimental values, typically within 1–50 meV.

The calculations start from the closed shell dications of Ra and element 120; two electrons are added, one at a time, to obtain the energies of the singly ionized and neutral atoms. The uncontracted universal basis set [23] was used, consisting of even-tempered Gaussian type orbitals, with exponents given by

$$\begin{aligned} \xi_n &= \gamma \delta^{(n-1)}, \quad \gamma = 106\,111\,395.371\,615, \\ \delta &= 0.486\,752\,256\,286. \end{aligned} \quad (4)$$

The basis set used for both Ra and element 120 consists of 37 *s* ($n = 1\text{--}37$), 31 *p* ($n = 5\text{--}35$), 26 *d* ($n = 9\text{--}34$), 21 *f* ($n = 13\text{--}33$), 16 *g* ($n = 17\text{--}32$), 11 *h* ($n = 21\text{--}31$), and 6 *i* ($n = 25\text{--}30$) functions. Virtual orbitals with energies over 200 hartree were omitted. The outer 52 electrons were correlated for both elements, leaving 36 core electrons of radium and 68 core electrons of element 120 uncorrelated. The size of the model space (P) was increased up to convergence of the calculated IPs; the final P contains 8s6p6d5f2g1h orbitals for Ra and 8s6p5d4f3g2h orbitals for element 120.

For heavy, and especially for superheavy elements, the contribution of QED effects beyond the frequency-independent Breit term might become non-negligible. In order to correct our calculated IPs for this contribution, we turn to the work of Thierfelder and Schwerdtfeger [24], who calculated the self-energy, vacuum polarization, and frequency-dependent Breit energy for group 1, 2, 11, 12, 13, and 18 elements. Their calculations were done within the picture of bound-state QED, using perturbation theory (for details see Ref. [24]). The composite effect of the three QED terms lowers the first IP of Ra and element 120 by 46.2 and 101.7 cm^{−1}, respectively.

B. Polarizabilities

Static dipole polarizabilities were obtained using the finite field approach [25,26], with atomic energies calculated for the free atoms and in the presence of a uniform electric field acting in the *z* direction, F_z . The energy of the atom in the presence of an electric field is given by

$$\begin{aligned} E(F_z) &= E(0) + F_z \left. \frac{\partial E(F_z)}{\partial F_z} \right|_{F_z=0} \\ &+ \frac{1}{2} F_z^2 \left. \frac{\partial^2 E(F_z)}{\partial^2 F_z} \right|_{F_z=0} + \dots \end{aligned} \quad (5)$$

The first term in this equation is the ground-state energy of the atom in the absence of the electric field, the second term contains the dipole moment, which vanishes for atoms, and α appears in the third term,

$$\alpha = -2 \frac{\partial^2 E(F_z)}{\partial^2 F_z}. \quad (6)$$

Atomic energy calculations were performed for $F_z = 0$, 0.0005, and 0.0010 a.u., and the polarizabilities were obtained by numerical differentiation. Good linearity of the energy shift with respect to F_z^2 was observed. The polarizabilities of neutral Ba, Ra, and element 120, as well as their singly and doubly charged ions, were calculated. These calculations, as well as the calculations of the EAs, described below, were carried out using the DIRAC08 computational program package [27].

Faegri's [28] dual family basis sets of uncontracted Gaussian-type orbitals was used for Ba and Ra. This type of basis set is not available for element 120; we therefore used a basis set constructed from Faegri's basis set for element 118, from Ref. [15]. The basis sets were augmented by adding diffuse and higher angular momentum functions until the calculated polarizabilities converged. The final basis sets were 24s22p16d12f4g1h for Ba, 26s23p18d13f5g2h for Ra, and 28s26p20d15f5g2h for element 120. Virtual orbitals with energies above 50 a.u. were omitted, and 28, 42, and 52 electrons were correlated for Ba, Ra, and element 120, respectively.

The 4c-Dirac-Coulomb Hamiltonian was used for the energy calculations, with an approximate estimate of the lowest-order relativistic correction to the two-electron term in the Hamiltonian provided by the Gaunt operator, $-e^2(\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2)/r_{12}$ [29]. The Gaunt interaction is included fully at the Dirac-Hartree-Fock (DHF) stage; at the correlation stage it is incorporated using the atomic mean-field integral (AMFI) approximation [30]. Gaunt interaction calculations are extremely demanding in computer resources; therefore, smaller basis

sets were used, $23s21p15d10f3g$ for Ba, $26s23p17d11f3g$ for Ra, and $28s25p19d12f4g$ for element 120. Calculations were performed with and without the Gaunt term using these basis sets, and the difference in the obtained polarizabilities constitutes the Gaunt contribution, which was added to the Dirac-Coulomb results for the large, converged basis set for each of the atoms.

Correlation was included by the relativistic single reference coupled cluster method with single, double, and perturbative triple excitations [RCCSD(T)]. To demonstrate the contribution of electron correlation to the calculated polarizabilities, we also present results obtained using the DHF, second-order Møller-Plesset perturbation theory (MP2), and RCCSD methods. In order to get an additional check on the results, calculations using the FSCC approach, outlined in Sec. II A, were also carried out.

