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Structure and stability of Xe_n^+ clusters

M. Amarouche,[a] G. Durand, and J. P. Malrieu

Laboratoire de Physique Quantique, Unité Associée au C.N.R.S. no. 505, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France

The equilibrium structure and energy of Xe_n^+ clusters ($n \leqslant 9$, $n = 13$ and 19) have been calculated using a model (of excitonic type) hamiltonian extracted from the potential curves of Xe_2^+ and Xe_2, and including spin–orbit coupling and three-body interactions between instantaneous induced dipoles. Due to the p nature of the valence AO, the hole delocalization proceeds along one direction but it rapidly becomes less favorable to delocalize the hole on an nth atom than to polarize a neutral atom situated around the $(n - 1)$ atoms linear cluster. Xe_3^+ and Xe_4^+ are therefore linear and generate two families of heavier clusters, obtained by polarizing neutral atoms situated on crowns around the axis of the Xe_3^+ or Xe_4^+ ionized cores. Each crown may bear up to five atoms and there are two crowns around Xe_3^+, three crowns around Xe_4^+, Xe_{13}^+, and Xe_{19}^+ appearing then as compact structures with filled crowns. Rules are given for the filling of the neutral crowns. The two families (Xe_3^+ supported and Xe_4^+ supported) are nearly degenerate in energies with numerous isomers. The calculated adiabatic ionization potential for Xe_{19} (10.1 eV) is in good agreement with the observed value for the bulk (9.8 eV).

I. INTRODUCTION

In the rapidly increasing field of atomic cluster studies,[1,2] the rare-gas clusters are especially attractive because of their (nearly) filled band electronic character. The neutral clusters are hold by dispersion forces and may be modelized through the close packing of hard spheres and additive two-body potentials. In the ionized clusters two supplementary effects are present, namely (i) the hole delocalization and (ii) the polarization energies.

A series of experimental observations are available concerning, besides the well-known dimers, trimers,[3,4] and heavier clusters;[5–8] the latter studies exhibit magic numbers for 3, 13, 16, and 19 for Xe_n^+. A rationalization of experimental evidences has been proposed by Haberland[9] who suggests that the delocalization spreads the hole on two centers only in a Xe_2^+ ion, which polarizes the surrounding neutral atoms. Dynamics studies have been performed within this model.[10,11] (A purely central charge model, without any delocalization, had been proposed in Ref. 8.)

Performing DIM calculations,[12,13] Hesslich and Kuntz[14] recently claimed that up to Ar_{12}^+, the cluster was essentially built around an Ar_3^+ cluster. The purpose of the present paper is twofold:

(i) through the study of heavier element clusters Xe_n^+, analyse the possible role of spin–orbit coupling;

(ii) reexamine the conflict between the X_2^+ and X_3^+ based models through a systematic study of the possible isomers X_n^+.

The model used in the present study is given in the next section; it is an excitonic-type of treatment whose parameters are extracted from Xe_2^+ potential curves. The main results appear in Sec. III.

II. MODEL HAMILTONIAN

Rather than using a usual molecular-orbital (MO) approach, which privilegiates the electronic delocalization through the use of symmetry-adapted MOs, the present model is of valence bond (VB) type. As well-known for a filled-band problem the ground state zeroth-order wave function may be written as an antisymmetrized product of atomic-like wave functions. Each atom in the cluster of n atoms keeps a s^2p^6 character, and disregarding the core electrons:

$$\Phi_0 = \mathscr{A} \prod_{i=1}^{n} (s_i \bar{s}_i x_i \bar{x}_i y_i \bar{y}_i z_i \bar{z}_i),$$

where the s and $p_{x,y,z}$ valence orbitals are supposed orthogonal, i.e., they have small orthogonalization tails on the neighbor atoms, but they basically keep a local (i.e., atomic) character. If one only considers the ionization of the p band (the s band being 11.3 eV above), the wave function of the electronic spin $S_z = 1/2$ ion may be written:

$$\Phi^+ = \sum_{i=1}^{n} \sum_{l=x,y,z} C_{il} a_{il} \Phi_0,$$

where a_{il} is an annihilation operator of an electron in the p_{il} spin orbital of β spin. The ionization is treated as a linear combination of local ionizations, and the model may therefore be called as excitonic. A similar picture[15] has been proposed and used for alkaline-earth positively charged clusters (Mg_n^+ and Mg_n^{++}).

A. The diatomic problem; definition of the parameters

For Xe_2^+ the symmetry results in a partition of the Hamiltonian into a Σ^+ part, concerning the holes in the (z-directed) σ AOs and two degenerate π parts. The 2×2 Σ^+ Hamiltonian, spanned by $a_{\overline{z1}}\Phi_0$ and $a_{\overline{z2}}\Phi_0$, has the form

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[a] Université de Tizi-Ouzou (Oued-Aissi).

$$\begin{pmatrix} IP + R_\sigma^+ & -F_\sigma^+ \\ -F_\sigma^+ & IP + R_\sigma^+ \end{pmatrix},$$

where the zero of energy is the energy of two isolated neutral atoms and IP is the *atomic* ionization potential. The lowest root is

$$\psi(\Sigma_u^+) = \frac{1}{\sqrt{2}}(a_{\overline{z1}} + a_{\overline{z2}})\Phi_0,$$

$$E(\Sigma_u^+) = IP + R_\sigma^+ - F_\sigma^+$$

and the upper one

$$\psi(\Sigma_g^+) = \frac{1}{\sqrt{2}}(a_{\overline{z1}} - a_{\overline{z2}})\Phi_0,$$

$$E(\Sigma_g^+) = IP + R_\sigma^+ + F_\sigma^+.$$

The parameter $R_\sigma^+ = \langle a_{\overline{z1}}\Phi_0 | H | a_{\overline{z1}}\Phi_0 \rangle$ represents the interaction between a σ-ionized and a neutral atom, including both repulsion and polarization effects, and is known as a function of the interatomic distance r_{12}:

$$R_\sigma^+ = [E(\Sigma_g^+) + E(\Sigma_u^+)]/2$$

if the potential curves of $^2\Sigma_u^+$ and $^2\Sigma_g^+$ are known from either experiment or good *ab initio* calculations. The integral F_σ^+ is the hopping integral responsible for the hole delocalization.
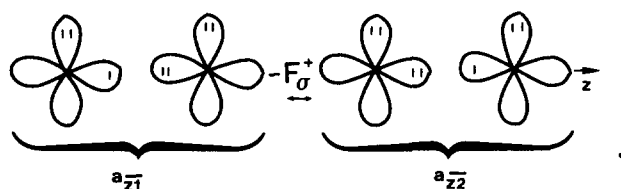
Its amplitude as a function of r_{12} is given by

$$F_\sigma^+ = [E(\Sigma_g^+) - E(\Sigma_u^+)]/2$$

and directly obtained from the dimer ion potential curves.

