Semiempirical Study of Rare Gas and Rare Gas-Hydrogen Ionic Clusters: \( R_n^+ , (R_nH)^+ \) and \( (R_nH_2)^+ \) for \( R = \text{Ar}, \text{Xe} \)

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Semiempirical Study of Rare Gas and Rare Gas-Hydrogen Ionic Clusters: $R_n^+$, $(R_nH)^+$ and $(R_nH_2)^+$ for $R = Ar, Xe$

The ionic rare gas clusters $Ar_n^+$ and rare gas-hydrogen clusters $(Ar_nH)^+$, $(Ar_nH_2)^+$ and $(Xe_nH)^+$ are studied by the semiempirical diatomics-in-ionic-systems (DILS) method. The $Ar_n^+$ clusters $(n > 3)$ are seen to have a structure of a linear $Ar^+$ core surrounded by $n-3$ neutral or almost neutral $Ar$ atoms. For $Xe_n^+$ $(n > 3)$, a symmetrical $Xe_n^+$ ionic core with the geometry of regular pyramid is formed. The rare gas-hydrogen clusters with one $H$ atom have a simple $R_n(RH)^+$ structure with $k$ neutral rare gas atoms attracted to the $(RH)^+$ molecule by polarization forces. Two $H$ atoms can bind with $Ar$ atoms to form unstable clusters $Ar_nH_2^+$ which dissociate to $(n-1)Ar + H + (ArH)^+$ through a high barrier of roughly $0.75$ eV. Two $H$ atoms and one $Xe^+$ ion are shown to form a collinear valence-bound $(XeHH)^+$ cluster whose dissociation energy is $0.46$ eV.
Semiempirical Study of Rare Gas and Rare Gas-Hydrogen Ionic Clusters: \( R_n^+ \), \((R\text{H})_n^+\) and \((R\text{H}_2)_n^+\) for \( R = \text{Ar}, \text{Xe} \)

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Abstract

The ionic rare gas clusters \( \text{Ar}_n^+ \) and \( \text{Xe}_n^+ \) and rare gas-hydrogen clusters \((\text{Ar}\text{H})_n^+\), \((\text{Ar}\text{H}_2)_n^+\), \((\text{Xe}\text{H})_n^+\) and \((\text{Xe}\text{H}_2)_n^+\) are studied by the semiempirical diatomics-in-ionic-systems (DIIS) method. The \( \text{Ar}_n^+ \) clusters \((n > 3)\) are seen to have a structure of a linear \( \text{Ar}_3 \) core surrounded by \( n-3 \) neutral or almost neutral \( \text{Ar} \) atoms. For \( \text{Xe}_n^+ \) \((n > 3)\), a symmetrical \( \text{Xe}_4^+ \) ionic core with the geometry of regular pyramid is formed. The rare gas-hydrogen clusters with one \( \text{H} \) atom have a simple \( R_k(\text{RH})^+ \) structure with \( k \) neutral rare gas atoms attracted to the \((\text{RH})^+\) molecule by polarization forces. Two \( \text{H} \) atoms can bind with \( \text{Ar} \) atoms to form quasistable clusters \( \text{Ar}_n\text{H}^+ \) which dissociate to \((n-1)\text{Ar} + \text{H} + (\text{ArH})^+\) through a high barrier of roughly 0.75 eV. Two \( \text{H} \) atoms and one \( \text{Xe}^+ \) ion are shown to form a collinear valence-bound \((\text{XeHH})^+\) cluster whose dissociation energy is 0.46 eV.

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I. Introduction

The simplest small clusters are formed by (i) rare gas atoms, (ii) rare gas atoms and nonpolar molecules and (iii) rare gas atoms and polar molecules. In all these clusters, electrons are strongly localized on the component molecules and rare gas atoms such that the particles are bound together only by dispersion (van der Waals) and in case (iii), weak polarization forces. Such clusters are usually called van der Waals (VDW) clusters. The rare gas atoms can also form, however, clusters in which electrons are partly delocalized, contributing to some valence forces between the particles involved. In particular, such delocalization takes place in neutral rare gas-halogen and ionic rare gas clusters.

As an example of neutral rare gas-halogen clusters, we can mention $\text{Xe}_n\text{Cl}$. The ground-state $\text{Xe}_n\text{Cl}$ clusters usually seem to be of the weakly-bound VDW-type. However, ab initio calculations of the $\text{XeCl}$ complex show that the large electron affinity of the Cl atom leads to a small but noticable electron delocalization which contributes about 50% of the $\text{XeCl}$ dissociation energy. This delocalization affects the structure of the $\text{Xe}_n\text{Cl}$ clusters and is responsible for the coupling between their ground state and excited ionic (i.e., charge transfer, $\text{Xe}_n^+\text{Cl}^-$) states. In these excited states the strongly-bound quasistable molecules $\text{Xe}_2^+\text{Cl}^-$ are formed which have been studied experimentally both in the gaseous and solid phases. The $\text{Xe}_2^+\text{Cl}^-$ molecule can attract more Xe atoms, mainly within Xe solid, forming $\text{Xe}_n^+\text{Cl}^-$ ($n > 2$) clusters.

The ionic rare gas clusters $\text{R}_n^+$ have been studied extensively both experimentally and theoretically. The smallest clusters $\text{R}_3^+$ have been detected, in particular, in Ar, Xe and Kr. Ab initio calculations of $\text{Ne}_3^+$ and $\text{Ar}_3^+$, as well as semiempirical calculations of $\text{Ar}_3^+$ and...
Xe$_3^+$, $^{27,29}$ show that the triatomic clusters $R_3^+$ have a symmetrical linear structure with the central atom bearing roughly 50% of the charge. Clusters with more than three atoms are found for all rare gas atoms, i.e., He$_n^+$, $^{30}$ Ne$_n^+$, $^{31}$ Ar$_n^+$ $^{27,32-36}$ Kr$_n^+$ $^{37}$ and Xe$_n^+$ $^{38,39}$ The large rare gas clusters $R_n^+$ with $n > 10$ demonstrate some magic numbers in their stabilization energy dependence on $n$. $^{33,35,37-43}$ The structure of the $R_n^+$ clusters with $n > 3$ is not completely clear. According to an experimental study, $^{35}$ the Ar$_3^+$ ion is the core in the Ar$_n^+$ clusters. Theoretical investigations which take into account the electron delocalization support this finding, at least for Ar$_n^+$ $^{26}$ and Xe$_n^+$ $^{29}$ and show that $R_4^+$ ions can also form a core of $R_n^+$ ($n > 4$) clusters. The involvement of $R_3^+$ and $R_4^+$ ions in the $R_n^+$ cluster formation allows one to conclude that models with the charge localized on one $^{33}$ or two $^{41,42}$ centers are unsatisfactory, at least for small $R_n^+$ clusters. As shown in Ref. $^{27}$ and $^{29}$, the charge can be shared even by more than four atoms.

Rare gas atoms can form not only the homonuclear clusters $R_n^+$ considered above but also ionic heteronuclear clusters which consist of either different rare gas atoms or rare gas atoms and valence-active atoms. The charge distribution and the structure of heteroatomic ionic clusters depend strongly on the relation between the ionization potentials of the atoms involved. For example, the ($Xe_nNe_m$)$^+$ cluster is obviously formed by a Xe$_n^+$ ionic core and neutral Ne atoms, since the ionization potential of Ne is much higher than that of Xe. In the case of valence-active atoms such as hydrogen, the situation becomes more complicated because of the formation of the valence-bonded molecules $H_2$, $H_3^+$, $H_3^+$ and ($RH$)$^+$. The ($RH_2$)$^+$ systems have been studied in the context of the $R^+ + H_2$ and $R + H_2^+$ chemical reactions (see, for example, Refs. $^{44-46}$). The ($ArH_2$)$^+$ potential energy surface has been calculated by the DIM method. $^{47}$ The study of the rare gas-hydrogen ionic clusters has
concentrated mainly on \( \text{ArH}_3^+ \) clusters, whose structure, by analogy with \( \text{HeH}_3^+ \), has been suggested to be a \( \text{H}_3^+ \) triangle with Ar at the vertex. This structure is supported by \textit{ab initio} calculations. The ionization potential of \( \text{Ar} \) (15.76 eV) is much higher than that of \( \text{H} \) (13.6 eV), so that the charge is located on the H atoms. A similar charge distribution is expected for the \( (\text{H}_2)_n \text{H}_3^+ \) ionic clusters, which have been studied experimentally, since the ionization potential of \( \text{H}_2 \) (15.43 eV) is also much higher than the \( \text{H} \) ionization potential. \textit{Ab initio} calculations of rare gas-hydrogen clusters with one H atom have been performed for \( \text{Ne}_n \text{H}_n^+ \) clusters. Due to the large difference between the Ne and H ionization potentials, the charge is strongly localized on \( \text{H}_n^+ \), and the Ne atoms are bound to \( \text{H}_n^+ \) mainly by polarization forces. A similar situation also occurs for clusters formed by aromatic cations and rare gas atoms. Since the ionization potentials of aromatic molecules are much smaller than those of rare gas atoms, the positive charge is located on the aromatic molecules, which thus attracts the rare gas atoms by polarization forces.

The brief survey presented above shows that the study of ionic clusters is a rapidly-developing field of research. Some of the experimental results, especially the discovery of the new (cluster) class of reactions, suggest possible practical applications of ionic clusters, such as in catalysis.

In this study we shall present a quantum chemical treatment of the relatively simple ionic clusters \( \text{R}_n^+ \) (\( \text{R,H}_n \)) and (\( \text{R}_n^+ \text{H}_2 \)). These systems are bound together not only by electrostatic forces but sometimes also by valence forces resulting from the electron (charge) delocalization, as discussed above for \( \text{R}_3^+ \) ions. In order to study theoretically the systems with ions where both electrostatic polarization and charge delocalization are of importance, we have previously developed the semiempirical diatomics-in-ionic-systems (DIIS)
method. This method was first applied to rare gas-halogen systems with excited ionic states like $\text{Xe}^+_n \text{Cl}^-$, $\text{Xe}^+_n \text{HCl}^-$, and we shall now use it to calculate the electronic structure of rare gas and rare gas-hydrogen ionic clusters.

In the next section we shall describe briefly the DIIS method, as well as some modifications which one needs to apply it to the systems under consideration. Sections III and IV deal with calculations of $\text{Ar}^+_n$, $(\text{Ar}_n \text{H})^+$ and $(\text{Ar}_n \text{H}_2)^+$ and of $\text{Xe}^+_n$, $(\text{Xe}_n \text{H})^+$ and $(\text{Xe}_n \text{H}_2)^+$, respectively. Section V given the Conclusions, and the Appendix presents the diatomic potentials.

II. Diatomics-in-Ionic-Systems (DIIS) Method

A. Closed-Shell Atoms with Electron Deficiency

Let us consider a polyatomic system $(A_1 A_2 \ldots A_J)^+$ consisting of $J$ closed-shell atoms or ions $A_i$ with one electron deficiency (hole) delocalized, generally speaking, between these atoms (ions). For example, the neutral rare gas-halogen system $R_n X$ is considered in DIIS as $(R_n X^-)^+$. The spin of a system with one electron deficiency is $S = \frac{1}{2}$. The DIIS wave function is presented as a linear combination of diabatic polyatomic wave functions with localized electron deficiency as

$$\Phi = \sum_{i=1}^{J} \sum_{\text{M}_i} C_{\text{im}} \Phi_{\text{im}},$$

(1)

where $\Phi_{\text{im}}$ is the diabatic wave function of the configuration $A_1 A_2 \ldots A_{\text{im}} \ldots A_J$, with the index $m$ indicating the orientation of the $A_i^+$ open shell ($M_i = 3$ for a P-symmetry $A_i^+$ shell). For example, $R_2 X$ is described by nine diabatic
configurations, namely $R^+RX^-$, $RR^+X^-$ and $RRX$ for $m = 1, 2, 3$. The rare gas ionic cluster $R_n^+$ is described by $3n$ diabatic configurations $R...R^+...R$. An ionic system consisting of $n$ rare gas atoms and one hydrogen atom $(R_nH)_n^+$ can be also treated by the DIIS method if the electron affinity of $H$ is neglected and singlet states only are considered. The $(R_nH)_n^+$ system is described by $3n + 1$ diabatic configurations, namely $R...R^+...RH (m = 1, 2, 3)$ and $R...R...RH^+ (m = 1)$.