C. Electron affinities

The EAs were calculated using the RCCSD(T) approach. Universal basis sets, described in Sec. II A, consisting of $34s32p25d20f8g2h$ functions for Ba, $33s31p25d20f8g2h$ functions for Ra, and $34s31p25d19f7g2h$ for element 120, were used. Convergence of the calculated EAs with respect to the size of the basis set was verified for the three atoms. Virtual orbitals with energies above 50 a.u. were omitted, and 28, 42, and 52 electrons were correlated for Ba, Ra, and element 120, respectively.

TABLE I. First and second ionization potentials (IP) and excitation energies (EE) of neutral Ra (cm^{-1}), compared with experiment [31] and other calculations. Average absolute errors ($\langle \Delta E \rangle$) are given.

	State	XIHFSCC ^a	IH1-FSCC ^b	CI + MBPT ^c	Expt.
IP1	$7s^1$ 2S	42608	42943	42531	42573
	+ QED ^d	42562			
EE	$7s7p$ 3P_0	13093	13183	12916	13078
	3P_1	14017	14102	13844	13999
	3P_2	16675	16805	16566	16689
	1P_1	20792	20823	20667	20716
	$6d7s$ 3D_1	14021	13827	13622	13716
	3D_2	14292	14102	13902	13994
	3D_3	14989	14839	14645	14707
	1D_2	17376	17159	17000	17081
	$7s8s$ 3S_1	26762	27128		26754
	$6d7p$ 3F_2	28328	28127		28038
	3F_3	30388	30306		30118
	3F_4	32603	32601		32368
	1D_2	31121	31178		30918
	$7s8p$ 3P_0	31126	31467		31086
	3P_1	31636	32245		31563
	3P_2	31934	32245		31874
IP2	$7s^0$ 1S	82080		82034	81842
$\langle \Delta E \rangle$	8 low EEs	139	108	102	
$\langle \Delta E \rangle$	all EEs	143	201		

^aPresent work.

^bReference [32].

^cReferences [13,14], empirical correction factors were employed.

^dSelf-energy, vacuum polarization, and frequency-dependent Breit energy contribution, amounting to -46.2 cm^{-1} (Ref. [24]).

III. RESULTS AND DISCUSSION

A. Ionization potentials and excitation energies

Table I contains the calculated IPs of Ra and Ra^+ and the transition energies of the neutral system. For all the calculated values, our results are in very good agreement with the experimental data, in particular for the first IP, where the QED corrections lower the calculated value to coincide with experiment. This indicates that the basis set and correlation effects were taken into account to the highest possible degree. The most recent high quality calculations of the electronic structure of Ra are the relativistic FSCC investigations of Landau *et al.* [32] and the CI + MBPT calculations of Dinh *et al.* [13,14]. The latter were empirically corrected by use of fitting factors, found by comparing calculated and experimental values for Ba; the present results achieve similar accuracy without such factors.

The first two IPs and the low excitation energies of element 120 are presented in Table II. The only previous investigation of the spectrum of this atom is of Ref. [14], carried out as described above, with empirical fitting factors obtained by comparing the computed and experimental values for Ra. Our results are again in good agreement with Ref. [14]. Another value of the IP of element 120 is from the work of Thierfelder *et al.* [15], calculated using the DC Hamiltonian and the FSCC approach. The value presented there, $44\,121 \text{ cm}^{-1}$, is significantly lower than the results of this work and Ref. [14], which may be attributed to a smaller basis set and use of a minimal model space consisting of the $8s$ orbital only.

The two IPs of element 120 are higher than the corresponding Ra values by about 5000 and 8000 cm^{-1} , respectively,

TABLE II. First and second ionization potentials (IP) and excitation energies (EE) of neutral element 120 (cm^{-1}).

	State	XIHFSCC ^a	CI + MBPT ^b
IP1	$8s^1$ 2S	47191	47296
	+ QED ^c	47089	
EE	$8s8p$ 3P_0	15648	15777
	3P_1	17587	17710
	3P_2	25192	25419
	1P_1	27513	27667
	$7d8s$ 3D_1	22903	22985
	3D_2	23034	23163
	3D_3	23782	23799
	1D_2	27247	27438
	$8s9s$ 3S_1	30862	
	$7d8p$ 3F_2	39703	
	3F_3	43969	
	3F_4	51846	
	1D_2	53036	
	$8s9p$ 3P_0	35463	
	3P_1	35595	
	3P_2	37369	
IP2	$8s^0$ 1S	89831	89931

^aPresent work.

^bReferences [13,14], empirical correction factors were employed.

^cSelf-energy, vacuum polarization, and frequency-dependent Breit energy contribution, amounting to -101.7 cm^{-1} (Ref. [24]).

TABLE III. Static dipole polarizabilities of Ba, Ra, and element 120, and their singly and doubly charged ions (a.u.).

	DHF	MP2	FSCCSD	RCCSD	RCCSD(T)
Ba	324.1	213.8	256.7	281.3	272.8
Ba ⁺	174.6	100.8	125.2	132.0	125.4
Ba ²⁺	10.5	10.3	10.4	10.4	10.4
Ra	293.4	193.0	235.7	251.8	242.8
Ra ⁺	114.2	84.0	106.0	110.9	105.9
Ra ²⁺	13.7	13.6	13.6	13.6	13.6
120	183.4	148.6	160.6	165.2	162.3
120 ⁺	83.3	65.7	71.6	73.3	72.0
120 ²⁺	21.6	20.5	20.9	20.9	20.9

due to the relativistic stabilization of the valence *s* orbital. The same trend is shown by the excitation energies, all of which are higher in element 120 than the corresponding values of Ra.