The π-symmetry potential curves $E(\Pi_g)$ and $E(\Pi_u)$

similarly define the parameter R_π^+, characteristic of the interaction between a π-ionized atom and a neutral atom and the F_π^+ π hopping integral, responsible for the hole delocalization in the π system

$$R_\pi^+ = [E(\Pi_g) + E(\Pi_u)]/2,$$

$$F_\pi^+ = [E(\Pi_g) - E(\Pi_u)]/2.$$

For X = Xe, the four basic parameters have been extracted from density-functional calculations of the $^2\Sigma_g^+$, $^2\Pi_u$, $^2\Pi_g$, and $^2\Sigma_u^+$ potential curves by Michels *et al.*[16] which after inclusion of the spin–orbit coupling (*vide infra*) give a nice agreement with experimental spectroscopic characteristics. Analytic fittings of the Σ_u^+ and Π_g potential curves by Morse functions and of the Π_u and Σ_g^+ potential curves by $(a + b/r)e^{-cr}$ repulsive functions have been performed through a least-square technique. The values of the parameters appear in Table I(A).

The spin–orbit (SO) contribution is included according to the semiempirical process proposed by Cohen and Schneider[17] as an interaction between $^2\Sigma^+$ and $^2\Pi$ states, the coupling constant being extracted from the asymptotic (i.e., atomic) splitting between $^2P_{3/2}$ and $^2P_{1/2}$ states. The Hamiltonian containing the SO coupling is written in Table II. Notice that the matrix is non-Hermitian. The resulting spectroscopic constants of the diatom are given in Table III; they differ from Michel *et al.*'s values by small deviations (due to the interpolation process) and they satisfactorily agree with experimental data[18]; this agreement is a crucial point for the quality of the model.

Figure 1 gives the r dependence of the four parameters. One should notice:

(i) the R^+ functions are attractive at long distances, due to polarization forces, before becoming repulsive around 7 bohrs. Notice that the repulsion is larger when the hole is in a π $5p$ AO since the $5p_z$ AO's are then filled, while for a σ hole the σ system, which presents the major overlap and therefore the largest contribution to the repulsion, only bears three electrons in two AOs.

TABLE I. (A) Analytic fitting of the potential curves of Xe$_2^+$ without spin–orbit coupling.

Diatomic	States	Analytical function	a_1(a.u.)	a_2(a.u.)	a_3(a.u.)
Xe$_2^+$	$^2\Sigma_u^+$	$a_2\{[1 - \exp - a_3(r - a_1)]^2 - 1\}$	5.977 71	0.050 863 5	0.685 974
	$^2\Pi_g$	$a_2\{[1 - \exp - a_3(r - a_1)^2 - 1]\}$	7.520 88	0.005 354 08	0.735 257
	$^2\Pi_u$	$(a_1 + a_2/r)\exp - a_3r$	$-35.120\ 9$	256.597	0.895 386
	$^2\Sigma_g^+$	$(a_1 + a_2/r)\exp - a_3r$	781.395	-2714.75	1.402 43

(B) Analytic fitting of the Xe$_2$ ($^1\Sigma_g^+$) ground state potential curve

| Diatomic state	Region of validity	Analytical function	b_1(a.u.)	b_2(a.u.)	b_3(a.u.)	b_4(a.u.)
$^1\Sigma_g^+$	$X<0.709$	$b_1 \exp - b_2 X$	280.027 1	13.441 5	$\cdots$	$\cdots$
	$0.709 < X < 0.75$	$\Sigma_{i=1}^{4} b_i X^{4-i}$	$-20.899\ 1$	46.703 4	$-34.982\ 8$	8.794 7
	$0.75 < X < 1.12$	$b_1\{[1 - \exp - b_2(X - 1)]^2 - 1\}$	0.000 849	6.279	$\cdots$	$\cdots$
	$X_1 = 1.12 < X < 1.4 = X_2$	$b_1 + (X - X_1)\{b_2 + (X - X_2) \times [b_3 + (X - X_1)b_4]\}$	$-0.000\ 594$	0.002 057	$-0.002\ 134$	$-0.017\ 78$
	$X>1.4$	$-b_1 X^{-6} - b_2 X^{-8}$	67.688 3	1771.803 5	$\cdots$	$\cdots$
	$X = r/r_e$	$r_e = 8.358\ 26$ a.u.				