The diagonal matrix elements of the DIIS wave function (1) have the physical interpretation as the energies of the diabatic configurations with fixed localization of the electron deficiency. If we consider only the pairwise interactions between atoms (ions), then the diagonal matrix elements are presented as a sum of diatomic interactions,

$$H_{im,im} = \sum_j W_j + \sum_{j_1 j_2 (\neq j_1)} W_{j_1 j_2} + U_1 + \sum_j U_{im,j}, \quad j, j_1, j_2 = 1, \ldots, n, (2)$$

where $W_j$ is the energy of the closed-shell atom $A_j$, $W_{j_1 j_2}$ is the diatomic potential between two closed-shell atoms, $A_{j_1} \cdot A_{j_2}$, $U_1$ is the energy of atom $A_1$ with an electron deficiency, and $U_{im,j}$ is the diabatic potential between the closed-shell atom $A_j$ and the atom with electron deficiency, $A_1^+$. The transformation of the potentials between $m$-oriented orbitals to the $\Sigma$ and $\Pi$ potentials is described in Ref. 9, where the expressions for the off-diagonal matrix elements are given as well. The atom $H$ is considered here as a closed shell atom. In the case of ionic systems, like $R_n^+$ or $(R_nH)_n^+$, the closed-shell atoms are neutral, and the atoms with electron deficiency are the ions $R^+$ or $H^+$. The diatomic potentials between neutral atoms, $W_{RR}$ and $W_{RH}$, are taken to be known from empirical studies or $ab\ initio$ calculations. The diabatic
potentials between neutral atoms and ions, such as $R^+ - R$, $R^+ - H$, $R - H^+$, have to be calculated since only adiabatic potentials, such as $W^+_{R_2}$ and $W(RH)^+$, are the physically-defined values.

The diabatic potentials $U_{im,j}$ can be found by considering the diatomic fragments within the DIIS approximation and solving the inverse problem of the $2 \times 2$ matrix eigenvalues, i.e., calculating the matrix elements for given eigenvalues. In the case of the homonuclear fragment $R_2^+$, the $2 \times 2$ matrix of the fragment is

$$
\begin{pmatrix}
U - E & V \\
V & U - E
\end{pmatrix} = 0,
$$

(3)

where $U$ is the $R^+ - R$ diabatic potential and $V$ is the exchange term in the $(R^+ R) - (R^+ R)$ coupling. Substituting into (3) the known adiabatic potentials $E^{(1)} = \Sigma_u^2$ and $E^{(2)} = \Sigma_g^2$ or $E^{(1)} = \Pi_g^2$ and $E^{(2)} = \Pi_u^2$, we can easily find the diabatic $R^+ R$ potential $U$ and the exchange term $V$ for $\Sigma$- or $\Pi$-symmetry. For the case of the heteroatomic fragment $(RH)^+$, there are two different diabatic potentials, $U^+_{RH}$ and $U_{RH^+}$,

$$
\begin{pmatrix}
U^+_{RH} - E & V \\
V & U_{RH^+} - E
\end{pmatrix} = 0.
$$

(4)

In order to find $U^+_{RH}$, $U_{RH^+}$ and $V$ for two given adiabatic potentials, for example, $E^{(1)} = \Sigma^1 \Sigma$ and $E^{(2)} = \Sigma^1 \Sigma$, one needs an extra empirical or ab initio value such as the static or transition dipole moment. After the diabatic
potentials $U_{im,j}$ and the exchange terms $V_{i_1m_1,i_2m_2}$ are determined from Eqs. (3) and (4), the diagonal matrix elements (2) and the off-diagonal matrix elements (presented in Ref. 9) can be calculated, and the wave function (1) and its energy spectrum can be found.

In the wave function presentation (1), the spin-orbit coupling is not taken into account, at least directly. Indirectly, the energy level shifts resulting from the spin-orbit coupling are incorporated into the system energy via the empirical or ab initio diatomic potentials which are used in the DIIS calculations as the input. By neglecting the spin-orbit coupling in the wave function, we are losing some of the excited states and are excluding from our consideration effects such as S-P mixing in collinear configurations.

B. Polarization Energy

In applying Eqs. (2)-(4), we need not care about the polarization component of the ion-atom interactions, since it is included in the empirical or ab initio potentials which we are suggesting to use. However, the polarization of atoms gives rise to the electrostatic dipole-dipole interaction which is of three-particle origin (ion-atom-atom) and cannot be considered in a pairwise way. The energy of the dipole-dipole interaction is usually small, although it is not necessarily negligible, and hence we intend to take it into account. Including this energy as a separate term $\Delta_i$ within the diagonal matrix element (2) and taking as zero the energy of the separated neutral atoms, we obtain

$$H_{im,im} = I_i + \sum_{j_1} \sum_{j_2>j_1} W_{j_1j_2} + \sum_j U_{im,j} + \Delta_i , \quad j,j_1,j_2 \neq i \quad (5)$$

where $I_i$ is the ionization potential of the $i$-th atom, and
A suggested form for the functional dependence on $R_{ij}$ is

$$
\gamma(R_{ij}) = \left[ 1 + \left( \frac{r_{1} + r_{2}}{R_{ij}} \right)^{12} \right]^{-1/3}
$$

(9)
where \( r_i \) and \( r_j \) are the ionic and atomic radii, respectively. For the case of the interaction between polarized neutral atoms, both \( r_i \) and \( r_j \) are atomic radii. When the interatomic separation \( R_{ij} \) is larger than the sum of atomic radii (non-overlapping atoms), the function \( \gamma \) is close to unity, i.e., the dipole approximation is valid. When the interatomic separation is smaller than the sum of atomic radii (overlapping atoms), the damping function decreases as \( R_{ij}^{-4} \), so that the ion-atom polarization energy (7) is saturated with a limiting value of \(-C_j/(r_i+r_j)^4\). The suggested form (9) for the \( R_{ij} \) dependence is of course arbitrary, but at least it describes in a proper way the asymptotic behavior. If the asymptotic conditions are fulfilled, the form of the dependence of \( \gamma \) on \( R_{ij} \) does not imply much about the results. According to our estimations, different reasonable models of the damping function \( \gamma(R_{ij}) \) vary the energy within a range of 0.03 eV only, mostly even much less. For the values \( r_i \) and \( r_j \) in (9), we shall use the atomic VDW radii.

C. \((R_n H_2)^+\) System

The ionic rare gas-hydrogen system \((R_n H_2)^+\) is described in the DIIS method as \( n \) closed-shell atoms (R) and two open-shell atoms (H) with one positively-charged hole. Each of the two diabatic configurations \( R\ldots RH^+H \) with a hole located on one of the H atoms is described by a wave function with a fixed \( s = \frac{1}{2} \) spin on the only open-shell atom (H). The situation is much more complicated in the diabatic configuration \( R\ldots R^+\ldots RHH \) when the hole is located on one of the \( n \) rare gas atoms. In this configuration there are three open-shell atoms \((R^+, H, H)\) with spins \( s = \frac{1}{2} \), which make two different spin states for a total spin \( S = \frac{1}{2} \). Consequently, each \( R\ldots R^+\ldots RHH \) configuration with fixed hole location is described by six diabatic wave functions which
differ from another not only by $p$-orbital orientation, like in expansion (1), but also by spin eigenfunctions. Taking into account the hole delocalization between all rare gas and hydrogen atoms, one expresses the DIIS wave function as the superposition of $6n+2$ diabatic wave functions,

\[ \Phi = \sum_{i=1}^{n} \sum_{m=1}^{3} \sum_{k=1}^{2} C_{imk} \Phi_{imk} + \sum_{j=1}^{2} C_{n+j} \Phi_{n+j} \quad , \quad (10) \]

where $\Phi_{n+j}$ describes the diabatic configuration with the charge on an H atom, $R...R.H^+$, $\Phi_{imk}$ describes the diabatic configuration $R\ldots R^+(i)\ldots R(n)^+H$ (the numbers in parentheses are the atomic indices) with the $m$-orientation of the $R^+$ $P$-shell, and $k$ indicates the spin configuration of the three $(R^+(i),H,H)$ uncoupled electrons. Following the usual DIM presentation of a triatomic wave function, we express the diabatic wave functions in terms of one-electron orbitals as

\[ \Phi_{i11} = -\frac{1}{\sqrt{2}} \left( |P_{ix}p_{iy}P_{iz}\bar{p}_{iz}s_1\bar{s}_2| - |P_{ix}p_{iy}P_{iz}\bar{p}_{iz}s_1s_2| \right) \prod_{j(\neq 1)} \Phi_j \quad (11) \]

\[ \Phi_{i12} = -\frac{1}{6} \left( 2|P_{ix}p_{iy}P_{iz}\bar{p}_{iz}s_1s_2| - |P_{ix}p_{iy}P_{iz}\bar{p}_{iz}s_1\bar{s}_2| \right. \]

\[ \left. - |P_{ix}p_{iy}P_{iz}\bar{p}_{iz}s_1\bar{s}_2| \right) \prod_{j(\neq 1)} \Phi_j \quad (12) \]

\[ \Phi_j = |P_{jx}\bar{p}_{jx}p_{jy}\bar{p}_{jy}p_{jz}\bar{p}_{jz}| \quad , \quad j = 1,2\ldots n \quad (13) \]

\[ \Phi_{n+1} = s_2 \prod_{j} \Phi_j \quad , \quad \Phi_{n+2} = s_1 \prod_{j} \Phi_j \quad . \quad (14) \]
where the bars denote the negative spin orientation, $p_{ix}$, $p_{iy}$, $p_{iz}$ are the p-orbitals of the i-th rare gas atom, and $s_1$ and $s_2$ are the 1s orbitals of the hydrogen atoms. The index $m = 1$ in $\Phi_{i11}$ and $\Phi_{i12}$ indicates the x-orientation of the $R^+_1$ shell. The diabatic functions $\Phi_{imk}$ for $m = 2$ (y-orientation) and $m = 3$ (z-orientation) are expressed by equations similar to Eqs. (11)-(12).