B. Polarizabilities

Table III contains polarizabilities of Ba, Ra, and element 120 and their singly and doubly charged ions, obtained using different correlation schemes. DHF significantly overestimates the polarizabilities of the neutral atoms and singly charged ions, and the second-order correction overshoots the mark, giving errors [with respect to RCCSD(T)] similar in size to calculations performed using DHF, but in the opposite direction. The differences between the results obtained using the different CC schemes occur because the Fock-space approach uses orbitals of the doubly charged ions, whereas the single reference scheme employs orbitals of the neutral atoms. The RCCSD(T) result is the most accurate, due to the inclusion of triple excitations; all three values for Ba fall within the error bars of the experimental 268(22) a.u. [33]. The doubly charged ions show negligible correlation effects due to the large gap between the highest occupied orbitals and the lowest unoccupied orbitals.

The contribution of the Gaunt term is between −0.5 and +0.2 a.u. for all the systems and correlation schemes. In our final values of the polarizabilities we correct the RCCSD(T) results for this contribution; QED effects can be safely neglected here.

Table IV contains the final polarizabilities, compared to the previously calculated and experimental values. The polarizability of Ba was investigated in numerous publications using a variety of methods. Here we compare our results with the most recent, relativistic *ab initio* investigations [34–38,41–43] and with experiment [33,39]. Our value for the neutral atom is in excellent agreement with all the previous publications, except for that of Roos *et al.* [38], which is significantly higher than all the other results and falls outside the experimental uncertainty. In case of the positively charged atom, the comparatively small error bars of the experimental value allow meaningful comparison to the experiment. Our value is in good agreement with the measured polarizability, as are the other theoretical investigations.

TABLE IV. Static dipole polarizabilities of Ba, Ra, and element 120 (a.u.).

α	Method	Reference
Ba		
272.7	RCCSD(T) + Gaunt	Present work
268(22)	Experimental	[33]
273.5	R-CI + MBPT ^a	[34]
273.9	DK + CCSD(T) ^b	[35]
275.5	ARPP + CCSD(T) ^c	[36]
268	RCCSD	[37]
312	DK + CASPT2 ^d	[38]
Ba ⁺		
125.3	RCCSD(T) + Gaunt	Present work
123.9(5)	Experimental	[39]
124.5	R-SDpT ^e	[41]
124.3	RCCSD(T)	[42]
123.1	DK + CCSD(T) ^b	[35]
122.4	ARPP + CCSD(T) ^c	[36]
Ba ²⁺		
10.4	RCCSD(T) + Gaunt	Present work
10.5	DK + CCSD(T) ^b	[35]
10.5	ARPP + CCSD(T) ^c	[36]
Ra		
242.8	RCCSD(T) + Gaunt	Present work
248.6	DK + CCSD(T) ^b	[35]
251.1	ARPP + CCSD(T) ^c	[36]
283	DK + CASPT2 ^d	[38]
Ra ⁺		
105.3	RCCSD(T) + Gaunt	Present work
105.4	DK + CCSD(T) ^b	[35]
107.4	ARPP + CCSD(T) ^c	[36]
104.5	RCCSD(T)	[42]
106.5	RMBPT	[43]
Ra ²⁺		
13.8	RCCSD(T) + Gaunt	Present work
13.7	DK + CCSD(T) ^b	[35]
13.4	ARPP + CCSD(T) ^c	[36]
120		
162.6	RCCSD(T) + Gaunt	Present work
120 ⁺		
72.1	RCCSD(T) + Gaunt	Present work
120 ²⁺		
20.9	RCCSD(T) + Gaunt	Present work

^aRelativistic configuration interaction (CI) combined with many-body perturbation theory (MBPT).

^bAll-electron scalar-relativistic Douglas-Kroll (DK) combined with CCSD(T).

^cSmall-core scalar-relativistic pseudopotential (ARPP) combined with CCSD(T).

^dDouglas Kroll, with complete active space second-order perturbation theory (CASPT2).

^eRelativistic all-order single-double partial triple excitation method [40].

The α of Ra has not been measured yet; we thus compare our results with the available theoretical estimates [35,36,38]. The Douglas-Kroll complete active space second-order perturbation theory (CASPT2) value of Roos *et al.* [38] is again higher than our results and other theoretical results, as was the case with Ba. Our value of 242.8 a.u. is slightly lower than both

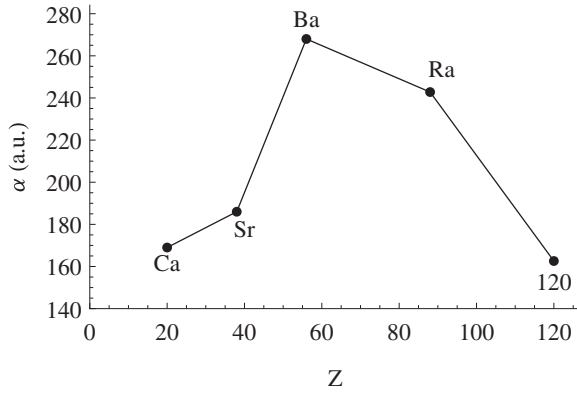


FIG. 1. Polarizabilities of group-2 elements (experimental for Ca [44], Sr [33], and Ba [33]; current calculations for Ra and element 120).

the all-electron Douglas-Kroll CCSD(T) and the small-core relativistic pseudopotential CCSD(T) values of Lim *et al.* [35,36] due, perhaps, to a more complete treatment of relativity in our approach. For both Ra^+ and Ra^{2+} , our results are in very good agreement with the earlier calculations [35,36,42,43].