TABLE II. Model Hamiltonian including SO coupling for the Xe_2^+ problem (with $\beta = \hbar^2/2\cdot\alpha$, where $\alpha = -23$ $(^2P_{3/2} - {}^2P_{1/2})$.

	z_1	$\bar{z}_1$	x_1	$\bar{x}_1$	y_1	$\bar{y}_1$	z_2	$\bar{z}_2$	x_2	$\bar{x}_2$	y_2	$\bar{y}_2$
z_1	R_σ^+			$-\beta$		$i\beta$	F_σ^+					
$\bar{z}_1$		R_σ^+	β		$i\beta$			F_σ^+				
x_1		β	R_π^+		$-i\beta$				F_π^+			
$\bar{x}_1$	$-\beta$			R_π^+		$i\beta$				F_π^+		
y_1		$-i\beta$	$i\beta$		R_π^+						F_π^+	
$\bar{y}_1$	$-i\beta$			$-i\beta$		R_π^+						F_π^+
z_2	F_σ^+						R_σ^+			$-\beta$		$i\beta$
$\bar{z}_2$		F_σ^+						R_σ^+	β		$i\beta$	
x_2			F_π^+					β	R_π^+		$-i\beta$	
$\bar{x}_2$				F_π^+			$-\beta$			R_π^+		$i\beta$
y_2					F_π^+			$-i\beta$	$i\beta$		R_π^+	
$\bar{y}_2$						F_π^+	$-i\beta$			$-i\beta$		R_π^+

(ii) the hole delocalization is about ten times larger in the σ system than in the π system: $|F_{\sigma\sigma}|/|F_{\pi\pi}| \cong 8.4$, 11.2, 15.0, for $r = 7$, 8, and 9 bohrs, respectively, which will appear to be the significant range of interatomic distances in the clusters. The hole delocalization will therefore be essentially one directional. Notice that attractive π type interactions may be essentially considered as polarization effects since for 8 bohrs for instance (i.e., close to the minima of $^2\Pi_g$ and $^2\Pi_u$ potential curves) $|F_\pi^+/R_\pi^+| \cong 1/3$. These remarks concerning the physical effects (repulsion, σ and π delocalization, polarization) will play a crucial role in the interpretation of the results.

B. Transfer to polyatomic systems

For a linear X_3^+ problem, directed along the z axis, the Σ^+ symmetry with $S_z = 1/2$ concerns a 3×3 matrix, spanned by $a_{\overline{z1}}\Phi_0$, $a_{\overline{z2}}\Phi_0$ and $a_{\overline{z3}}\Phi_0$:
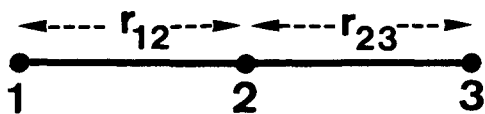
We assume that one may write the Hamiltonian matrix elements as

$$\langle a_{\overline{z1}}\Phi_0|H|a_{\overline{z1}}\Phi_0\rangle = IP + R_\sigma^+ (r_{12}) + R(r_{23}) + R_\sigma^+ (r_{13}),$$

where R is the neutral–neutral interatomic potential

$$\langle a_{\overline{z1}}\Phi_0|H|a_{\overline{z2}}\Phi_0\rangle = -F_\sigma^+ (r_{12}),$$

$$\langle a_{\overline{z1}}\Phi_0|H|a_{\overline{z3}}\Phi_0\rangle = -F_\sigma^+ (r_{13}),$$

$$\langle a_{\overline{z2}}\Phi_0|H|a_{\overline{z2}}\Phi_0\rangle = IP + R_\sigma^+ (r_{12}) + R_\sigma^+ (r_{23}) + R(r_{13}).$$

This assumption expresses that (i) the hopping integrals are transfered from the bicentric problem. (ii) The diagonal terms, relative to a localized ion with the hole on atom i, is the sum of interatomic ion–neutral interactions between the ion and the neutral atoms and of neutral–neutral interactions between neutral atoms. This last type of interaction, which did not apear in the X_2^+ problem, must be introduced; the $R(r)$ potential is spherical and may be obtained from collisional and spectroscopic experimental informations. In the present study the Xe_2 ground state potential curve has been fitted by a repulsive $A \exp(-Br)$ short-range potential adopted from Foreman et al.[19] for $r < 5.93$ bohrs; a Morse function in the well region $6.26 < r < 9.41$ bohrs extracted from Ref. 20; a long range C_6/r_6 behavior.[20] The values of the parameters are given in Table I(B).

TABLE III. Spectroscopic constants of the lowest states of Xe_2^+ including spin–orbit coupling.

State	Experimental data[a]		This work		Michel's values[b]	
	r_e (bohrs)	D_e (hartrees)	r_e (bohrs)	D_e (hartrees)	r_e (bohrs)	D_e (hartrees)
$A\,^2\Sigma_{1/2u}^+$	5.99	0.0379	6.04	0.0396	6.01	0.0393
$B\,^2\Pi_{3/2g}$		0.0067	7.52	0.0053	7.38	0.0054
$C\,^2\Pi_{3/2u}$		<0.0018	8.28	0.0024	7.55	0.0015
$B\,^2\Pi_{1/2g}$	repulsive curve at 8.24 bohrs	0.002	9.94	0.0002	repulsive	curve
$C\,^2\Pi_{1/2u}$	8.24	0.0069	7.67	0.0077	7.50	0.0076
$D\,^2\Sigma_{1/2g}^+$		<0.002	8.73	0.0014	repulsive	curve

[a] Reference 18.
[b] Reference 16.
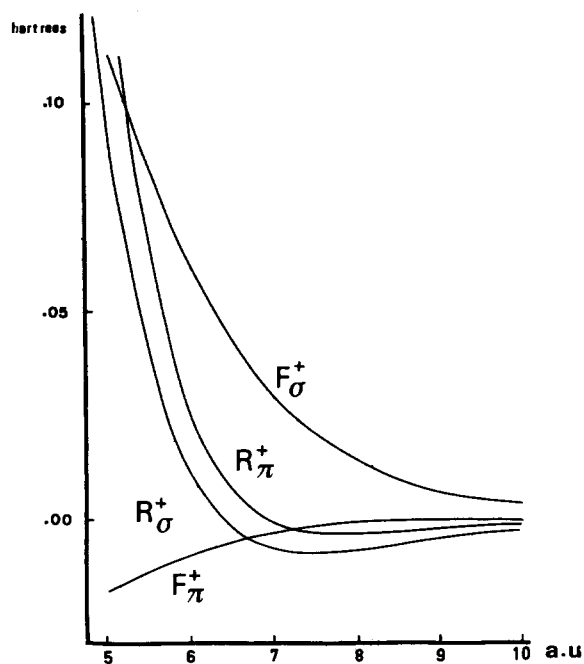
FIG. 1. r dependence of the four parameters R_σ^+, F_σ^+, R_π^+, F_π^+.