The p-orbitals of the diabatic functions (11)-(13) are oriented along fixed x,y,z-axes. When the diabatic functions are used to form the $H$-matrix, the x,y,z oriented p-orbitals have to be transformed to $\Sigma$ and $\Pi$ orientatations of diatomic fragments. This transformation for arbitrary located atoms is performed by an $S$ matrix whose elements are

$$S_{ij,\Sigma} = (x_j - x_i)/R_{ij} , \quad S_{ij,\Pi} = r_{ij}/R_{ij} , \quad S_{ij,\pi} = 0 \quad (15a)$$

$$S_{ij,\Sigma} = (y_j - y_i)/R_{ij} , \quad S_{ij,\Pi} = -(x_j - x_i)(y_j - y_i)/(R_{ij}r_{ij})$$

$$S_{ij,\pi} = (z_j - z_i)/r_{ij} \quad (15b)$$

$$S_{ij,\Sigma} = (z_j - z_i)/R_{ij} , \quad S_{ij,\Pi} = -(x_j - x_i)(z_j - z_i)/(R_{ij}r_{ij})$$

$$S_{ij,\pi} = -(y_j - y_i)/r_{ij} \quad (15c)$$

$$r_{ij} = \sqrt{(y_j - y_i)^2 + (z_j - z_i)^2} \quad (16)$$

where $x_i$, $y_i$ and $z_i$ are the i-th atom coordinates, $R_{ij}$ is the interatomic separation, and the $\Pi$-orientation of the $R^+_1$ P-shell is indicated by $\Pi$ when located in the plane formed by $R_{ij}$ and the x-axis, and by $\pi$ when perpendicular
to this plane. We shall also use later the following combinations of the \( S \) values:

\[
T_{ij,m} = S_{ij,m}^2 + S_{ij,m\pi}^2 \quad (17a)
\]

\[
T_{ij,m_1m_2} = S_{ij,m_1} S_{ij,m_2} + S_{ij,m_1\pi} S_{ij,m_2\pi} \quad (17b)
\]

Applying both the DIIS\(^9\) and DIM\(^{47,58}\) approaches and using the diabatic functions (11)-(14), we obtain the \((6n+2)\times(6n+2)\) \( H \)-matrix which we shall simply display without going into the details of its construction. The diagonal matrix element for \( R^{(1)\ldots R^{+}(1)\ldots R^{(n)} H^{(n+1)} H^{(n+2)} } \) is

\[
H_{imk,imk} = I_R + \sum_{j_1}^{n-1} \sum_{j_2>j_1}^n W_{j_1,j_2} + \sum_{j=1}^n [S_{ij,m\Sigma} U_{ij,\Sigma} + T_{ij,m} U_{ij,\Pi}]
+ \sum_{j_1=1}^n \sum_{j=1}^2 W_{j_1,n+j} + \sum_{j=1}^2 [S_{ij,n+j,m\Sigma} O^{(k)}_{i,n+j,\Sigma} + T_{ij,n+j,m} O^{(k)}_{i,n+j,\Pi}]
+ \omega^{(k)}_{n+1,n+2} \quad j_1,j_2 \neq i \quad k = 1,2 \quad (18)
\]

\[
o^{(1)}_{i,n+j,\Sigma} = \frac{1}{4} U_{i,n+j,\Sigma} + \frac{3}{4} U_{i,n+j,\Sigma} \\
\]

\[
o^{(2)}_{i,n+j,\Sigma} = \frac{3}{4} U_{i,n+j,\Sigma} + \frac{1}{4} U_{i,n+j,\Sigma} \quad (19a)
\]

\[
o^{(k)}_{i,n+j,\Pi} \quad (19b)
\]

and the same for \( O^{(k)}_{i,n+j,\Pi} \). In Eqs. (18)-(19), \( I_R \) is the rare gas ionization potential, \( W_{j_1,j_2} \) are the \( R-R \) potentials, \( W_{j_1,n+j} \) are the \( R-H \) potentials,\}
The diagonal matrix element for $R...R^+_H(n+1)^H(n+2)$ is

$$H_{n+1,n+1} = I_H + \sum_{j_1} \sum_{j_2 (j_2 > j_1)} W_{j_1,j_2} + \sum_{j=1}^{n-2} (W_{j,n+2} + U_{n+1,j}) + U_{n+1,n+2},$$

and the same for $H_{n+3,n+2}$. In Eq. (20), $U_{n+1,j}$ are the $H^+_R$ potentials, and $U_{n+1,n+2}$ is the $H^+_R-H^+_H$ diabatic potential.

The off-diagonal matrix element between two $R(1)...R^+(n)^H(n+1)^H(n+2)$ configurations with different $(k = 1,2)$ spin orientations are:

$$H_{im1,im2} = \frac{\sqrt{3}}{4} \sum_{j=1}^{2} (-1)^{J-1} \left( S_{i,n+j,m}^2 \left( (3U_{i,n+j,\Sigma} - U_{i,n+j,\Sigma}) + T_{i,n+j,m} (3U_{i,n+j,\Pi} - 2U_{i,n+j,\Pi}) \right) \right).$$

The off-diagonal matrix elements between two $R(1)...R^+(i)...R(n)^H(n+1)^H(n+2)$ configurations with different $(m_1,m_2)$ orbital orientations are:

$$H_{im1,k,im2,k} = \sum_{j=1}^{n} \left( S_{ij,m_1,\Sigma} S_{ij,m_2,\Sigma} U_{ij,\Sigma} + T_{ij,m_1,m_2} U_{ij,\Pi} \right).$$
\[
H_{i_1m_1,i_2m_2}^{1,2} = H_{i_2m_2,i_1m_1}^{1,2} = \frac{\beta}{4} \sum_{j=1}^{2} (-1)^{j-1} S_{i,n+j,m_1} \Sigma S_{i,n+j,m_2} \Sigma \times (3U_{i,n+j,\Sigma} - U_{i,n+j,\Sigma}) + T_{i,n+j,m_1m_2} (3U_{i,n+j,\Pi} - U_{i,n+j,\Pi})\]
\]

(23)

The off-diagonal matrix elements between the configurations

\[R(1)\cdots R(1_i)\cdots n(n+1)R(n+2)\] and \[R(1)\cdots R(1_i)\cdots R(n+1)R(n+2)\] are

\[
H_{i_1m_1,i_2m_2}^{1,2} = H_{i_2m_2,i_1m_1}^{1,2} = S_{i_1i_2m_1} \Sigma S_{i_2i_1m_2} \Sigma V_{i_1i_2}^{\Sigma} + (S_{i_1i_2m_1} \Pi S_{i_2i_1m_2} \Pi + S_{i_1i_2m_1} \Sigma S_{i_2i_1m_2} \Sigma) V_{i_1i_2}^{\Pi}
\]

(24)

\[
H_{i_1m_1,i_2m_2}^{1,2} = 0
\]

(25)

where \(V_{i_1i_2}^{\Sigma}\) and \(V_{i_1i_2}^{\Pi}\) are the exchange terms of the \((R(1_i)R(1_{i_2}))-(R(1_i)R(1_{i_2}))\) coupling (see Eq. (3)). The off-diagonal matrix elements between the configuration \(R(1)\cdots R(1)R(n)R(n+1)R(n+1)\) and the configurations \(R(1)\cdots R(1)R(n)R(n+1)R(n+1)\) and \(R(1)\cdots R(1)R(n)R(n+1)R(n+2)\) are

\[
H_{i_1n+j}^{1,2} = -S_{i,n+j,m} \Sigma V_{i,n+j,\Sigma}, \quad j = 1,2
\]

(26)
\[ H_{i+2,m} = \sqrt{3}(-1)^{j-1} H_{i,m} + H_{i,1} \], \quad j = 1, 2 \tag{27} \\

where \( V_{i,m+1,\Sigma} \) is the exchange term in the \((R^+H)\cdot(RH^-)\) coupling (see Eq. (4)). The \( \Pi \)-component of the coupling is zero. The off-diagonal matrix element between the configurations \( R(1) \cdots R(n)H^+(n+1)H^+(n+2) \) and \( R(1) \cdots R(n)H^+(n+1)H^+(n+2) \) is equal to the exchange term of the \((H^+H)-(HH^+)\) coupling in the \( H_2^+ \) molecule (see Eq. (3)), \\

\[ H_{n+1,m+2} = V_{n+1,m+2} \]. \tag{28} \\

When the delocalization of the charge is neglected (i.e., setting the exchange terms \( V \) equal to zero), we obtain for \( R \cdots R^+ \cdots RHH \) the usual DIM matrix elements.

The diabatic potentials \( U_{i,j,\Sigma} \) and \( U_{i,j,\Pi} \) of the \( R^+R \) diatomic fragments (Eqs. (18) and (22)), as well as \( U_{n+1,m} \) of the \( H^+H \) fragment (Eq. (20)), are found by the inverse solution of Eq. (3), as described in Subsection II.A above. The situation is much more complicated for the diabatic potentials \( U_{i,n+1,\Sigma} \) and \( U_{i,n+1,\Pi} \) (Eqs. (19), (21) and (23)) and \( U_{n+1,m} \) (Eq. (20)) of the \( R^+H \) and \( RH^+ \) diatomic fragments. In our approach, the \((RH)^+\) diatomic fragment is described by a \( 3 \times 3 \) matrix which is obtained by removing to infinity all other atoms. Using Eqs. (18), (20), (26) and (27), we have

\[
\begin{vmatrix}
\frac{1}{4} U_{i,n+1} + \frac{3}{4} U_{i,n+1} - E & \frac{\sqrt{3}}{4} (3 U_{i,n+1} - U_{i,n+1}) & V_{i,n+1} \\
\frac{\sqrt{3}}{4} (3 U_{i,n+1} - U_{i,n+1}) & \frac{1}{4} U_{i,n+1} + \frac{3}{4} U_{i,n+1} - E & -\sqrt{3} V_{i,n+1} \\
V_{i,n+1} & -\sqrt{3} V_{i,n+1} & U_{n+1,i} - E \\
\end{vmatrix} = 0 .
\tag{29}
\]
where we have simplified the notation by dropping the subscript $\Sigma$ for the

$$(R(i)H_{(n+1)})^+$$

fragment. Using the $(RH)^+$ potentials $^1W_{i,n+1}$ and $^3W_{i,n+1}$

(asymptotic to $R^++H$) and $W_{n+1,i}$ (asymptotic to $R+H^+$) as the eigenvalues $E^{(1)}$,

$E^{(2)}$ and $E^{(3)}$ for Eq. (29), we can find numerically the diabatic potentials

$^1U_{i,n+1}$, $^3U_{i,n+1}$ and $U_{n+1,i}$. The construction of the exchange term $V_{i,n+1}$ of

the $(RH)^+$ diatomic fragment was described in Subsection II.A (see Eq. (4)).

The diabatic $\Pi$-potentials $^1U_{i,n+j,\Pi}$ and $^3U_{i,n+j,\Pi}$ coincide with the adiabatic

$^1W_{i,n+j,\Pi}$ and $^3W_{i,n+j,\Pi}$ potentials, since the exchange term $V_{i,n+j,\Pi}$ is equal
to zero. The adiabatic diatomic potentials of the diatomic fragments $R_2$, $H_2$, $RH$, $R_2^+$, $H_2^+$ and $(RH)^+ \text{ for } R = Ar,Xe$ are presented in the Appendix.

III. Argon and Argon-Hydrogen Ionic Clusters $Ar_n^+$, $(Ar,H)_n^+$ and $(Ar,H_2)_n^+$

Considering the structure of rare gas-hydrogen ionic clusters, we have
decided to look at $Ar$ and $Xe$, since they are expected to form different kinds
of clusters with $H$ due to the difference in their ionization potentials.

Specifically, the $Ar$ ionization potential ($т_{Ar} = 15.76 \text{ eV}$) is much higher than
the $H$ ionization potential ($т_{H} = 13.6 \text{ eV}$), whereas the $Xe$ ionization potential
($т_{Xe} = 12.13 \text{ eV}$) is smaller than that of $H$, which leads to different charge
distributions in the argon-hydrogen and xenon-hydrogen clusters. But before
considering the rare gas-hydrogen systems, we shall present the results of
calculations on the rare gas ionic clusters $Ar_n^+$ and $Xe_n^+$.

A. $Ar_n^+$ Clusters

The results of the calculations of the small ionic clusters $Ar_3^+$, $Ar_4^+$, $Ar_5^+$ and $Ar_6^+$ are presented in Table 1 and, partly, in Fig. 1. We shall
now compare these results with the known experimental and theoretical results
which have been obtained for the $Ar_n^+$ clusters.
According to experimental studies of the simplest cluster, $\text{Ar}_3^+$, its energy of dissociation, $\text{Ar}_3^+ \rightarrow \text{Ar}_2^+ + \text{Ar}$, is about 0.2 eV.\textsuperscript{17,21,23,59,60} There are two alternative structures of the $\text{Ar}_3^+$ cluster, namely an asymmetrical $\text{Ar}_2^+\text{Ar}$ structure with the charge concentrated on $\text{Ar}_2^+$ and a structure with the charge distributed among all three atoms. In the case of the $\text{Ar}_2^+\text{Ar}$ structure, where the neutral atom is bound to the $\text{Ar}_2^+$ molecule by polarization forces, the triangle geometry is expected to be the most stable one.\textsuperscript{61} When the charge is delocalized among all three atoms, the exchange interaction contributes significantly to the binding so that the symmetrical linear geometry is expected to be the most stable configuration. The first quantum chemistry calculation, performed by the approximate $X_\alpha$ method, gave preference to the asymmetrical triangle structure.\textsuperscript{62} However, the CI ab initio calculations,\textsuperscript{24,25} as well as semiempirical calculations,\textsuperscript{27,29} found the symmetrical linear configuration to be the most stable one. The experimental spectral data, unfortunately, cannot provide direct evidence about the $\text{Ar}_3^+$ geometry. The conclusions made by the indirect analysis of the experimental data are contradictory. Whereas some of the experimental works confirm the symmetrical linear $\text{Ar}_3^+$ structure,\textsuperscript{17,35,63} other papers substantiate the asymmetrical $\text{Ar}_2^+\text{Ar}$ structure, either of triangular\textsuperscript{61} or linear\textsuperscript{19,64} geometry.