Static atomic polarizability is linked to the atomic size, which in turn may be approximated by the cube of the radius of the maximal charge density of the valence orbital (ns orbital in the case of the group-2 elements studied here), $[R_{\max}(ns)]^3$. For the neutral atoms and the singly charged ions, α increases from Ca to Ba and then decreases toward element 120 (Fig. 1), which can be explained by the strong relativistic contraction of the ns orbital. The polarizability of element 120 (162.6 a.u.) is thus similar to that of Ca (169 ± 17 a.u. [44]). To the best of our knowledge, the only previous *ab initio* value for α of element 120 is provided by the nonrelativistic restricted HF calculations of Koch and Andrae [45]. However, as the nonrelativistic HF approach does not account for the relativistic contraction of the ns orbital, the α obtained there is overestimated (568 a.u.).

In the case of the doubly charged ions, a different trend is observed, defined by the outer $(n-1)p_{3/2}$ orbital, which expands in the group with the increase in the atomic number. Thus, 120^{2+} has the highest polarizability of the three ions considered here.

C. Electron affinities

The EAs of the rare-earth elements have received considerable attention in the late 80s and early 90s, prompted by the prediction [46] and subsequent experimental confirmation [47] of a stable negative ion of Ca in the $[Ar]4s^2 4p\ (^2P)$ state. A large number of results have been published for Ba, using a variety of theoretical methods, all of them establishing a stable negative ion in a $[Xe]6s^2 6p$ ground state, with an IP of 110–200 meV, depending on the method [48–59]. The importance of relativistic effects and of electron correlation for obtaining the proper ground-state configuration and accurate value of the EA is shown in all these publications. In 1995 the EA of Ba was measured as 144.62 ± 0.06 meV, using a combination of laser photodetachment and resonance ionization spectroscopy [60]. A number of theoretical publications also predict the EA of Ra in the $[Rn]7s^2 7p$ ground state, putting it between 70

TABLE V. Electron affinities of Ba, Ra, and element 120 (meV), compared to experiment (for Ba) and to other theoretical values.

EA	Method	Reference
Ba[−], [Xe]6s²6p, ²P		
−142	DHF	Present work
70	RCCSD	Present work
138	RCCSD(T)	Present work
144.62	Experimental	[60]
148	MCHF + rel. shift corrections ^a	[51]
160	Pseudorelativistic MCHF	[55]
110	PP + CI + Polarization contributions ^b	[54]
217	MCDF ^c	[56]
145	RMBPT + Breit ^d	[57]
186	Polarization potential + RMBPT	[58]
Ra[−], [Rn]7s²7p, ²P		
−99	DHF	Present work
42	RCCSD	Present work
82	RCCSD(T)	Present work
>50	Experimental	[62]
70	Pseudo-relativistic MCHF	[55]
148	RMBPT	[61]
140	Polarization potential + RMBPT	[59]
120[−] [118]8s²8p, ²P		
−121	DHF	Present work
−2	RCCSD	Present work
21	RCCSD(T)	Present work

^aMulticonfiguration Hartree-Fock (MCHF); relativistic corrections include mass-velocity, spin-spin contact, and Darwin terms.

^bLarge-core relativistic pseudopotential (PP) combined with configuration interaction (CI) approach.

^cMulticonfiguration Dirac-Fock (MCDF) method.

^dRelativistic many-body perturbation theory (RMBPT) including the Breit term.

and 150 meV [48,50,55,59,61]. The stability of Ra^- was confirmed experimentally in 1993 by means of accelerator mass spectrometry, and a lower limit of 50 meV was set for the EA of this atom [62]. The EA of element 120 was estimated in our earlier publication [16] as 52 meV, based on fitting the EAs obtained using the FSCC method to the experimental values for the lighter homologues and extending this fit to Ra and element 120.

Table V shows the calculated and (when available) experimental EAs of Ba, Ra, and element 120. The experimental EA of Ba is quite close to our calculated value, and we believe that the other calculated EAs, for Ra and element 120, are of similar quality. Table V also includes the best previously published EA values. They are mostly from the 1990s and of necessity employ less accurate methods for treating relativity and/or correlation.

The negatively charged ions of the group-2 elements are particularly interesting systems, since the outer electron is bound to a closed shell atom mainly by the long-range (polarization) interactions. This outer electron polarizes the large and thus easily polarizable neutral atoms, so that the bond is formed due to the strong electron correlation effects. A very good correlation is therefore observed between the polarizabilities of the group-2 atoms (see Fig. 1) and their EAs [Fig. 2(a)]. Both quantities increase from Ca to