Before inclusion of the spin–orbit coupling, the Σ^+ part of the Hamiltonian is a 3×3 matrix, and so are the π blocks, which involve F_π^+ interactions and R_π^+ contributions to the diagonal. The spin–orbit operator couples the Σ^+ and Π parts. The overall complex matrix is of dimension 18, i.e., $6n$ for a n-atom cluster.

For nonlinear structures and for any cluster, the problem will be expressed using general Cartesian coordinates and therefore p_x, p_y, p_z AOs. The two-body effective interactions are obtained through well-known rotations into the bicentrally directed local coordinates.

In multicenter problems a further correction must be introduced, namely, the interaction between induced dipoles. This is a third-order correction in the perturbative expansion and a three-body effect. When the hole is located on the atom I, it induces dipole moments μ_{JI} on all the other atoms:

$$\mu_{JI} = \alpha \frac{r_{IJ}}{r_{IJ}^3},$$

where $\alpha (= \alpha_J)$ is the polarizability of the instantaneously neutral Xe atoms [α has been taken as 36.3 (a.u.^{3})[21]]. The interaction between the induced dipoles on atoms J and K ($\neq I$) created by the hole and atom I is given by

$$\delta_I = \sum_{J \neq K} \sum \left(\frac{\mu_{JI} \cdot \mu_{KI}}{r_{JK}^3} - 3 \frac{(\mu_{JI} \cdot r_{JK})(\mu_{KI} \cdot r_{JK})}{r_{JK}^5} \right).$$

The diagonal energies relative to the six determinants where the hole is located on atom I are shifted by this quantity. Notice that our VB type model, which describes the resonance between locally ionized situations, introduces, besides the static polarization effect included in single-determinantal Hartree–Fock pictures, the *dynamic* polarization effects, i.e., the instantaneous repolarization of the atoms around the

hole, which is a correlation effect. The importance of this effect (its dominance over the static polarization when the number of atoms increases) has been demonstrated and illustrated in a recent paper.[22] The model also includes the dynamic interaction between induced dipoles.

The present model essentially differs from DIM calculations on Ar_n^+ by (i) the inclusion of SO coupling and (ii) the inclusion of (induced-dipole)–(induced-dipole) interactions.

III. RESULTS

A. Hole delocalization vs polarization: Xe_3^+ to Xe_5^+

As shown by previous *ab initio*[23,24] and DIM[14] calculations on Ar_3^+, the noble-gas trimer cation is linear. Table IV gives the results for Xe_3^+. The most stable structure is linear with a charge of $-0.52\, e^-$ on the central atom. It is bound by 0.36 eV with respect to $Xe_2^+ + Xe$. This extra stabilization is due to the hole delocalization on the third atom which results in a bond lengthening with respect to Xe_2^+. The directionality of the hole delocalization is responsible for the linearity. A second minimum appears at 0.25 eV above; it is an isosceles triangle, and is of intermolecular nature $Xe_2^+ \cdots Xe$ as appears from the charge on the remote atom which is only $-0.004\, e^-$. The 0.11 eV stability with respect to the $Xe_2^+ + Xe$ asymptote is due to polarization forces. The saddle point between the two equilibrium structures is 0.25 eV above the linear one, but only 0.03 eV above the secondary minimum.

One may notice that the SO coupling has not a major influence on the shape of the potential surface; without SO the stability of the linear structure with respect to the $(Xe_2^+ + Xe)$ asymptote is 0.38 eV. As expected the SO coupling favors the π or perpendicular delocalization and thus diminishes the height of the saddle point and secondary minimum above the linear structure, but this is a minor effect (≈ 0.02 eV). This tendency is confirmed by the analysis of the bending force constant of the linear structure, which is decreased by 12% under the SO effect.

The delocalization on a *third* center brings 33% of the stabilization energy obtained by the delocalization on *two* centers. This ratio is much larger than for Ar cluster

TABLE IV. Xe_3^+ equilibrium distances (in bohrs) and binding energies (in eV) relative to the dissociation into atoms with (SO) and without (NSO) spin–orbit coupling.

		r_1(a.u.)	r_2(a.u.)	r_3(a.u.)	Be (eV)	δ Be (eV) relative to linear structure
Linear	SO	6.28	$= r_1$	$= r_1 + r_2$	1.442	$\cdots$
	NSO	6.22	$= r_1$	$= r_1 + r_2$	1.762	$\cdots$
Isosceles	SO	8.03	$= r_1$	6.06	1.189	0.252
	NSO	8.11	$= r_1$	5.99	1.485	0.277
Saddle point	SO	6.04	7.83	10.48	1.156	0.286
	NSO	5.97	7.87	10.45	1.455	0.306

$$[E(Ar_2^+) - E(Ar^+ + Ar) = 1.33 \text{ eV}^{25},$$

$$E(Ar_3^+) - E(Ar_2^+ + Ar) = 0.21 \text{ eV}^{26}]$$

but it remains smaller than what expected from a simple Hückel model (introducing only the delocalization) which would predict a ratio $\sqrt{2}$ for the binding energies X_3^+/X_2^+.

The Xe_3^+ problem introduces the basic physics of the problem, namely the conflict between hole delocalization which occurs along one direction, and the polarization of neutral atoms around a rather localized hole. This conflict will be illustrated in the series of heavier clusters but one may already notice that extending the hole to a longer and longer linear chain will bring less and less extra energy. It is well known that the energy of the highest MO of a linear chain is given by

$$\epsilon_n = -2\beta \cos \frac{n\pi}{n+1} = 2\beta \cos \frac{\pi}{n+1},$$

where β is the hopping integral between two adjacent $2p_z$ AO; then ϵ_n tends towards the asymptotic value -2β as n^{-2}. Delocalization towards a new atom along the linear chain will bring less and less energy when the chain length increases, and besides a certain value of n it will become preferrable to add the supplementary atom in a perpendicular direction, the polarization energy becoming larger than the extra delocalization energy. Xe_4^+ actually prefers a linear geometry, i.e., a delocalization on four atoms (cf. Fig. 2), but the charge on the external atoms is rather weak (-0.09 e^-); the stabilization energy with respect to $Xe_3^+ + Xe$ is only 0.15 eV. There exists a planar isomer based on a Xe_3^+ (nearly) linear structure, the extra atom being essentially neutral ($q = -0.002 e^-$), and remaining at quite long distances of both the central and one external atom of Xe_3^+ ($r = 8.05$–8.10 bohrs). This atom is polarized by Xe_3^+, and the polarization energy stabilizes the complex by 0.09 eV. This isomer is therefore 0.06 eV only above the linear minimum.