Such discrepancy in the conclusions is due, most probably, from the features of the $\text{Ar}_2^+$ potential energy surface. Since $\text{Ar}_3^+$ has a very flat $\text{Ar}_2^+\text{Ar}$ potential,\textsuperscript{19,28,64} the vibrational motion shifts, for the most part, the $\text{Ar}_3^+$ configuration far away from the equilibrium configuration, thus significantly affecting the electronic transitions. This problem has been considered in detail by Gidea and Amarouche,\textsuperscript{28} who calculated the potential energy surfaces of $\text{Ar}_3^+$ by a method similar to DIIS. A trajectory study performed on these potential energy surfaces shows that the symmetrical linear
Ar$_3^+$ minimum energy configuration alone provides the spectrum close to the experimental one, if one takes into account the vibrational motion.\textsuperscript{28}

In our calculations the triatomic cluster Ar$_3^+$ has a symmetrical linear equilibrium configuration, in accord with other calculations.\textsuperscript{24-28} The $\Sigma_k \rightarrow \Sigma_g$ transition energy in the equilibrium configuration is found in our calculations to be equal to 2.26 eV, close to the other theoretical values of 2.36 eV\textsuperscript{24} and 2.34 eV.\textsuperscript{28} Our $\Sigma_k \rightarrow \Sigma_g$ transition moment is 8.8 D, compared to the \textit{ab initio} value of 8.24 D.\textsuperscript{24} For the Ar-Ar distance at the equilibrium configuration, our calculation gives $R = 2.59$ Å, exactly the same as the semiempirical calculation of Gadea and Amarouche\textsuperscript{28} but slightly less than \textit{ab initio} calculations (2.62 Å).\textsuperscript{25} The Ar$_3^+$ -- Ar$_2^+$ + Ar dissociation energy in our calculation is $D = 0.203$ eV, close to the experimental values of 0.22 eV\textsuperscript{17,61} and 0.18 ± 0.05 eV.\textsuperscript{21} Other calculations give values a little bit lower than our dissociation energies, namely, 0.18 eV,\textsuperscript{24} 0.16 eV,\textsuperscript{25} 0.20 eV\textsuperscript{27} and 0.17 eV.\textsuperscript{28}

The most stable Ar$_4^+$ cluster, according to our calculations, is formed by an Ar$_3^+$ ion and almost neutral ($q = +0.002$) Ar atom separated from the nearest charged atom by 3.68 Å (see Table 1 and Fig. 1.III). The dissociation energy for the Ar$_4^+$ -- Ar$_3^+$ + Ar detachment process is found to be equal to $D = 0.047$ eV, a typical energy of the polarization attraction. Another Ar$_4^+$ cluster is found in an asymmetrical linear configuration with one almost neutral ($q = +0.01$) atom separated from the nearest atom of Ar$_3^+$ by 3.3 Å (see Table I and Fig. 1.V). The dissociation energy of this quasistable configuration is $D = 0.031$ eV, and the potential barrier of the transition to the most stable configuration (Fig. 1.III) is about 0.001 eV only. In the DIM calculation,\textsuperscript{27} the linear configuration with the dissociation energy of 0.043 eV is found to be the most stable one. According to experimental studies,\textsuperscript{20,65} the spectrum
of $\text{Ar}_n^+$ and other small $\text{Ar}_n^+$ clusters is similar to the $\text{Ar}_3^+$ spectrum, so that the conclusion is made that the $\text{Ar}_n^+$ ($n > 3$) clusters have a structure of $\text{Ar}_3^+\text{Ar}_{n-3}^-$. This experimental finding supports our result that $\text{Ar}_3^+\text{Ar}$ is the most stable structure for the $\text{Ar}_4^+$ cluster. A similar result is obtained for $\text{Ar}_5^+$ and $\text{Ar}_6^+$ (see below). Like in the experimental studies, the spectrum of the most stable $\text{Ar}_4^+$ cluster is found to be similar to that of $\text{Ar}_3^+$ (Table 2.III). It consists of two transitions with large transition moments and transition energies close to one another and to the $^2\Sigma^+_g$ excitation energy of $\text{Ar}_3^+$, so that they give one absorption band with its center close to that of the $\text{Ar}_3^+$ absorption. It is interesting to note that in the $\text{Ar}_4^+$ excitation states a strong charge transfer takes place, which makes it impossible to describe the excited $(\text{Ar}_4^+)^*$ cluster as an $(\text{Ar}_3^+)^*\text{Ar}$ structure (Table 2). Save for the transitions which resemble the $^2\Sigma^+_u \rightarrow ^2\Sigma^+_g$ transition of $\text{Ar}_3^+$, we find also in $\text{Ar}_4^+$ a low-energy (1.79 eV) transition with a small transition moment of $\mu = 0.7$ D (Table 2).

In addition to the $\text{Ar}_4^+$ clusters with the ground-state $\text{Ar}_3^+\text{Ar}$ structure, we find a quasistable symmetrical configuration with all atoms bearing the same charge of $q = +0.25$, (Table 1.IV). In this configuration, $\text{Ar}_4^+$ has the geometry of a regular pyramid with a separation of 2.836 Å between every two atoms. The energy of this fully-symmetrical structure is only 0.1 eV above the energy of the most stable $\text{Ar}_4^+$ cluster. The spectrum of the symmetrical $\text{Ar}_4^+$ cluster is quite different from that of $\text{Ar}_3^+$. The transition energy to the three lowest excited states which form a degenerate level is only 1.46 eV, compared to 2.26 eV for the first allowed transition in $\text{Ar}_3^+$ (Table 2). The symmetrical $\text{Ar}_4^+$ configuration is separated from the stable $\text{Ar}_3^+\text{Ar}$ configuration by a high barrier of roughly 0.25 eV.
The $\text{Ar}_5^+$ and $\text{Ar}_6^+$ clusters are formed in a similar way as the stable $\text{Ar}_4^+$ cluster, i.e., by a $\text{Ar}_3^+$ ion and neutral or almost neutral Ar atoms. The energy of one Ar atom detachment is 0.05 eV for $\text{Ar}_5^+$ and 0.06 for $\text{Ar}_6^+$ (Table 1). The $\text{Ar}_5^+$ and $\text{Ar}_6^+$ spectra are similar to the spectrum of the stable $\text{Ar}_4^+$ cluster (Table 2.III). The experimental studies confirm that $\text{Ar}_3^+$ is an ionic core in small $\text{Ar}_n^+$ clusters. However, in large $\text{Ar}_n^+$ clusters, $n \geq 15$, the $\text{Ar}_2^+$ molecule was found to be the most stable ionic core. The transition from the $\text{Ar}_3^+$ to $\text{Ar}_2^+$ core with an increase of cluster size can be explained by the polarization effects. The energy of the neutral atoms polarization by the ionic is slightly larger for the $\text{Ar}_2^+$ than $\text{Ar}_3^+$ core because of the difference in their dimension. In small $\text{Ar}_n^+$ clusters, this difference in polarization energy is small compared to the $\text{Ar}_3^+$ dissociation energy, and consequently it is not expected to affect the core structure. In large $\text{Ar}_n^+$ clusters, the polarization energy is close to that in solid Ar where, according to our estimations, the difference between the polarization energies of the $\text{Ar}_2^+$ and $\text{Ar}_3^+$ cores lies somewhere between 0.3 and 0.6 eV. This energy difference is larger than the $\text{Ar}_3^+$ dissociation energy, so that the $\text{Ar}_2^+$ core may become more stable than the $\text{Ar}_3^+$ one.

B. (Ar$_n$H$^+$) Clusters

The structure of the (ArH)$^+$ clusters is simple: all of them are formed by an (ArH)$^+$ ionic molecule and n-1 neutral Ar atoms which are bound to (ArH)$^+$ by polarization forces (Table 3). Since in the (ArH)$^+$ molecule the H atom bears more charge than the Ar atom ($q_H = +0.569$), the neutral Ar atoms are located on the H side of the (ArH)$^+$ ion (Fig. 2). The simplest (Ar$_n$H)$^+$ cluster, Ar(ArH)$^+$, has a bent geometry with the neutral Ar atom at a distance of 2.81 Å from H. In the Ar$_2$(ArH)$^+$, Ar$_3$(ArH)$^+$ and Ar$_4$(ArH)$^+$ clusters, the
neutral atoms are located symmetrically around the \((\text{ArH})^+\) molecular axis at the distances of 2.79 Å, 2.79 Å and 2.84 Å, respectively. In the \(\text{Ar}_6\)(\(\text{ArH}\))^+ clusters, two of the Ar atoms are more tightly bound to \((\text{ArH})^+\) than the other four Ar atoms. In the sequence of \(\text{Ar}_k\)(\(\text{ArH}\))^+ clusters, the H charge increases monotonically with \(k\). The energy of an Ar atom detachment from an \(\text{Ar}_k\)(\(\text{ArH}\))^+ cluster is relatively large, varying from 0.09 eV for \(k = 6\) to 0.19 eV for \(k = 3\). The electronic spectrum of the \(\text{Ar}_k\)(\(\text{ArH}\))^+ clusters is practically the same as the spectrum of the isolated \((\text{ArH})^+\) molecule. The \(\text{Ar}_k\)(\(\text{ArH}\))^+ clusters can probably be detected by studying their rotational spectrum, since the \(\text{Ar}_k\)(\(\text{ArH}\))^+ dipole moment depends strongly on \(k\) (Table 3).

C. \(\text{Ar}_n\text{H}_2^+\) Clusters

The ionization potential of Ar (15.76 eV) is close to the ionization potential of the \(\text{H}_2\) molecule (15.426 eV), which leads to strong coupling between the states \(\text{Ar}^+\text{H}_2^+\) and \(\text{ArH}_2^+\). This coupling affects significantly the potential energy surfaces of the \((\text{ArH}_2)^+\) system, which have been calculated by the DIM method. We shall not consider here the \((\text{ArH}_2)^+\) potential energy surfaces, i.e., we shall not consider the energy \(E\) as a function of the interatomic distances \(R_{\text{Ar-H}(1)}\), \(R_{\text{Ar-H}(2)}\) and \(R_{\text{H-H}}\), but restrict our task to the study of ionic clusters formed by the Ar atom or atoms and the \(\text{H}_2\) molecule. The calculation of the \((\text{ArH}_2)^+\) system is performed by the modified DIIS method described in Subsection II.C above.