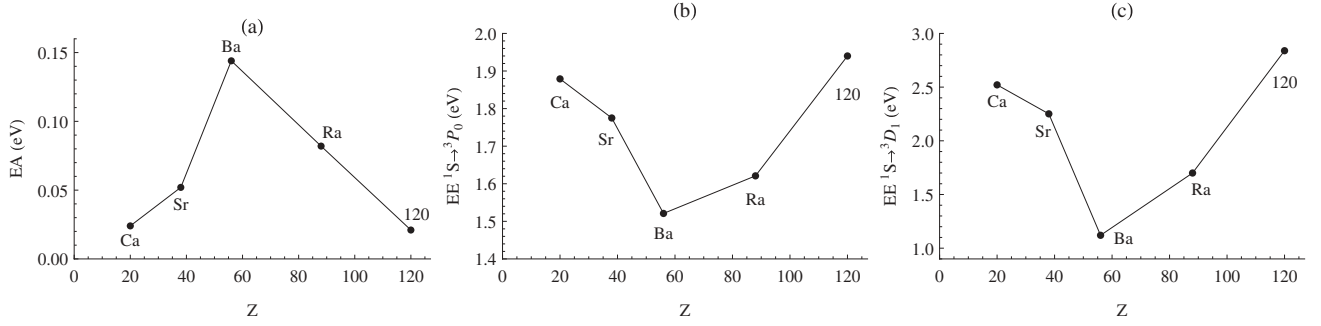


FIG. 2. (a) Electron affinities (experimental for Ca [47], Sr [63], and Ba [60]; current calculations for Ra and element 120); (b) energies of the $1S \rightarrow 3P_0$ transitions; and (c) energies of the $1S \rightarrow 3D_1$ transitions of the group-2 elements (eV). Transition energies of element 120 are taken from the current work (Table II); for the lighter homologues experimental values [31] are used.

Ba and then decrease toward element 120. Thus, the least polarizable atom among the elements discussed here, element 120 ($\alpha = 163$ a.u.), has the lowest EA.

The importance of the correlation effects in the negatively charged ions is seen from our data of Table V. Thus, while the use of the CCSD method turns the EAs of Ba and Ra to positive (compared to the uncorrelated values), it is still insufficient to stabilize the 120 anion. For these anions, which are systems with three electrons out of a rare-gas closed shell, the contribution of the triple excitations is extremely important,

doubling the EAs of Ba and Ra, causing the value for Ba to approach the experimental one, and turning the EA of element 120 from negative to positive.

The attached electron occupies the vacant np orbital in all the atoms in the group, leading to a $2P$ ground state. Figure 2(b) in Ref. [16] presents a qualitative picture of the 4c-DFT energies of the group-2 elements. There it can be seen that for all the considered elements, apart from Ba, the np orbital is indeed the lowest vacant one. This is also indicated by the $1S \rightarrow 1,3P$ transitions of the neutral atoms, which are the lowest transitions of all the group-2 elements, except Ba. The energies of these transitions decrease from Ca to Ba and increase toward element 120, due to the predominance of the relativistic stabilization over the orbital effect on ns orbitals from the sixth row on [Fig. 3(b)]. It was also shown in our earlier work [Ref. [16], Fig. 2(b)] that the $(n-1)d$ orbitals lie in the same energy region as the np orbitals. Thus the excitations of the type $1S \rightarrow 1,3D$ provide an additional essential contribution to the correlation energy and stabilization of the negative ions. A similar relationship was established by Fuentealba *et al.* [54] for the lighter group-2 elements. Figure 3(c) shows that the trend in these transitions coincides with that of the $1S \rightarrow 1,3P$ ones. The correlation energy contribution is inversely proportional to the $ns - np$ and the $ns - (n-1)d$ energy separation, which increases in group 2 from Ba to element 120 (reflected by the increasing energies of the $1S \rightarrow 1,3P$ and $1S \rightarrow 1,3D$ transitions). Thus, the contribution of correlation effects to the EAs decreases from Ba to element 120; nevertheless, it is still sufficient to stabilize the 120⁻ ion.

The group-2 EAs exhibit a trend reversal at Ba; the lowest value for element 120 out of the atoms considered here is

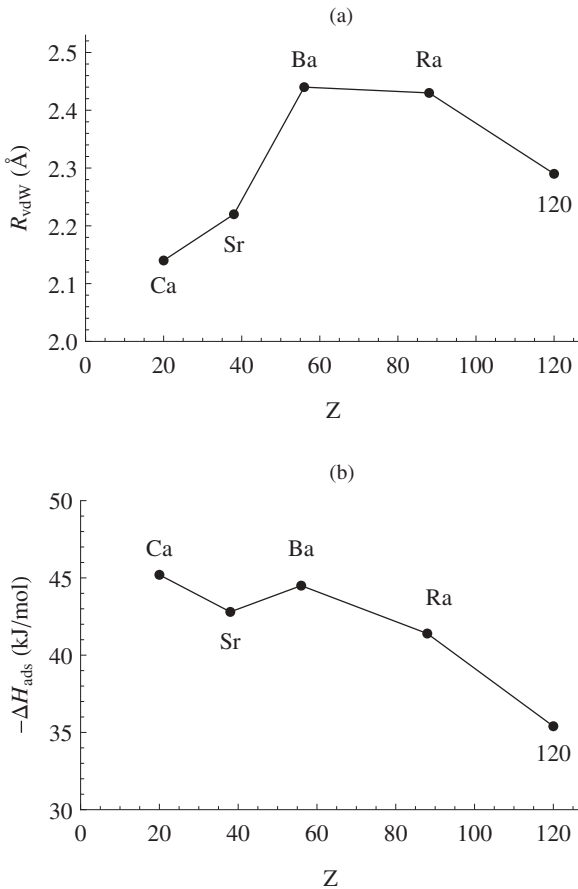


FIG. 3. (a) Van der Waals radii and (b) adsorption enthalpies of group-2 atoms on Teflon.