One might be tempted to see the linear Xe_4^+ structure as $Xe\cdots(Xe_2^+)\cdots Xe$, i.e., a Xe_2^+ core polarizing two external atoms in axial position, but the charges on these atoms are much larger than on the extra atom of the isomer (Xe_3^+) Xe, and the bond lengths are 1.4 bohrs shorter than in this isomer and we think it is preferable to consider this linear structure as kept by a hole delocalization on four atoms.
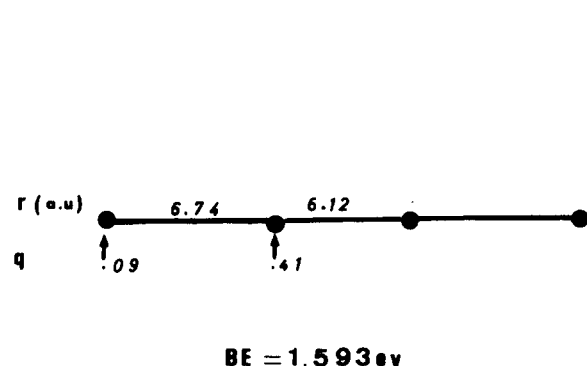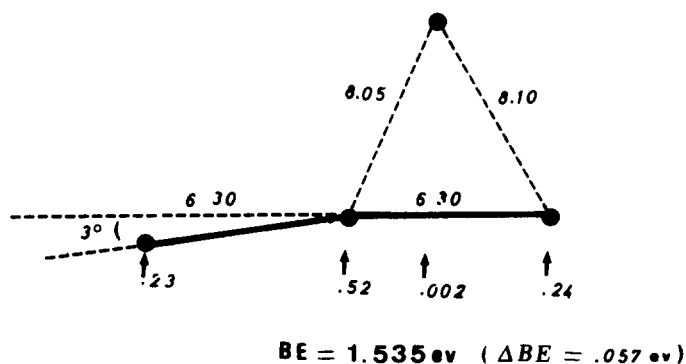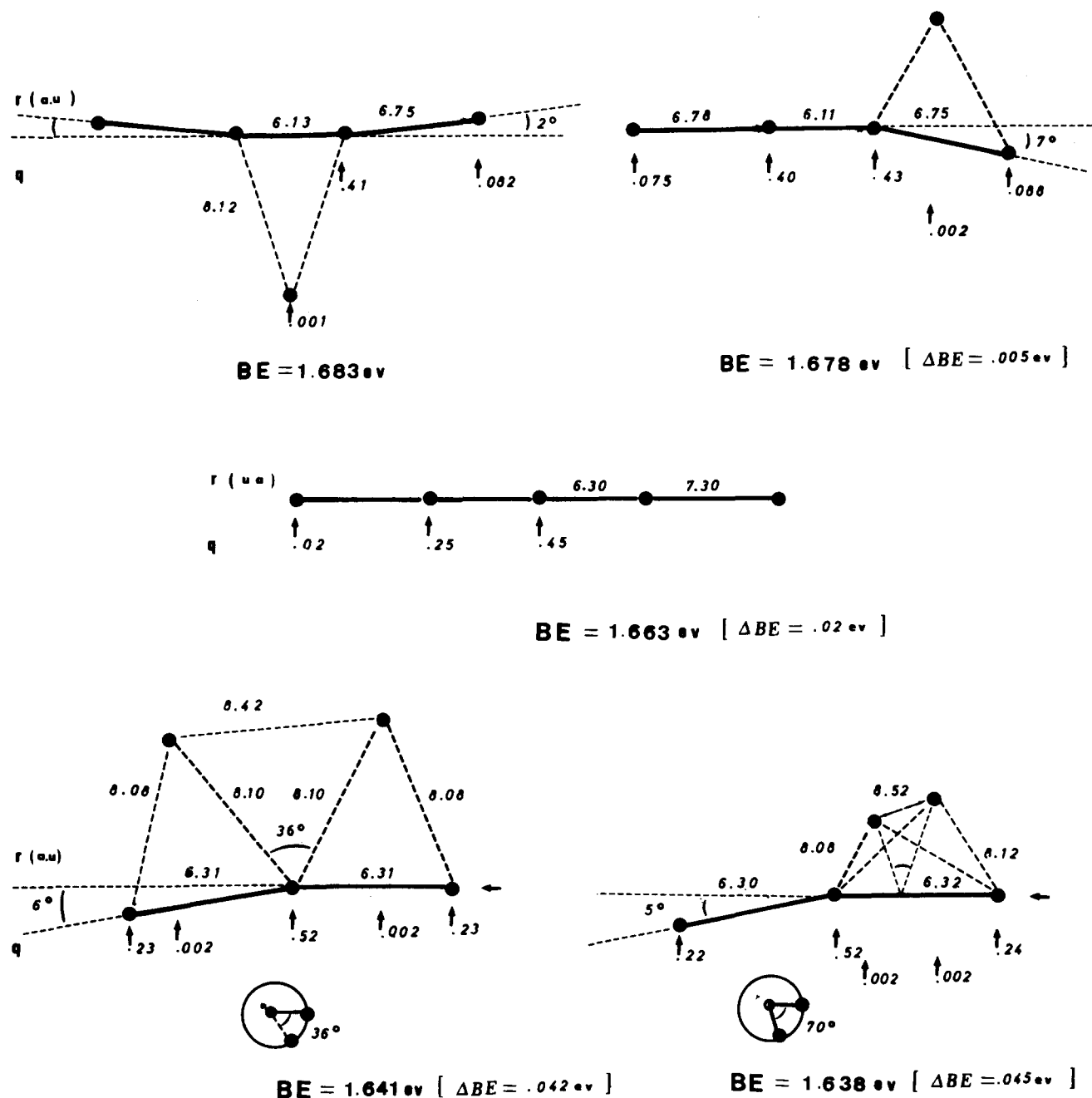
Going to Xe_5^+ (cf. Fig. 3), one may see that increasing the delocalization extent is no longer more stabilizing than polarizing appropriately positioned atoms around a smaller core; the linear Xe_5^+ cluster is actually 0.02 eV above the lowest minimum which is of (Xe_4^+) Xe character with the external Xe polarized by the most charged internal atoms of linear Xe_4^+. Keeping a linear Xe_4^+ core and adding the outer atom on the external bond leads to an almost degenerate minimum ($\Delta BE = -0.005$ eV). If two neutral atoms are added on the Xe_3^+ core, they may be brought upon either on two different bonds of Xe_3^+, or on the same bond of Xe_3^+. Notice from Figs. 2 and 3 that the neutral atoms on a Xe_3^+ core seem to have the same interatomic distance ($\cong 8.08$ bohrs) to the atoms of the Xe_3^+ core, i.e., belong to similar crowns around the Xe_3^+, axis. Labeling the two crowns as crowns 1 and 2 according to the following scheme:
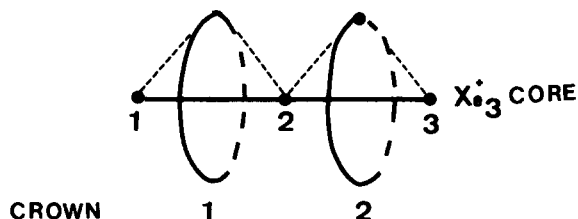