The \((\text{ArH}_2)^+\) clusters can be formed by \(\text{Ar}^+ + \text{H}_2\) (-4.746 eV), \(\text{Ar} + \text{H}_2^+\) (-4.95 eV) and \(\text{H} + (\text{ArH})^+\) (-6.215 eV). It follows that the most stable \((\text{ArH}_2)^+\) cluster is expected to be formed by the \((\text{ArH})^+\) molecule and H atom. However, the polarization attraction of the H atom to the \((\text{ArH})^+\) ion is so
weak that, according to our calculation, no (ArH₂)⁺ cluster can be formed. The ionic (ArH₂)⁺ cluster can be formed in a quasistable configurations only. We find that the quasistable (ArH₂)⁺ cluster with the lowest energy is formed by an almost neutral Ar atom (q = 0.02) and the H₂⁺ molecular ion with an H-H separation of 1.05 Å, slightly shorter than in the isolated H₂⁺ (1.06 Å). The Ar atom is located in a plane perpendicular to the H₂⁺ axis at a distance of 2.935 Å from the H₂⁺ center (Fig. 2). The energy of the Ar detachment is relatively large, D = 0.193 eV. The ArH₂⁺ cluster is separated from the stable state of separated (ArH)⁺ and H by a high barrier of, roughly, 0.75 eV. The saddle point for the ArH₂⁺ → H + (ArH)⁺ dissociation lies in the collinear configuration with the interatomic distances R_{H-H} = 1.5 Å and R_{Ar-H} = 1.2 Å. Unfortunately, in the DIM calculation the geometry of Fig. 2 was not studied so we do not have a comparison for our results.

The ArₙH⁺ clusters with a few Ar atoms have a structure similar to that of ArH₂⁺ (see Fig. 2 and Table 4). In all of these clusters up to n = 5, the Ar atoms are located in a plane perpendicular to the H₂⁺ axis at distances of about 3 Å. The energy of the Ar detachment is 0.19-0.2 eV, slowly decreasing with n for n > 2. The common charge of the Ar atoms slightly increases with n reaching q = ±0.075 in Ar₅H⁺. The decrease of the H₂⁺ charge with n leads to some decrease of the H-H interatomic distance, which is 1.03 Å in Ar₅H⁺. The larger ArₙH⁺ clusters (n > 5) are expected to be much less stable than the clusters presented in Table 4. The photoabsorption spectrum of the ArₙH⁺ clusters is very different from the H⁺ spectrum, since the lowest excited states are built up by charge transfer to Ar atoms and the formation of ArₙH⁺ (Table 4).
IV. Xenon and Xenon-Hydrogen Clusters $\text{Xe}_n^+$, $(\text{Xe}_n\text{H})^+$ and $(\text{Xe}_n\text{H}_2)^+$

A. $\text{Xe}_n^+$ Clusters

The results of the calculations of the small ionic clusters $\text{Xe}_3^+$, $\text{Xe}_4^+$, $\text{Xe}_5^+$ and $\text{Xe}_6^+$ are presented in Table 5 and (partly) in Fig. 3. In our calculations, the triatomic cluster $\text{Xe}_3^+$ has a symmetrical linear structure with 50% of the charge at the central atom, in accord with other calculations.\(^{24,29}\) Our calculation gives 3.38 Å for the Xe-Xe separation in $\text{Xe}_3^+$, compared to 3.47 Å\(^{24}\) and 3.32 Å\(^{29}\) in other calculations. The $\text{Xe}_3^+ \rightarrow \text{Xe}_2^+ + \text{Xe}$ dissociation energy in our calculation is $D = 0.20$ eV, which is 0.07 eV lower than the experimental value of 0.27 eV.\(^{22}\) Our dissociation energy is almost exactly halfway between the values of 0.12 eV\(^{24}\) and 0.36 eV\(^{26}\) obtained in two other calculations. For the $^2\Sigma_u^+ \rightarrow ^2\Sigma_g^+$ transition energy from the equilibrium point, we obtain $T = 1.87$ eV, a little bit higher value than in Ref. 24 (1.60 eV).

Our results obtained for $\text{Xe}_n^+$ clusters with $n > 3$ are quite different from those obtained in Ref. 29. According to our calculations, the most stable $\text{Xe}_4^+$ cluster has a structure of a regular pyramid, like $\text{Ar}_4^+$ (Fig. 1.IV), and the lowest energy quasistable $\text{Xe}_4^+$ cluster has a structure $\text{Xe}_3^+\text{Xe}$ with the weakly-charged atom ($q \approx 0.014$) located to the side of the $\text{Xe}_3^+$ axis (Table 5, Fig. 3). We find also a quasistable linear symmetrical $\text{Xe}_4^+$ cluster which energy lies 0.012 eV above the $\text{Xe}_3^+\text{Xe}$. In contrast to this, in Ref. 29 the most stable $\text{Xe}_4^+$ structure (Xe detachment energy of 0.159 eV) is just the linear symmetrical one. A structure like our regular pyramid (Fig. 3.III) was not found in Ref. 29 at all. We find the collinear $\text{Xe}_4^+$ cluster V to be separated from the bent geometry $\text{Xe}_3^+\text{Xe}$ cluster IV by a small barrier of 0.03 eV. The $\text{Xe}_3^+\text{Xe}$ cluster IV which can be formed easily as the result of the attachment of Xe to $\text{Xe}_3^+$ (attachment energy of 0.08 eV) is separated by a high
barrier of approximately 0.3 eV from the most stable Xe\textsuperscript{+} cluster, III. It follows that the Xe\textsubscript{3}X cluster can exist for a relatively long time when the temperature is not high.

The clusters Xe\textsubscript{5}\textsuperscript{+} and Xe\textsubscript{6}\textsuperscript{+} are presented in Table 5 for both the Xe\textsubscript{4}\textsuperscript{+}X\textsubscript{n-4} and Xe\textsubscript{3}\textsuperscript{+}X\textsubscript{n-3} structures. The energy of Xe detachment varies in the interval 0.07-0.11 eV. The binding energy of the attached atoms is derived from polarization forces, since these atoms are almost neutral.

In the family of Xe\textsubscript{3}\textsuperscript{+}X\textsubscript{n-3} clusters (IV, VII and IX in Table 5), the strongest transition is to the excited state similar to \( ^2\Sigma^+ \) of Xe\textsubscript{3}\textsuperscript{+}, i.e., with a very small charge on the central Xe\textsubscript{3}\textsuperscript{+} atom. In some of these clusters, an important portion of the charge is transferred in this excited state from Xe\textsubscript{3}\textsuperscript{+} to the attached atoms, for example, q = 0.38 in the Xe\textsubscript{3}\textsuperscript{+} cluster IV. As in the case of the Ar\textsubscript{3}\textsuperscript{+}Ar\textsubscript{n-3} clusters, the transition energy is not affected much by the charge transfer, so that in the Xe\textsubscript{3}\textsuperscript{+}X\textsubscript{n-3} clusters a strong photoabsorption is expected in the same range as in Xe\textsubscript{3}\textsuperscript{+}. In addition to this \( \Sigma_u \rightarrow \Sigma_g^+ \)-like transition, more allowed transitions with smaller transition energy are found in the Xe\textsubscript{3}\textsuperscript{+}X\textsubscript{n-3} clusters (Table 6).

In the symmetrical Xe\textsubscript{4}\textsuperscript{+} configuration III, there is threefold degenerate level with an energy of 1.20 eV above the ground state (and a transition moment of 2.7 D). In Xe\textsubscript{4}\textsuperscript{+}Xe and Xe\textsubscript{4}\textsuperscript{+}Xe\textsubscript{2}, two of the excited states remain degenerate with almost the same excitation energy as in Xe\textsubscript{4}\textsuperscript{+}, whereas the third state excitation energy is lowered by about 0.15 eV. The linear Xe\textsubscript{4}\textsuperscript{+} cluster has only one strong transition \( \Sigma_u \rightarrow \Sigma_g^+ \), whose energy is 1.46 eV, about 0.4 eV less than in Xe\textsubscript{3}\textsuperscript{+}Xe. The differences between the spectra of Xe\textsubscript{4}\textsuperscript{+} III (regular pyramid), Xe\textsubscript{3}\textsuperscript{+}Xe IV and Xe\textsubscript{4}\textsuperscript{+} V (linear) may help in the experimental search for the most stable Xe\textsubscript{4}\textsuperscript{+} cluster.
B. (XeH)\(^+\) Clusters

As in the case of the (Ar\(_n\))\(^+\) clusters, the (Xe\(_n\))\(^+\) clusters are formed by the (XeH)\(^+\) molecule which attracts more neutral Xe atoms. Since in the (XeH)\(^+\) molecule the Xe atom bears most of the charge, the neutral Xe atoms are located on the rare gas atom side of (XeH)\(^+\) (Fig. 4). The Xe(XeH)\(^+\) cluster is found to have a linear geometry with a Xe + (XeH) dissociation energy of 0.046 eV, which is much less than the Ar(ArH)\(^+\) dissociation energy (0.163 eV). The energy of the Xe detachment in the Xe\(_k\)(XeH)\(^+\) clusters varies in the interval 0.04-0.08 eV (Table 7). The charge of H in (XeH)\(^+\) slightly decreases when the number of attached neutral atoms increases. The spectrum of the Xe\(_k\)(XeH)\(^+\) clusters is practically the same as that of isolated (XeH)\(^+\).

C. (Xe\(_n\)H\(_2\))\(^+\) Clusters

The most stable (Xe\(_n\)H\(_2\))\(^+\) clusters are expected to be formed by charged Xe atoms and a neutral H\(_2\) molecule, since the H\(_2\) ionization potential is about 3.3 eV higher than that of Xe. The calculation of the simplest, (XeH\(_2\))\(^+\), system shows the existence of a strongly-bound cluster with the energy of the Xe\(^+\) + H\(_2\) dissociation of D = 0.456 eV. This cluster has a linear geometry with the Xe-H distance of 1.79 Å, 0.18 Å larger than in the (XeH)\(^+\) molecule, and the H-H distance of 0.81 Å, 0.07 Å larger than in H\(_2\) molecule (Fig. 4). Almost a whole charge is concentrated on the Xe atom (q = 0.955), but the valence bond between Xe\(^+\) and H\(_2\) is strong. The excitation energies for the allowed transitions (in the equilibrium configuration) are 10.76 eV and 18.56 eV, whereas in H\(_2\) there is one transition, 19.2 eV, and in (XeH)\(^+\) there are two transitions but with energies of 7.93 eV and 13.3 eV.

The structure of (Xe\(_n\)H\(_2\))\(^+\) clusters with more than one Xe atom is quite different from that of (XeH\(_2\))\(^+\) due to the formation of Xe\(_2^+\) or Xe\(_3^+\) molecules.
All \((\text{Xe}_n\text{H}_2)^+\) clusters that we have studied \((n > 1)\) have the structure \(\text{Xe}_n^+\text{H}_2\) with a practically neutral \(\text{H}_2\) molecule. In the most stable \(\text{Xe}_2^+\text{H}_2\) cluster, the axis of both molecules are perpendicular to one another (Fig. 4). The dissociation energy of this cluster is 0.084 eV. In the \(\text{Xe}_3^+\text{H}_2\) clusters three Xe atoms form, in contrast to the free \(\text{Xe}_3^+\) cluster, a triangular \(\text{Xe}_3^+\) system with Xe-Xe distances in the interval 3.50-3.58 Å. In one of the \(\text{Xe}_3^+\text{H}_2\) isomers with the \(\text{Xe}_3^+\text{H}_2 \rightarrow \text{Xe}_3^+ + \text{H}_2\) dissociation energy of \(D = 0.108\) eV, the \(\text{Xe}_3^+\) plane is perpendicular to the \(\text{H}_2\) axis with its center located on this axis at 3.08 Å from the \(\text{H}_2\) center. In another isomer \((D = 0.097\) eV), \(\text{H}_2\) is located in the \(\text{Xe}_3^+\) plane. In contrast to the \(\text{Xe}_k(\text{XeH})^+\) clusters, in \(\text{Xe}_n^+\text{H}_2\) clusters \((n \geq 2)\), the valence binding affects to a certain degree the cluster structure.

V. Conclusions

1. The semiempirical diatomics-in-molecules (DIIS) method\(^9\) proves to be an effective tool to treat rare gas \(R_n^+\) and rare gas-hydrogen \((\text{RH})^+\) ionic clusters. The DIIS results obtained for the triatomic \(\text{Ar}_3^+\) and \(\text{Xe}_3^+\) clusters are close to those obtained in other studies.