TABLE VI. IPs, EAs (meV), and α (a.u.) of Ba, Ra, and element 120 (present calculations unless referenced otherwise).

	Ba	Ra	120
IP1	5.212 ^a	5.278 ^a	5.851
IP2	10.004 ^a	10.147 ^a	11.137
EA	0.145 ^b	0.082	0.021
α	272.7	242.8	162.6

^aReference [31].

^bReference [60].

mainly due to the relativistic stabilization and contraction of the $8s$ atomic orbital. Final recommended atomic properties of Ba, Ra, and element 120 are given in Table VI.

IV. VOLATILITY OF GROUP-2 ATOMS

Following the eventual discovery of suitable isotopes of element 120, its volatility might be studied using some advanced chromatography (vacuum) techniques that can cope with the extremely short lifetimes of its isotopes. To guarantee the transport of element 120 through Teflon capillaries from the target chamber to the chemistry setup, its ΔH_{ads} on Teflon should be known. For this purpose, the following model of the van der Waals type adatom-slab interaction [64] may be used:

$$E(x) = -\frac{3}{16} \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right) \frac{\alpha_{\text{at}}}{\left(\frac{1}{\text{IP}_{\text{slab}}} + \frac{1}{\text{IP}_{\text{at}}} \right) x^3}, \quad (7)$$

where IP_{at} and IP_{slab} are the IPs of the adatom and the slab, ε is the dielectric constant of the surface material, α_{at} is the polarizability of the adatom, and x is the adatom-surface separation distance, approximated by the van der Waals radius (R_{vdW}) of the adsorbed atom. The R_{vdW} values of Ra and element 120 were obtained via a correlation between the known R_{vdW} in group 2 [65] and the R_{max} of the valence ns atomic orbitals [12]; they are 2.43 Å for Ra and 2.29 Å for element 120 (Table VII). The trend of R_{vdW} in group 2 [Fig. 3(a)] follows that of atomic radii (Fig. 4(a) in Ref. [16]). The $-\Delta H_{\text{ads}}$ values of group-2 elements on Teflon obtained using Eq. (7) for $\varepsilon = 2.04$ and $\text{IP}_{\text{slab}} = 10.12$ eV [66] are also given in Table VII. The relatively low value for element 120, $-\Delta H_{\text{ads}} = 35.4$ kJ/mol, indicates that this atom should be easily transported through the Teflon capillaries to the chemistry setup. The trend in the $-\Delta H_{\text{ads}}$ is displayed in Fig. 3(b). It is remarkable that this trend follows that of the predicted ΔH_{sub} of the group-2 metals, as well as that of $-\Delta H_{\text{ads}}$ on gold (Figs. 6(a) and 9 in Ref. [16]). The trends in all three properties are defined by the trends in the energies of both the ns and $(n-1)d$ atomic orbitals of the group-2 elements (see Ref. [16] for discussion).

The calculated ΔH_{ads} of element 120 can be used to predict the relative yield of this element at the end of an inert transport capillary or a column, taking into account the half-life $T_{1/2}$ of the studied isotope and the parameters of the capillary or column. The following equation is used,

$$\frac{N}{N_0} = \exp \left(-\frac{\ln 2}{T_{1/2}} \right) t_R. \quad (8)$$

Here N_0 is the number of particles (atoms) entering the column, N is the number of particles exiting the column, and t_R is the retention time in the column. The latter is given by

the following equation [67],

$$t_R = \frac{z_A a_z}{Q} \frac{u_m}{4} \tau_0 \exp \left(\frac{-\Delta H_{\text{ads}}}{k_B T_c} \right), \quad (9)$$

where z_A is the mean coordinate of the adsorption zone, a_z is the column surface area per unit length, Q is the volume flow rate, u_m is the mean velocity of two-dimensional gas molecules, τ_0 is the elementary adsorption sojourn time, k_B is the Boltzmann constant, and T_c is the temperature of the column. For an open Teflon column or a capillary with an inner diameter of 2 mm, length of 1 m, and $Q = 1$ l/min, at room temperature, the relative yield of the $^{295}\text{120}$ isotope with $T_{1/2} = 1$ s was calculated as 77%. The low adsorption enthalpy of element 120 means that in this case the yield of this atom at the end of the column or capillary is not determined by its volatility, but rather by the lifetime of a given isotope with respect to the transport time.

V. SUMMARY AND CONCLUSION

We have calculated the ionization potentials, excitation energies, and electron affinities of element 120 and the polarizabilities of its neutral and singly and doubly charged states in the framework of the 4c-Dirac-Coulomb Hamiltonian. Electron correlation is treated using the intermediate Hamiltonian FSCC approach for the IPs and EEs and by the relativistic single reference CCSD(T) method for the EAs and polarizabilities. To estimate the accuracy of the results, we have calculated the same atomic properties of Ba and Ra, the lighter homologues of element 120, for which experimental data are available. Our results are in excellent agreement with the known experimental values for the homologues, and similar accuracy is expected for the predictions for element 120.