CROWN   1   2

one may introduce a compact notation (Xe_3^+, n_1, n_2) for an $(3 + n_1 + n_2)$ atom cluster, which means that n_1 (respectively, n_2) atoms are put on the crown 1 (respectively, crown 2). The lowest energy isomer of that type for Xe_5^+ is $(Xe_3^+,1,1)$, but $(Xe_3^+,2,0)$ is almost degenerate (the difference in energy is only 0.003 eV).

The optimum distance between two neutral atoms appears from Fig. 3 to be close to 8.4–8.5 bohrs, i.e., close to the interatomic equilibrium distance of Xe_2, as expected. If the two neutral atoms i and j belong to the same crown, centered on the atoms 1 and 2 of Xe_3^+, the resulting angle between the planes $(1, i, 2)$ and $(1, j, 2)$ is 70°; one may therefore put up to five atoms on the same crown $(360°/5 = 72°)$. If the two neutral atoms belong to two different crowns, the compromise between charged–neutral and neutral–neutral interatomic distances results in an angle between the planes $(1,i,2)$ and $(2,j,3)$ of 36°, i.e., half of 72°, and the second crown is therefore simply rotated from the first one by an angle insuring a staggered conformation:

BE $= 1.593$ ev

BE $= 1.535$ ev   ($\Delta BE = .057$ ev)

FIG. 2. Xe_4^+ isomers.

BE = 1.683 ev

BE = 1.678 ev [ΔBE = .005 ev]

BE = 1.663 ev [ΔBE = .02 ev]

BE = 1.641 ev [ΔBE = .042 ev]

BE = 1.638 ev [ΔBE = .045 ev]

FIG. 3. Xe$_5^+$ isomers.

Analogously one sees that starting from a Xe$_4^+$ core, one may add the neutral polarized atoms on either the internal crown or one of the external crowns, and one will characterize a cluster of Xe$_4^+$ core as (Xe$_4^+$, n_1, n_2, n_3) according to the number of neutral atoms bonded to atoms 1 and 2 (n_1), 2 and 3 (n_2) and 3 and 4 (n_3):
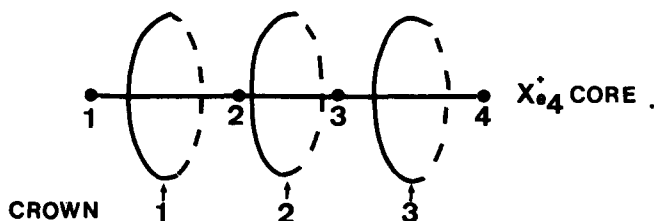
B. Larger clusters: Xe$_6^+$ to Xe$_9^+$, Xe$_{13}^+$, and Xe$_{19}^+$

The linear hole delocalization cannot exceed five atoms; for Xe$_6^+$ the linear isomer is 0.27 eV above the lowest structure. One may therefore consider that all isomers belong to one of two families, characterized by the core Xe$_4^+$ or Xe$_3^+$. As appears in Table V, Xe$_6^+$ lowest isomers are (Xe$_4^+$, 1, 1, 0) and (Xe$_4^+$, 0, 2, 0) which are nearly degenerate (by 0.002 eV). The lowest member of the Xe$_3^+$ family is 0.027 eV above, and one may notice that in the (Xe$_3^+$, 2, 1) structure the atom in the second crown is bound to the two atoms of the upper crown, in order to obtain three neutral–neutral interactions; the isomer (Xe$_3^+$, 2, 1)′ is 0.015 eV above since it only has two neutral–neutral interactions:

$$\left(X_{\scriptscriptstyle\bullet 3}^{+},2,1\right) \qquad \left(X_{\scriptscriptstyle\bullet 3}^{+},2,1\right)'$$

The filling of the crowns therefore obeys the requirement of maximizing the number of neutral–neutral interactions.

This law is valid in the Xe_4^+ family, as seen for Xe_7^+, Xe_8^+, and Xe_9^+ (Table V) and the Xe_4^+ core seems to remain preferred by approximately 0.03 eV over the best candidates of the Xe_3^+ family.