2. According to our calculation, there are two very different isomers of \(R_4^+\) clusters. One has the structure of a \(R_3^+\) ion and almost neutral \(R\) atom, whereas the other isomer has the symmetrical geometry of a regular pyramid with all four atoms bearing the same charge. We find the \(\text{Ar}_3^+\text{Ar}\) and the symmetrical \(\text{Xe}_4^+\) clusters to be the most stable isomers, so that \(\text{Ar}_n^+\) \((n = 4-6)\) and \(\text{Xe}_n^+\) \((n = 5,6)\) to have ionic cores \(\text{Ar}_3^+\) and \(\text{Xe}_4^+\), respectively. The experimentally detected transition from the \(\text{Ar}_3^+\) to \(\text{Ar}_2^+\) ionic core in large \((n \geq 15)\) \(\text{Ar}_n^+\) clusters results, most probably from the polarization energy increase.
3. The \((RnH)_n^+\) clusters have the structure of a \((RH)^+\) molecule and \(n-1\) neutral \(R\) atoms. The neutral rare gas atoms are located at the \(H\) side of the \((ArH)^+\) molecule in the \((ArH)^+Ar_{n-1}\) clusters and at the \(Xe\) side of the \((XeH)^+\) molecule in the \((XeH)^+Xe_{n-1}\) clusters.

4. In order to consider the \((RnH_2)_n^+\) clusters, we have modified the DIIS method by including into the DIIS wave function some DIM components which describe \(3\Sigma\) and \(3\Pi\) states of the \(R^+H\) fragments. We find that the \(Xe^+\) ion forms with \(H_2\) molecule a stable \((D_e = 0.46\) eV\) collinear cluster \((XeHH)^+\) with the strong contribution of valence forces. When more \(Xe\) atoms are involved, the cluster is formed by \(Xe^+_n(n > 1)\) ion and \(H_2\) molecule which are bound one to another by polarization forces only. In the case of \(Ar\) atoms, we do not find any stable ionic \((ArH_2)_n^+\) clusters. The quasistable clusters are formed by slightly-charged \(Ar\) atoms and \(H_2^+\) ionic molecule.

VI. Acknowledgments

This research was supported in part by the National Science Foundation under Grant CHE-8922288 and the Office of Naval Research. IL thanks the State University of New York at Buffalo for its hospitality in Summer 1989 when this research was initiated.

Appendix: Diatomic Potentials and Exchange Terms

The matrix elements within the DIIS method are expressed in terms of the potentials and exchange terms of diatomic fragments (see Sec. II). In the \(R_n^+\), \((R,H)^+\) and \((R,H_2)^+\) ionic clusters considered in this work, there are the following neutral and ionic diatomic fragments: \(R_2, H_2, RH, R_2^+, H_2^+\) and \((RH)^+\). The potentials of the neutral fragments, \(W_{ij}\), are used directly in the matrix elements expressions. The adiabatic potentials of the ionic fragments,
W\textsubscript{ij}, are needed for the calculations of the diabatic potentials U\textsubscript{ij} (see Eqs. (3), (4) and (29)). When the heteronuclear fragment (RH)	extsuperscript{+} is considered, one needs also the exchange term V which has to be defined independently from the potentials. The potentials are given in eV and the distances in Å.

**A. Neutral Fragments R\textsubscript{2}, H\textsubscript{2} and RH**

We need the following potentials of the neutral fragments: \textsuperscript{1}\Sigma\textsubscript{RR}, \textsuperscript{1}\Sigma\textsubscript{HH}, \textsuperscript{1}\Sigma\textsubscript{RH} and \textsuperscript{3}\Sigma\textsubscript{HH} (the last one is for (R\textsubscript{n}H\textsubscript{2})\textsuperscript{+} only). The R\textsubscript{2} potentials are taken as a sum of a repulsive exponential term and an attractive dispersion term,

\[ W_{\text{ArAr}}(\textsuperscript{1}\Sigma) = 6940 \exp[-3.6R] - 60/R^6 , \tag{A.1} \]

which provides the empirical\textsuperscript{68} values \( R_e = 3.76 \) Å and \( D_e = 0.012 \) eV and fits the \textit{ab initio} potential\textsuperscript{69} at small R, and

\[ W_{\text{XeXe}}(\textsuperscript{1}\Sigma) = 24000 \exp[-3.17R] - 320/R^6 , \tag{A.2} \]

which provides the empirical\textsuperscript{70} values \( R_e = 4.47 \) Å and \( D_e = 0.023 \) eV and fits the \textit{ab initio} potential\textsuperscript{71} at small R.

The ground-state H\textsubscript{2} potential is described by a modified (for large R) Morse function,\textsuperscript{58}

\[ W_{\text{HH}}(\textsuperscript{1}\Sigma) = 4.746 G(G-2)g \tag{A.3} \]

\[ G = \exp[-a(R-R_e)] \tag{A.4} \]

\[ g = \exp[-b(R-R_e)^3] . \tag{A.5} \]
In Eqs. (A.4) and (A.5), \( R_e = 0.7417 \text{ Å} \), and the parameters \( a = 1.9446 \text{ Å}^{-1} \) and \( b = 0.1215 \text{ Å}^{-3} \) are found by fitting the exact \( \text{H}_2 \) potential. The accuracy of the fit is generally within 0.05 eV for \( R > 0.53 \text{ Å} \). The repulsive \( ^3\Sigma \) potential of \( \text{H}_2 \) is described by an anti-Morse function,

\[
W_{\text{HH}}(\Sigma) = 1.963 \ G(G-2)G \text{,} \tag{A.6}
\]

where the G-function parameter is \( a = 1.805 \text{ Å}^{-1} \) and the g-function parameter is \( b = 0.1215 \text{ Å}^{-3} \). The potential (A.6) fits the exact potential.

The RH potential is described by a Lennard-Jones potential with the empirical parameters for \( \text{ArH} \) of \( R_e = 3.62 \text{ Å} \) and \( D_e = 4.15 \text{ meV} \) and for \( \text{XeH} \) of \( R_e = 3.93 \text{ Å} \) and \( D_e = 6.85 \text{ meV} \).

\[
W_{\text{ArH}}(\Sigma) = 0.0166(\frac{3.22}{R})^{12} - (\frac{3.22}{R})^{6} \tag{A.7}
\]

\[
W_{\text{XeH}}(\Sigma) = 0.0274(\frac{3.5}{R})^{12} - (\frac{3.5}{R})^{6} \tag{A.8}
\]

### B. Ionic Homonuclear Fragments \( R_2^+ \) and \( H_2^+ \)

We need the following adiabatic potentials of the ionic homonuclear fragments: \( ^2\Sigma_u^+ \), \( ^2\Sigma_g^+ \), \( ^2\Pi_u \) for \( R_2^+ \) and \( \sigma_g \), \( \sigma_u \) for \( H_2^+ \). The attractive \( ^2\Sigma_u^+ \) and \( ^2\Pi_g \) potentials of \( R_2^+ \) are described as a sum of Morse function and the polarization term \( P \). For argon these are expressed as

\[
W_{(\text{ArAr})}(^2\Sigma_u^+) = 1.184 \ G(G-2) + P_{\text{Ar}} \text{,} \quad R_e = 2.48 \text{,} \quad a = 2.0 \tag{A.9}
\]

\[
W_{(\text{ArAr})}(^2\Pi_g) = 0.025 \ G(G-2) + P_{\text{Ar}} \text{,} \quad R_e = 3.2 \text{,} \quad a = 2.3 \tag{A.10}
\]
\[ P_{Ar} = -11.7\left(1 + \left(\frac{2.8}{R}\right)^{12}\right)^{1/3}/R^4, \]  
(A.11)

where \( R_e \) and \( a \) in (A.9) and (A.10) are the parameters of the G-function (A.4), and the number 3.8 in (A.11) is twice the radius of the Ar atom. We assume the \( \text{Ar}^+ \) radius to be equal to the neutral Ar radius \( r_{Ar} = 1.9 \) Å. For xenon we have

\[ W_{(\text{XeXe})}^{(+\Sigma_u)} = 1.0 \, G(G-2) + P_{\text{Xe}} , \quad R_e = 3.22 , \quad a = 155 \]  
(A.12)

\[ W_{(\text{XeXe})}^{(+\Pi_g)} = 0.01 \, G(G-2) + P_{\text{Xe}} , \quad R_e = 3.8 , \quad a = 3.0 \]  
(A.13)

\[ P_{\text{Xe}} = -2.91\left(1 + \left(\frac{4.4}{R}\right)^{12}\right)^{1/3}/R^4. \]  
(A.14)

The Xe and \( \text{Xe}^+ \) radii are both taken as equal to \( r_{\text{Xe}} = 2.2 \) Å, so that twice the double radius in (A.14) is 4.4 Å.

The repulsive potentials of \( \text{R}_2^+ \) are described by a sum of a polarization term \( P \) and anti-Morse function for the \( \Sigma_g \) state or exponential function for the \( \Pi_u \) state:

\[ W_{(\text{ArAr})}^{(+\Sigma_g)} = 0.9 \, G(G+2) + P_{\text{Ar}} , \quad R_e = 2.48 , \quad a = 1.72 \]  
(A.15)

\[ W_{(\text{ArAr})}^{(+\Pi_u)} = 1290 \exp[-2.8R] + P_{\text{Ar}} \]  
(A.16)

\[ W_{(\text{XeXe})}^{(+\Sigma_g)} = 0.78 \, G(G+2) + P_{\text{Xe}} , \quad R_e = 3.22 , \quad a = 1.45 \]  
(A.17)

\[ W_{(\text{XeXe})}^{(+\Pi_u)} = 6.910 \exp[-2.75R] + P_{\text{Xe}} \]  
(A.18)
The ground-state potentials (A.9) and (A.12) provide the empirical dissociation energies\(^75\) of \(D_e = 1.24\) eV for \(Ar_2^+\) and \(D_e = 1.08\) eV for \(Xe_2^+\). The excited-state potentials (A.10), (A.13) and (A.15)-(A.18) fit the \textit{ab initio} potentials of Ref. 75.

The exact ground-state potential \(\sigma_g\) of the \(H_2^+\) molecular ion\(^76\) has been fit by a Morse function in Ref. 77 (there is a misprint in Ref. 77 on p. 17: \(a = 0.6678\) should be \(a = 0.678\)). In order to improve the fitting at small \(R\), we have added a repulsive exponential component to the Morse function. At large \(R\), the fitting is improved by the \(g\)-function (A.5),

\[
W^{\sigma_g} = 810.7 \exp[-11.34R] + 2.795 G(G-2)g
\]

with the following parameters for the \(g\)- and \(G\)-functions: \(R_e = 1.054\) Å, \(a = 1.281\) Å, \(b = 0.0067\) Å\(^3\). The accuracy of the fit is within 0.015 eV for \(R > 0.74\) Å. The equilibrium distance of the potential (A.19) is 1.06 Å, slightly larger than the parameter \(R_e\) for the \(G\)- and \(g\)-functions. The dissociation energy of the potential (A.19) is \(D_e = 2.79\) eV. The excited \(\sigma_u\) potential\(^76\) is fit by an anti-Morse potential,

\[
W^{\sigma_u} = 3.014 G(G+2)g, \quad R_e = 1.054, \quad a = 1.379, \quad b = 0.0067
\]

The polarization component of the potentials (A.19) and (A.20) is

\[
P_H = -4.8[1 + \left(\frac{12}{R}\right)^{12}]^{-1/3}/R^4
\]
where 1.7 is the H radius.