The atomic properties of the heavier group-2 elements are largely determined by their valence ns orbital, which experiences strong relativistic stabilization and contraction. Thus, the first and second IPs of element 120 (5.851 and 11.137 eV) are higher than those of Ra (5.278 and 10.147 eV), as are all the calculated excitation energies. The polarizability of element 120 (163 a.u.) is lower than that of Ra, due to the contraction of the $8s$ orbital. Element 120 has a positive EA of 0.021 eV due to the strong correlation effects; it is, however, the lowest among the atoms considered here due to the relativistic contraction of the $8s$ orbital. The α and EA of Ra, which have not been yet measured, are predicted to be $\alpha(\text{Ra}) = 242.8$ a.u. and $\text{EA}(\text{Ra}) = 0.082$ eV. Based on the calculated atomic properties of element 120, its ΔH_{ads} on Teflon is estimated as 35.4 kJ/mol, which is low enough to allow an easy transport of this atom through the Teflon capillaries to the chemistry setup.

ACKNOWLEDGMENTS

The authors are thankful to A. Yakushev for performing the Monte Carlo simulations. A.B. thanks the Helmholtz Institute Mainz for financial support and P. Schwerdtfeger and A. Punnett for valuable discussions.

TABLE VII. Van der Waals radii (Å) and adsorption enthalpies, $-\Delta H_{\text{ads}}$ (kJ/mol), of group-2 atoms on Teflon.

	Ca	Sr	Ba	Ra	120
R_{vdW}^a	2.14	2.22	2.44	2.43	2.29
$-\Delta H_{\text{ads}}$	45.2	42.8	44.5	41.4	35.4

^aData for Ca through Ba are from Ref. [65].