A simple physical picture arises from these variational results including full geometry optimization. One has three types of contributions to the energy:

(1) Hole-delocalization energy (E_{hd}) (which is nonadditive but transferable if the hole extension is kept).

(2) Neutral atom polarization energy by a given core (E_{pol}), which may tentatively be considered as additive for that given core and a given position of the atom (i.e., its crown).

(3) Neutral–neutral interactions (E_{nn}) which are additive. As a support to this analysis one may mention that the optimized interatomic distances are almost the same as those appearing in the light clusters. In the whole (Xe_3^+, n_1, n_2) series the interatomic distances between the positively charged atoms or between the positively charged and neutral atoms only vary by less than $\pm$ 0.04 bohr. The largest variations concern the weak neutral–neutral interatomic distances which are between 8.44 and 8.56 bohrs. The same trends are observed in the (Xe_4^+, n_1, n_2, n_3) frame. A numerical systematics of energetics has been obtained from the preceding calculations for up to Xe_6^+:

$$E_{hd}^{(3)} = 1.441 \text{ eV} \quad \text{for } Xe_3^+ \text{ core},$$

$$E_{hd}^{(4)} = 1.593 \text{ eV} \quad \text{for } Xe_4^+ \text{ core},$$

$$E_{pol}^{(3)} = 0.093 \text{ eV} \quad \text{for an } Xe_3^+ \text{ core},$$

$$E_{pol}^{(4)} = 0.090 \text{ eV} \quad \text{(respectively 0.086 eV) for an } Xe_4^+$$

core in the central crown (2) [respectively, external crowns (1 or 3)]

E_{nn} varies from 0.010 eV for two atoms in the same crown around Xe_3^+ or Xe_4^+ (internal crown) to 0.013 eV for atoms

belonging to two different crowns of Xe_3^+ or to the same external crown of Xe_4^+ and to 0.015 eV for two atoms of adjacent crowns of Xe_4^+. When applied to Xe_7^+, Xe_8^+, and Xe_9^+, this series (i) correctly predicts the preferred isomers and (ii) slightly overestimates the binding energies.

Even if this additive systematics enables one to predict the qualitative structure of heavier clusters, a full geometry optimization becomes costly, due to the large number of degress of freedom. One may take benefit of the fact that the two crowns around Xe_3^+ are filled up for Xe_3^+ (Xe_3^+,5,5), which keeps a high symmetry of order 5; this is a distorted icosahedral structure, the atoms of one axis bearing the positive charge. The optimized geometries are given in Fig. 4(a); remember that the neutral Xe_{13} icosahedral cluster would have all interatomic distances of 8.09 and 8.51 bohrs for the internal and surface bonds, respectively. The binding energy for Xe_{13}^+ is 2.51 eV.

One may notice as well that starting from the Xe_4^+ core hole and filling up the three crowns will lead to a Xe_{19}^+ (Xe_4^+,5,5,5) compact cluster with a symmetry of order 5. The relaxed geometry is given in Fig. 4(b) and the binding energy is 3.17 eV.
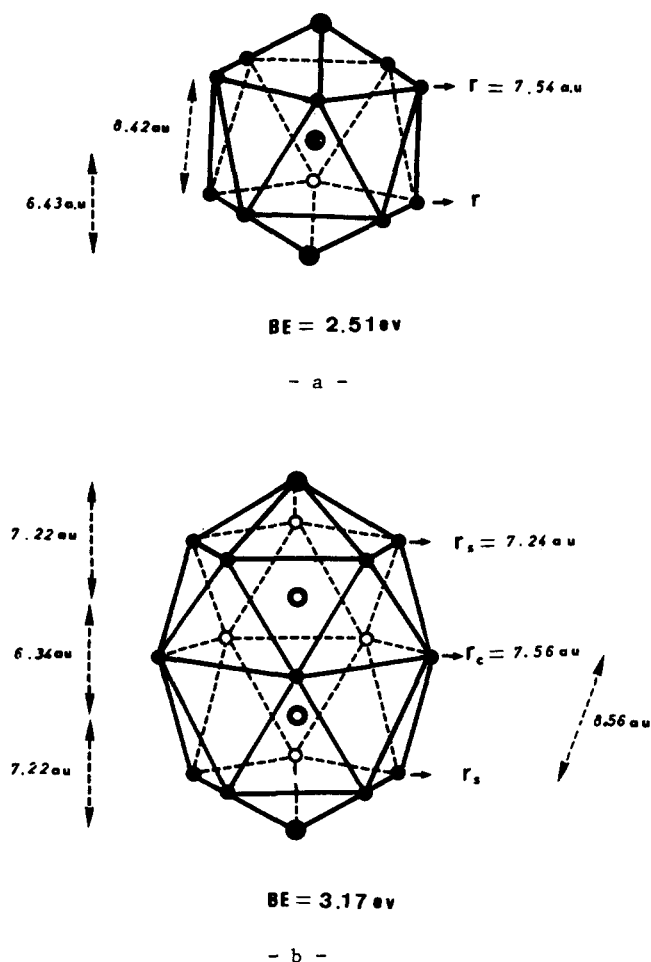
C. Vertical and adiabatic ionization potentials

Xe_{19}^+ appears therefore more stable than $Xe^+ + 18$ independent atoms by 3.2 eV; since the ionization potential of Xe is 12.12 eV one might think that the ionization potential of Xe_{19} is $12.1 - 3.2$ eV $= 8.9$ eV, i.e., below the bulk ionization potential (9.8 eV).[27] But one should notice that Xe_{19} has a non-negligible binding energy and the ionization potentials for Xe_n must be calculated from their optimal geometry energy. Using the simple two-body potential given previously the geometries of neutral clusters have been optimized up to Xe_{19} adding atoms above the faces of the Xe_7 pentagonal bipyramid. Table VI gives the neutral clusters binding energies and vertical and adiabatic ionization potentials. One may notice that

(i) The relaxation energy of the ion (i.e., difference between vertical and adiabatic ionization potentials) decreases since it is 0.64 eV for Xe_9, 0.33 eV for Xe_{13}, and 0.27 eV for Xe_{19}.