C. Ionic Heteronuclear Fragment \((RH)^+\)

In order to find from Eq. (4) or (29) the \((RH)^+\) diabatic \(\Sigma\) potentials \(U\), one needs three adiabatic potentials, namely \(1\Sigma\) and \(3\Sigma\) asymptotic to \(R^+ + H\) and \(1\Sigma\) asymptotic to \(R + H^+\). The adiabatic potentials are described as a sum of an attractive (Morse) or repulsive (anti-Morse or exponential) potential and the polarization term \(P\). The adiabatic \(\Sigma\) potentials of \((ArH)^+\) are expressed as follows:

\[
W_{(ArH)}^{+\, 1\Sigma} = 3.157 \, G(G-2) + P_{Ar} \quad , \quad R_e = 1.266 , \quad a = 1.94 \quad (A.22)
\]

\[
W_{(ArH)}^{+\, 3\Sigma} = 2.75 \, G(G+2) + P_{H} + 2.16 \quad , \quad R_e = 1.266 , \quad a = 1.2 \quad (A.23)
\]

\[
W_{(ArH)}^{+\, 3\Sigma} = 600 \, \exp [-1.8R] + P_{H} + 2.16 \quad (A.24)
\]

\[
P_{Ar} = 11.7[1 + \left(\frac{1.9}{R}\right)^{12}]^{-1/3}/R^4 \quad (A.25)
\]

\[
P_{H} = 4.8[1 + \left(\frac{3.6}{R}\right)^{12}]^{-1/3}/R^4 \quad (A.26)
\]

In (A.22) and (A.23), \(R_e\) and \(a\) are the parameters for the G-function (A.4), and in (A.23) and (A.24) the number 2.16 presents the difference between the ionization potentials of Ar and H. In the polarization terms (A.25) and (A.26), 1.9 is the Ar radius and 3.6 is the sum of the Ar and H radii. The ground-state \((ArH)^+\) equilibrium distance \(R_e = 1.266\) Å in the potential (A.22) is equal to the experimental value.\(^{78,79}\) This potential provides the ab
initio dissociation energy \( D_e = 4.055 \text{ eV} \). The \textit{ab initio} ground-state potential of Ref. 80 is used to find the parameter \( a \) of (A.22). The excited-state potentials (A.23) and (A.24) are found by fitting the \textit{ab initio} potentials of Ref. 81. The (ArH)\(^+\) exchange term \( V \) is found from Eq. (4) by fitting the \textit{ab initio} dipole moment, \( 80 \) which is close to the experimental value \( 81 \) at the equilibrium point,

\[
V = -95.5 \, R^2 \exp[-2.42R] \quad (A.27)
\]

The adiabatic \( \Sigma \) potentials of \((\text{XeH})^+\) are as follows:

\[
W(\text{XeH})^+ (^1\Sigma) = 4.03 \, G(G-2) + P_H \quad , \quad R_e = 1.61 \quad , \quad a = 1.56 \quad (A.28)
\]

\[
W(\text{XeH})^+ (^1\Sigma) = 73 \exp[-1.3R] + P_{\text{Xe}} + 1.47 \quad (A.29)
\]

\[
W(\text{XeH})^+ (^3\Sigma) = 1.3 \, G(G+2) + P_H \quad , \quad R_e = 1.61 \quad , \quad a = 1.56 \quad (A.30)
\]

\[
P_H = -4.8[1 + \left(\frac{2.8}{R}\right)^{12}]^{-1/3} / R^4 \quad (A.31)
\]

\[
P_{\text{Xe}} = -2.91[1 + \left(\frac{2.2}{R}\right)^{12}]^{-1/3} / R^4 \quad . \quad (A.32)
\]

In (A.29), 1.47 presents the difference between the ionization potentials of \( H \) and \( \text{Xe} \). In the polarization terms (A.31) and (A.32), 3.9 is the sum of the \( \text{Xe} \) and \( H \) radii and 2.2 is the \( \text{Xe} \) radius. The ground-state \((\text{XeH})^+\) equilibrium distance \( R_e = 1.61 \, \text{Å} \) in the potential (A.28) is equal to the experimental value. \( 82 \) The potential (A.28) provides the \textit{ab initio} \( 83 \) dissociation energy \( D_e = 4.05 \text{ eV} \), a value close to the experimental dissociation energy of \( D_e = 3.8 \) eV. \( 84 \) The parameter \( a \) of (A.28) is found by fitting the \textit{ab initio} potential of Ref. 83. The excited-state potentials (A.29) and (A.30) are found by
fitting the ab initio potentials of Ref. 85. The \((\text{XeH})^+\) exchange term \(V\) is found from Eq. (4) by fitting the ab initio dipole moment, \(^{83}\)

\[
V = -57.7 \ R^2 \ \text{exp}[-2.0 \ R] \quad .
\] (A.33)

The \(\Pi\) potentials of \((\text{ArH})^+\) are obtained by fitting the ab initio potentials of Ref. 81,

\[
W_{(\text{ArH})^+}^{(1\Pi)} = 423 \ \text{exp}[-3.9R] + P_H + 2.16 \quad .
\] (A.34)

\[
W_{(\text{ArH})^+}^{(3\Pi)} = 90 \ \text{exp}[-1.2R] + P_H + 2.16 \quad ,
\] (A.35)

where \(P_H\) is given by (A.26). The \(\Pi\) potentials of \((\text{XeH})^+\) are obtained by fitting the ab initio potentials of Ref. 85,

\[
W_{(\text{XeH})^+}^{(1\Pi)} = 370 \ \text{exp}[-2.74R] + P_H \quad .
\] (A.36)

\[
W_{(\text{XeH})^+}^{(3\Pi)} = 430 \ \text{exp}[-2.74R] + P_H \quad ,
\] (A.37)

where \(P_H\) is given by (A.31).
References


Table 1. Structure of the ionic clusters $\text{Ar}_n^+$ and ionic molecule $\text{Ar}_2^+$. The distances (R) are in Å, and the energies (E,D) in eV.

<table>
<thead>
<tr>
<th>N</th>
<th>$\text{Ar}_n^+$</th>
<th>Structure 1)</th>
<th>R 2)</th>
<th>R 3)</th>
<th>q 4)</th>
<th>E</th>
<th>Dissociation Products</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\text{Ar}_2^+$</td>
<td></td>
<td>2.48</td>
<td></td>
<td></td>
<td>-1.240</td>
<td>$\text{Ar}^+ + \text{Ar}$</td>
<td>1.240</td>
</tr>
<tr>
<td>II</td>
<td>$\text{Ar}_3^+$</td>
<td>linear</td>
<td>2.59</td>
<td></td>
<td></td>
<td>-1.443</td>
<td>$\text{Ar}_2^+ + \text{Ar}$</td>
<td>0.203</td>
</tr>
<tr>
<td>III</td>
<td>$\text{Ar}_4^+$</td>
<td>$(\text{Ar}_3^+)<em>z(\text{Ar})</em>{xz}$</td>
<td>2.59</td>
<td>3.68</td>
<td>0.002</td>
<td>-1.490</td>
<td>$\text{Ar}_3^+ + \text{Ar}$</td>
<td>0.047</td>
</tr>
<tr>
<td>IV</td>
<td>$\text{Ar}_4^+$</td>
<td>regular pyramid</td>
<td>2.836</td>
<td></td>
<td></td>
<td>-1.480</td>
<td>$\text{Ar}_2^+ + 2\text{Ar}$</td>
<td>0.240</td>
</tr>
<tr>
<td>V</td>
<td>$\text{Ar}_4^+$</td>
<td>linear</td>
<td>2.59</td>
<td>3.3</td>
<td>0.01</td>
<td>-1.474</td>
<td>$\text{Ar}_3^+ + \text{Ar}$</td>
<td>0.031</td>
</tr>
<tr>
<td>VI</td>
<td>$\text{Ar}_5^+$</td>
<td>$(\text{Ar}_3^+)_z(\text{Ar}<em>2)</em>{xy}$</td>
<td>2.59</td>
<td>3.68</td>
<td>0</td>
<td>-1.540</td>
<td>$(\text{Ar}<em>4^+)</em>\text{III} + \text{Ar}$</td>
<td>0.050</td>
</tr>
<tr>
<td>VII</td>
<td>$\text{Ar}_5^+$</td>
<td>$(\text{Ar}_3^+)_z(\text{Ar}<em>2)</em>{xz}$</td>
<td>2.59</td>
<td>3.61</td>
<td>0.002</td>
<td>-1.540</td>
<td>$(\text{Ar}<em>4^+)</em>\text{III} + \text{Ar}$</td>
<td>0.050</td>
</tr>
<tr>
<td>VIII</td>
<td>$\text{Ar}_5^+$</td>
<td>$(\text{Ar}_3^+)_z(\text{Ar}<em>2)</em>{xz}$</td>
<td>2.59</td>
<td>3.68</td>
<td>0.003</td>
<td>-1.537</td>
<td>$(\text{Ar}<em>4^+)</em>\text{III} + \text{Ar}$</td>
<td>0.047</td>
</tr>
<tr>
<td>IX</td>
<td>$\text{Ar}_6^+$</td>
<td>$(\text{Ar}_3^+)_z(\text{Ar}<em>2)</em>{xy}(\text{Ar})_x$</td>
<td>2.59</td>
<td>3.61</td>
<td>0.001</td>
<td>-1.601</td>
<td>$(\text{Ar}<em>5^+)</em>\text{VI} + \text{Ar}$</td>
<td>0.061</td>
</tr>
</tbody>
</table>

1) The subscripts $z$, $xz$, etc. denote the location along an axis or in a plane (see Fig. 1.II-V).

2) Distance between adjacent charged atoms.

3) Distance from a neutral or weakly-charged atom to the nearest charged atom.

4) Common charge of all weakly-charged atoms.
Table 2. Transition energy $T$ in eV and transition moment $\mu$ in Debyes of the allowed transitions in $\text{Ar}_{2}^{+}$ and $\text{Ar}_{4}^{+}$. $q$ is the charge distribution in the excited states.

<table>
<thead>
<tr>
<th>N</th>
<th>$\text{Ar}_{n}^{+}$</th>
<th>$T$</th>
<th>$D$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>$\text{Ar}_{3}^{+}$</td>
<td>2.26</td>
<td>8.8</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>$\text{Ar}_{3}^{+}\text{Ar}$</td>
<td>2.24</td>
<td>8.8</td>
<td>0.30</td>
<td>0.01</td>
<td>0.34</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.19</td>
<td>6.8</td>
<td>0.10</td>
<td>0.04</td>
<td>0.24</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.79</td>
<td>6.8</td>
<td>0.27</td>
<td>0.37</td>
<td>0.15</td>
<td>0.21</td>
</tr>
<tr>
<td>V</td>
<td>$\text{Ar}_{4}^{+}$ linear</td>
<td>1.97</td>
<td>8.2</td>
<td>0.24</td>
<td>0.01</td>
<td>0.26</td>
<td>0.49</td>
</tr>
<tr>
<td>IV</td>
<td>$\text{Ar}_{4}^{+}$ pyramid</td>
<td>1.46</td>
<td>2.1</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.46</td>
<td>2.1</td>
<td>0.30</td>
<td>0.30</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.46</td>
<td>2.1</td>
<td>0.20</td>
<td>0.20</td>
<td>0.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>

1) For $N$, see Table 1.
Table 3. Structure of the ionic clusters $\text{Ar}_k(\text{ArH})^+$ and ionic molecule $(\text{ArH})^+$. The distances $(R)$ are in Å, the energies $(E)$ in eV and the dipole moment $(\mu)$ in Debyes.

$$
\begin{array}{cccccc}
\text{Ar}_k(\text{ArH})^+ & q_H^{1)} & R_{\text{Ar-H}}^{2)} & R_{\text{Ar-Ar}}^{2)} & \mu & E \\
(\text{ArH})^+ & 0.569 & 2.78 & -4.055 \\
\text{Ar}(\text{ArH})^+ & 0.579 & 2.81 & 3.70 & 5.98 & -4.218 & 0.163 \\
\text{Ar}_2(\text{ArH})^+ & 0.591 & 2.79 & 3.81 & 6.32 & -4.395 & 0.177 \\
\text{Ar}_3(\text{ArH})^+ & 0.601 & 2.79 & 3.72 & 6.23 & -4.586 & 0.191 \\
\text{Ar}_4(\text{ArH})^+ & 0.609 & 2.84 & 3.57 & 4.94 & -4.760 & 0.174 \\
\text{Ar}_6(\text{ArH})^+ & 0.614 & 2.84 & 3.17 & 3.87 & 3.38 & 3.33 & -4.947 & 0.094 \\
\end{array}
$$

1) Charge of the H atom in $(\text{ArH})^+$

2) $R_{\text{Ar-H}}$ and $R_{\text{Ar-Ar}}$ are the distances from the neutral atom to H and Ar of $(\text{ArH})^+$, respectively. For $\text{Ar}_6(\text{ArH})^+$ there are two different Ar-H and Ar-Ar distances.
Table 4. Structure of the ionic clusters $\text{Ar}_n\text{H}_2^+$ and ionic molecule $\text{H}_2^+$. The distances (R) are in Å, the energies in eV and the dipole moments ($\mu$) in Debyes.