- [1] C. E. Düllmann, A. Yakushev, J. Khuyagbaatar, D. Rudolph *et al.*, Tech. Rep. PHN-NUSTAR-SHE-02 (GSI Helmholtzzentrum für Schwerionenforschung, Darmstadt, Planckstrasse 1, D-64291 Germany, 2011).
- [2] S. Hofman, S. Heinz, D. Ackerman *et al.*, Tech. Rep. PHN-NUSTAR-SHE-01 (GSI Helmholtzzentrum für Schwerionenforschung, Darmstadt, Planckstrasse 1, D-64291 Germany, 2011).
- [3] V. Zagrebaev and W. Greiner, *Phys. Rev. C* **78**, 034610 (2008).
- [4] A. Sobiczewski, *Acta Phys. Pol. B* **42**, 024707 (2011).
- [5] B. Fricke and J. Waber, *Actinides Rev.* **1**, 433 (1971).
- [6] B. Fricke, W. Greiner, and J. Waber, *Theor. Chim. Acta* **21**, 235 (1971).
- [7] B. Fricke, *Struct. Bond.* **21**, 89 (1975).
- [8] V. Pershina, *Chem. Rev.* **96**, 1977 (1996).
- [9] P. Schwerdtfeger and M. Seth, in *Encyclopedia of Computational Chemistry* (Wiley & Sons, New York, 2002).
- [10] V. Pershina, in *Relativistic Methods for Chemists* (Springer, New York, 2010).
- [11] J. T. Waber, D. T. Cromer, and D. Liberman, *J. Chem. Phys.* **51**, 664 (1969).
- [12] J. Desclaux, *At. Data Nucl. Data Tables* **12**, 311 (1973).
- [13] T. H. Dinh, V. A. Dzuba, V. V. Flambaum, and J. S. M. Ginges, *Phys. Rev. A* **78**, 022507 (2008).
- [14] T. H. Dinh, V. A. Dzuba, V. V. Flambaum, and J. S. M. Ginges, *Phys. Rev. A* **78**, 054501 (2008).
- [15] C. Thierfelder, P. Schwerdtfeger, A. Koers, A. Borschevsky, and B. Fricke, *Phys. Rev. A* **80**, 022501 (2009).
- [16] V. Pershina, A. Borschevsky, and J. Anton, *J. Chem. Phys.* **136**, 134317 (2012).
- [17] J. Sucher, *Phys. Rev. A* **22**, 348 (1980).
- [18] Y. Ishikawa, R. Baretty, and R. Binning, *Chem. Phys. Lett.* **121**, 130 (1985).
- [19] E. Eliav, U. Kaldor, and Y. Ishikawa, *Phys. Rev. A* **49**, 1724 (1994).
- [20] E. Eliav, U. Kaldor, and Y. Ishikawa, *Phys. Rev. A* **50**, 1121 (1994).
- [21] E. Eliav, M. J. Vilkas, Y. Ishikawa, and U. Kaldor, *J. Chem. Phys.* **122**, 224113 (2005).
- [22] A. Borschevsky, E. Eliav, Y. Ishikawa, and U. Kaldor, *Phys. Rev. A* **74**, 062505 (2006).
- [23] G. L. Malli, A. B. F. Da Silva, and Y. Ishikawa, *Phys. Rev. A* **47**, 143 (1993).
- [24] C. Thierfelder and P. Schwerdtfeger, *Phys. Rev. A* **82**, 062503 (2010).
- [25] U. Kaldor, *J. Phys. B* **6**, 71 (1973).
- [26] H. J. Monkhorst, *Int. J. Quantum Chem.* **11**, 421 (1977).
- [27] DIRAC, a relativistic *ab initio* electronic structure program, Release DIRAC08 (2008), written by L. Visscher, H. J. Aa. Jensen, and T. Saue, with new contributions from R. Bast, S. Dubillard, K. G. Dyall, U. Ekström, E. Eliav, T. Fleig, A. S. P. Gomes, T. U. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, P. Norman, J. Olsen, M. Pernpointner, K. Ruud, P. Salek, and J. Sikkema, see <http://dirac.chem.vu.nl>.
- [28] K. Faegri, *Theor. Chim. Acta* **105**, 252 (2001).
- [29] J. Gaunt, *Proc. R. Soc. London, Ser. A* **122**, 513 (1929).
- [30] B. Schimmelpfennig, L. Maron, U. Wahlgren, C. Teichteil, H. Fagerli, and O. Gropen, *Chem. Phys. Lett.* **286**, 267 (1998).
- [31] C. Moore, *Atomic Energy Levels*, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (US) US GPO, Washington, DC, 1971).
- [32] A. Landau, E. Eliav, Y. Ishikawa, and U. Kaldor, *J. Chem. Phys.* **113**, 9905 (2000).
- [33] H. L. Schwartz, T. M. Miller, and B. Bederson, *Phys. Rev. A* **10**, 1924 (1974).
- [34] S. Porsev and A. Derevianko, *JETP* **102**, 195 (2006).
- [35] I. S. Lim and P. Schwerdtfeger, *Phys. Rev. A* **70**, 062501 (2004).
- [36] I. S. Lim, H. Stoll, and P. Schwerdtfeger, *J. Chem. Phys.* **124**, 034107 (2006).
- [37] B. K. Sahoo and B. P. Das, *Phys. Rev. A* **77**, 062516 (2008).
- [38] B. Roos, V. Veryazov, and P.-O. Widmark, *Theor. Chem. Acc.* **111**, 345 (2004).
- [39] E. L. Snow and S. R. Lundeen, *Phys. Rev. A* **76**, 052505 (2007).
- [40] M. S. Safronova, W. R. Johnson, and A. Derevianko, *Phys. Rev. A* **60**, 4476 (1999).
- [41] U. I. Safronova, *Phys. Rev. A* **81**, 052506 (2010).
- [42] B. K. Sahoo, R. G. E. Timmermans, B. P. Das, and D. Mukherjee, *Phys. Rev. A* **80**, 062506 (2009).
- [43] U. I. Safronova, W. R. Johnson, and M. S. Safronova, *Phys. Rev. A* **76**, 042504 (2007).
- [44] T. M. Miller and B. Bederson, *Phys. Rev. A* **14**, 1572 (1976).
- [45] V. Koch and D. Andrae, *Int. J. Quant. Chem.* **111**, 891 (2011).
- [46] C. F. Fischer, J. B. Lagowski, and S. H. Vosko, *Phys. Rev. Lett.* **59**, 2263 (1987).
- [47] D. J. Pegg, J. S. Thompson, R. N. Compton, and G. D. Alton, *Phys. Rev. Lett.* **59**, 2267 (1987).
- [48] L. Kim and C. H. Greene, *J. Phys. B* **22**, L175 (1989).
- [49] S. H. Vosko, J. B. Lagowski, and I. L. Mayer, *Phys. Rev. A* **39**, 446 (1989).
- [50] Y. Guo and M. A. Whitehead, *Phys. Rev. A* **40**, 28 (1989).
- [51] C. F. Fischer, *Phys. Rev. A* **39**, 963 (1989).
- [52] W. R. Johnson, J. Sapirstein, and S. A. Blundell, *J. Phys. B* **22**, 2341 (1989).
- [53] G. F. Gribakin, B. V. Gul'tsev, V. K. Ivanov, and M. Y. Kuchiev, *J. Phys. B* **23**, 4505 (1990).
- [54] P. Fuentealba, A. Savin, H. Stoll, and H. Preuss, *Phys. Rev. A* **41**, 1238 (1990).
- [55] R. Cowan and M. Wilson, *Phys. Scr.* **43**, 244 (1991).
- [56] W. P. Wijesundera, S. H. Vosko, and F. A. Parpia, *J. Phys. B* **29**, 379 (1996).
- [57] E. N. Avgoustoglou and D. R. Beck, *Phys. Rev. A* **55**, 4143 (1997).
- [58] A. Glushkov, V. Efimov, T. Buyadzi, S. Dankov, and V. Polishchuk, *J. Appl. Spectrosc.* **64**, 114 (1997).
- [59] S. Malinovskaya, A. Polevoi, A. Kivganov, V. Efimov, N. Serbov, A. Drozdov, and I. Shpinareva, *Russ. Phys. J.* **41**, 1010 (1998).
- [60] V. V. Petrunin, J. D. Voldstad, P. Balling, P. Kristensen, T. Andersen, and H. K. Haugen, *Phys. Rev. Lett.* **75**, 1911 (1995).
- [61] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and D. P. Sushkov, *Phys. Rev. A* **44**, 2823 (1991).
- [62] X.-L. Zhao, M.-J. Nadeau, M. A. Garwan, L. R. Kilus, and A. E. Litherland, *Phys. Rev. A* **48**, 3980 (1993).
- [63] H. H. Andersen, V. V. Petrunin, P. Kristensen, and T. Andersen, *Phys. Rev. A* **55**, 3247 (1997).
- [64] V. Pershina and T. Bastug, *Chem. Phys.* **311**, 139 (2005).
- [65] P. Pykkö, *Chem. Rev.* **97**, 597 (1997).
- [66] David R. Lide, Editor, *CRC Handbook of Chemistry and Physics*, 88th ed. (CRC Press, Boca Raton, FL, 2007).
- [67] I. Zvara, *The Inorganic Radiochemistry of Heavy Elements* (Springer, New York, 2008).