(ii) The adiabatic ionization potentials seem to approach the experimental bulk asymptote from above ($IP^{adiab} = 10.14$ eV for Xe_{13} and 10.06 eV for Xe_{19}).

TABLE V. Lowest isomers of Xe_6^+ to Xe_9^+; structure (see the text) and binding energy from variational calculations and from an additive systematics (in parentheses).

Xe_6^+	Nature	$(Xe_4^+,1,1,0)$	$(Xe_4^+,0,2,0)$	$(Xe_4^+,2,0,0)$	$(Xe_3^+,2,1)$	$(Xe_3^+,2,1)'$	$(Xe_3^+,3,0)$
	BE (eV)	1.784	1.782	1.777	1.757	1.742	1.736
Xe_7^+	Nature	$(Xe_4^+,2,1,0)$	$(Xe_4^+,1,2,0)$	$(Xe_4^+,0,3,0)$	$(Xe_3^+,2,2)$	$(Xe_3^+,3,1)$	
	BE (eV)	1.899 (1.898)	1.898 (1.899)	1.877 (1.882)	1.872 (1.874)	1.853 (1.861)	
Xe_8^+	Nature	$(Xe_4^+,1,2,1)$	$(Xe_4^+,2,2,0)$	$(Xe_4^+,3,1,0)$	$(Xe_3^+,3,2)$	$(Xe_3^+,5,0)$	
	BE (eV)	2.014 (2.015)	2.011 (1.998)	1.990 (1.997)	1.981 (1.990)	$\cdots$ (1.960)	
Xe_9^+	Nature	$(Xe_4^+,2,3,0)$	$(Xe_4^+,3,2,0)$				
	BE (eV)	2.118 (2.128)	2.097 (2.127)				

FIG. 4. Optimal structures of Xe_{13}^+ (a) and Xe_{19}^+ (b).

IV. DISCUSSION AND CONCLUSION

Our simple model Hamiltonian makes possible the calculation of Xe_n^+ clusters up to $n = 19$. Of course one of the conclusions is the large number of nearly degenerate isomers, a result already obtained by Hesslich and Kuntz

TABLE VI. Neutral clusters binding energies and vertical and adiabatic ionization potentials.

n	Binding energies (eV)	Vertical IP (eV)	Adiabatic IP (eV)
2	− 0.0229	11.34	10.63
3	− 0.0693	11.15	10.32
4	− 0.1386	11.06	10.24
5	− 0.2082	10.94	10.21
6	− 0.2796	10.97	10.18
7	− 0.3707	10.81	10.16
8	− 0.4409	10.75	10.12
9	− 0.4902	10.70	10.06
10	− 0.6181	10.56	⋯
11	− 0.7132	10.54	⋯
12	− 0.8235	10.48	⋯
13	− 0.9587	10.47	10.14
14	− 1.0295	10.46	⋯
15	− 1.0646	10.44	⋯
16	− 1.2107	10.43	⋯
17	− 1.3009	10.42	⋯
18	− 1.4088	10.39	⋯
19	− 1.5384	10.33	10.06

from DIM calculations for Ar_n^+.[14] Since our model Hamiltonian is basically similar to a DIM Hamiltonian it should lead to similar results. Differences might be due to two supplementary inputs included in our model:

(i) The spin–orbit coupling, which appears to have a minor effect, allowing a somewhat larger folding of the linear core Xe_3^+ or Xe_4^+, but this concerns small angles (< 10°).

(ii) The (induced-dipole)–(induced-dipole) three-body effect. We have repeated all calculations without this term. Since the three-body effect is essentially repulsive, the binding energies were somewhat larger; the adiabatic ionization potentials for large clusters were too low (below the bulk value), i.e., 9.49 eV for Xe_{13} and 9.15 eV for Xe_{19}. This effect is therefore important. It is a little larger in the Xe_3^+ family than in the Xe_4^+ one, since for instance $(Xe_3^+,2,0)$ is more stable by 0.01 eV than $(Xe_4^+,0,1,0)$ when it is omitted.

One should mention that polarization of neighbor atoms should in principle be screened to some extent in order to avoid redundancy with electron hopping,[15] and our estimate of the (induced-dipole)–(induced-dipole) interaction is perhaps somewhat overestimated. In view of that uncertainty it seems reasonable to conjecture that the two series based on Xe_3^+ and Xe_4^+ cores are in competition and quite degenerate. This fundamental remark reconciliates two hypothetic structures proposed for the Xe_n^+ clusters, which may almost indifferently be built from Xe_3^+ (rather than Xe^+) or Xe_4^+ (rather than Xe_2^+) cores.

The experimental magic numbers observed for Xe_{13}^+ and Xe_{19}^+ are not easy to interpret, but one may notice that they correspond to clusters which represent a complete packing for *both* the neutral and the positively charged clusters, and for which the relaxation energy is quite small. The abundance of clusters of a given mass observed in mass spectroscopy is a result of several intricate factors regarding the neutral cluster stability, the ionization intensity, the stability of the positive clusters, the fission efficiencies, and at this stage we do not pretend to interpret these exceptional peaks. A further work will try to leave the present purely static level of description and to make a step towards a more dynamic picture. Two questions will be studied:

(1) The heights of the potential energy saddle points between the various minima will be studied in order to see whether one may really speak of structures or whether the cluster must be seen as a dynamic drop. This aspect will concern: (a) the movement of neutral atoms from one crown to another within a family, (b) the change from one family to another and (c) the change of the hole direction. (2) The fission and aggregation processes.

To finish one should insist on the importance of the directionality of the hole delocalization; it is responsible for the linear structure of the core–hole and for its small extent. When going to an analogous problem where the hole is created in a s band instead of a p band (namely, Mg_n^+ instead of rare gas_n^+) the hole extent is no longer directional and concerns a larger number of atoms.[22] In that sense the rare-gas positively charged clusters are especially simple.

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