<table>
<thead>
<tr>
<th>$\text{Ar}_n\text{H}_2^+$</th>
<th>$q_{\text{H}_2^+}$</th>
<th>$R_{\text{H-H}}$</th>
<th>$R_{\text{Ar}}$</th>
<th>$\mu$</th>
<th>$E$</th>
<th>$\text{Ar}^-$ Detachment</th>
<th>$T$</th>
<th>$\mu$</th>
<th>$T$</th>
<th>$\mu$</th>
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<tbody>
<tr>
<td>$\text{H}_2^+$</td>
<td>1.0</td>
<td>1.06</td>
<td>0</td>
<td>-2.790</td>
<td>11.8</td>
<td>2.5</td>
<td></td>
<td></td>
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<tr>
<td>$\text{ArH}_2^+$</td>
<td>0.98</td>
<td>1.05</td>
<td>2.935</td>
<td>12.3</td>
<td>-2.983</td>
<td>0.193</td>
<td>5.65</td>
<td>1.9</td>
<td></td>
<td></td>
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<tr>
<td>$\text{Ar}_2\text{H}_2^+$</td>
<td>0.964</td>
<td>1.05</td>
<td>2.94</td>
<td>9.02</td>
<td>-3.183</td>
<td>0.200</td>
<td>5.83</td>
<td>2.0</td>
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<tr>
<td>$\text{Ar}_3\text{H}_2^+$</td>
<td>0.95</td>
<td>1.04</td>
<td>2.95</td>
<td>5.15</td>
<td>-3.377</td>
<td>0.194</td>
<td>5.58</td>
<td>0.8</td>
<td>5.89</td>
<td>2.3</td>
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<td>$\text{Ar}_4\text{H}_2^+$</td>
<td>0.936</td>
<td>1.03</td>
<td>2.955</td>
<td>1.65</td>
<td>-3.568</td>
<td>0.191</td>
<td>5.71</td>
<td>0.9</td>
<td>5.94</td>
<td>2.5</td>
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<td>$\text{Ar}_5\text{H}_2^+$</td>
<td>0.926</td>
<td>1.03</td>
<td>2.995</td>
<td>0</td>
<td>-3.754</td>
<td>0.186</td>
<td>5.44</td>
<td>1.7</td>
<td>5.92</td>
<td>2.2</td>
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1) Distance from the Ar atoms to the center of $\text{H}_2^+$. The adjacent Ar atoms are separated by 3.7 Å ($n = 2-4$) and 3.52 Å in symmetrical $\text{Ar}_5\text{H}_2^+$. 
Table 5. Structure of the ionic clusters $\text{Xe}_n^+$ and ionic molecule $\text{Xe}_2^+$. (See Table 1 for the footnotes.)

<table>
<thead>
<tr>
<th>N</th>
<th>$\text{Xe}_n^+$ structure</th>
<th>$R_{1}$</th>
<th>$R_{2}$</th>
<th>$q_{4}$</th>
<th>$E$</th>
<th>Dissociation Products</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\text{Xe}_2^+$</td>
<td>3.22</td>
<td>-1.08</td>
<td></td>
<td></td>
<td>$\text{Xe}_2^+ + \text{Xe}$</td>
<td>1.08</td>
</tr>
<tr>
<td>II</td>
<td>$\text{Xe}_3^+$ linear</td>
<td>3.383</td>
<td>-1.277</td>
<td></td>
<td></td>
<td>$\text{Xe}_2^+ + \text{Xe}$</td>
<td>0.197</td>
</tr>
<tr>
<td>III</td>
<td>$\text{Xe}_4^+$ regular pyramid</td>
<td>3.646</td>
<td>-1.480</td>
<td></td>
<td></td>
<td>$\text{Xe}_2^+ + 2\text{Xe}$</td>
<td>0.40</td>
</tr>
<tr>
<td>IV</td>
<td>$\text{Xe}_4^+$ $\text{(Xe}_3^+\text{)}<em>2\text{(Xe)}</em>{xz}$</td>
<td>3.384</td>
<td>4.19</td>
<td>0.014</td>
<td>-1.356</td>
<td>$\text{Xe}_3^+ + \text{Xe}$</td>
<td>0.079</td>
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<tr>
<td>V</td>
<td>$\text{Xe}_4^+$ linear</td>
<td>3.315</td>
<td>3.65</td>
<td>0.184</td>
<td>-1.346</td>
<td>$\text{Xe}_3^+ + \text{Xe}$</td>
<td>0.069</td>
</tr>
<tr>
<td>VI</td>
<td>$\text{Xe}_5^+$ $\text{(Xe}_4^+\text{)}<em>3\text{(Xe)}</em>{xz}$</td>
<td>3.646</td>
<td>4.40</td>
<td>0.001</td>
<td>-1.568</td>
<td>$\text{Xe}_4^+ + \text{Xe}$</td>
<td>0.088</td>
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<tr>
<td>VII</td>
<td>$\text{Xe}_5^+$ $\text{(Xe}_3^+\text{)}<em>2\text{(Xe)}</em>{xz}$</td>
<td>3.383</td>
<td>4.24</td>
<td>0.005</td>
<td>-1.439</td>
<td>$\text{Xe}_3^+\text{Xe} + \text{Xe}$</td>
<td>0.083</td>
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<tr>
<td>VIII</td>
<td>$\text{Xe}_6^+$ $\text{(Xe}_4^+\text{)}_3\text{Xe}_2$</td>
<td>3.644</td>
<td>4.40</td>
<td>0</td>
<td>-1.637</td>
<td>$\text{Xe}_4^+\text{Xe} + \text{Xe}$</td>
<td>0.069</td>
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<tr>
<td>IX</td>
<td>$\text{Xe}_6^+$ $\text{(Xe}_3^+\text{)}<em>2\text{(Xe)}</em>{xz}$</td>
<td>3.375</td>
<td>4.20</td>
<td>0.021</td>
<td>-1.547</td>
<td>$\text{Xe}_3^+\text{Xe}_2 + \text{Xe}$</td>
<td>0.108</td>
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Table 6. Transition energies $T$ (eV) and moments $\mu$(D) of the $Xe_3^+Xe_k$ allowed transitions.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$Xe_3^+Xe_k$</th>
<th>$T$</th>
<th>$\mu$</th>
<th>$T$</th>
<th>$\mu$</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>$Xe_3^+$</td>
<td>1.87</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>IV</td>
<td>$Xe_3^+Xe$</td>
<td>1.86</td>
<td>8.3</td>
<td>1.66</td>
<td>3.6</td>
<td>1.17 1.7</td>
</tr>
<tr>
<td>VII</td>
<td>$Xe_3^+Xe_2$</td>
<td>1.86</td>
<td>11</td>
<td></td>
<td></td>
<td>1.15 1.7</td>
</tr>
<tr>
<td>IX</td>
<td>$Xe_3^+Xe_3$</td>
<td>1.88</td>
<td>7.9</td>
<td>1.82</td>
<td>4.5</td>
<td>1.23 1.6</td>
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</tbody>
</table>

1) For $N$, see Table 6.
Table 7. Structure of the ionic clusters $\text{Xe}_k(\text{XeH})^+$ and ionic molecule $(\text{XeH})^+$.

<table>
<thead>
<tr>
<th>$\text{Xe}_k(\text{XeH})^+$</th>
<th>$q_\text{H}$</th>
<th>$R_{\text{Xe-H}}$</th>
<th>$R_{\text{Xe-Xe}^+}$</th>
<th>$\mu$</th>
<th>$E$</th>
<th>Xe Detachment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{XeH})^+$</td>
<td>0.282</td>
<td></td>
<td></td>
<td>1.54</td>
<td>-4.050</td>
<td></td>
</tr>
<tr>
<td>$\text{Xe}(\text{XeH})^+$</td>
<td>0.280</td>
<td>6.07</td>
<td>4.46</td>
<td>11.5</td>
<td>-4.096</td>
<td>0.046</td>
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<tr>
<td>$\text{Xe}_2(\text{XeH})^+$</td>
<td>0.279</td>
<td>5.95</td>
<td>4.50</td>
<td>12.7</td>
<td>-4.156</td>
<td>0.060</td>
</tr>
<tr>
<td>$\text{Xe}_3(\text{XeH})^+$</td>
<td>0.278</td>
<td>5.96</td>
<td>4.56</td>
<td>13.3</td>
<td>-4.235</td>
<td>0.079</td>
</tr>
<tr>
<td>$\text{Xe}_4(\text{XeH})^+$</td>
<td>0.277</td>
<td>5.91</td>
<td>4.62</td>
<td>12.4</td>
<td>-4.297</td>
<td>0.062</td>
</tr>
<tr>
<td>$\text{Xe}_5(\text{XeH})^+$</td>
<td>0.275</td>
<td>5.73</td>
<td>4.85</td>
<td>10.7</td>
<td>-4.372</td>
<td>0.038</td>
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</table>

1) Charge of the H atom in $(\text{XeH})^+$.

2) $R_{\text{Xe-H}}$ and $R_{\text{Xe-Xe}^+}$ are the distances from the neutral atom to H and Xe of $(\text{XeH})^+$, respectively.
Figure Captions

Fig. 1. $\text{Ar}_3^+$ and $\text{Ar}_4^+$ geometry. The Roman numerals indicate the clusters (the same as in Table 1). The numbers without a sign are distances in Å, and the numbers with the + sign are the atomic charges.

Fig. 2. Geometry of the ionic clusters $\text{Ar}(\text{ArH})^+$, $\text{Ar}_2(\text{ArH})^+$ and $\text{ArH}_2^+$. For notations, see Fig. 1.

Fig. 3. Geometry of $\text{Xe}_3^+$ and $\text{Xe}_4^+$. For notations, see Fig. 1. The Roman numerals indicate the clusters (see Table 5).

Fig. 4. Geometry of the ionic clusters $\text{Xe}(\text{XeH})^+$, $\text{Xe}_2(\text{XeH})^+$, $(\text{XeH}_2)^+$ and $\text{Xe}_2^+\text{H}_2$. For notations, see Figs. 1 and 3.
\[ \text{Xe}_3^{+}, \text{II} \quad \text{Xe}_4^{+}, \text{IV} \quad \text{Xe}_4^{+}, \text{V} \]

\[ \begin{align*}
\text{z} & : +0.25 \\
3.383 & \\
\text{z} & : +0.5 \\
3.383 & \\
\text{z} & : +0.25 \\
3.383 & \\
\text{x} & : +0.251 \\
3.384 & \\
\text{z} & : +0.495 \\
3.384 & \\
\text{z} & : +0.24 \\
3.383 & \\
\text{z} & : +0.092 \\
3.653 & \\
\text{x} & : +0.408 \\
3.653 & \\
\text{x} & : +0.092 \\
3.653 & \\
\end{align*} \]
Fig. 4

$\text{Xe} (\text{XeH})^+$

$\text{Xe}_2 (\text{XeH})^+$

$(\text{XeH}_2)^+$

$\text{Xe}^+ \text{H}_2$

- $\text{H}$
- $\text{Xe}$
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