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Theory of the electron affinity of clusters of rare-gas atoms

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The electron affinity of small clusters of rare-gas atoms like Ar_n, Kr_n, and Xe_n is calculated using a dielectric continuum model. Thus, we obtain for Xe_n a positive electron affinity for approximately $n > 10$. For small clusters ($n \simeq 12$) the excess electron is only weakly bound in a diffuse orbital. For larger clusters ($n > 25$) we conclude that $\mathrm{Xe}_n{}^-$ is very stable. The clusters $\mathrm{Kr}_n{}^-$ and $\mathrm{Ar}_n{}^-$ are strongly stable only when they are much larger ($n > 100$).

A single rare-gas atom has no electron affinity because of its closed electronic shell. Liquid Ar, Kr, and Xe can solvate excess electrons in a delocalized quasifree state.[1] These electrons have a high mobility.[2,3] The attractive interaction between the solvated electron and the rare-gas atoms arises from the induced polarization of the atoms and is stronger than the effect of the repulsive short-range interaction. Thus the energy of the electron is lower than in the vacuum. In view of this, one expects a transition from zero or no electron affinity for small clusters to a positive electron affinity for large clusters. In the following, the size dependence of the electron affinity and the localization of the excess electron in rare-gas atom clusters is studied in detail. Note that so far this problem has not been studied very much experimentally. Haberland *et al.*[4] have tried to produce and detect $\mathrm{Xe}_n{}^-$ clusters for $n < 13$, but without success. Theoretical studies by Thirumalai[5] use a statistical superposition of electron-atom interaction potentials to obtain a rough estimate of $n \simeq 50$ for the smallest sizes of stable Xe_n^-. This is a rough upper limit and it is important to improve this estimate. Another study by Antoniewicz *et al.*[6] shows that large dielectric spheres could bind electrons at their surface. However, no attempt was made to study the electron affinity of clusters or rare-gas atoms and the localization of the excess electron inside these clusters.

We thus proceed as follows. The quasifree electrons in liquid rare gas form a band. The energy V_0 of the bottom of this band determines the solvation energy; thus if $V_0 < 0$ the liquid has a positive electron affinity and if $V_0 > 0$ then there is no electron affinity. This energy V_0 has been determined from the photoelectric effect with photoelectron emission into the liquid.[2,3] It is convenient to divide V_0 into three distinct parts,[1] $V_0 = V_R + V_{PN} + V_{PF}$. The interaction V_R with the repulsive Hartree-Fock pseudopotential of the electrons of the rare-gas atoms[1] increases the energy of the quasifree electron. The attractive polarization interaction between the electron and the rare-gas atoms is much faster than the movement of the excess electron and essentially instantaneous. $V_{PN}(\mathbf{r})$ is the potential energy due to this interaction with the atoms which are in the immediate vicinity of the position $\mathbf{r}$ of the electron. $V_{PF}(\mathbf{r})$ is the potential energy due to the atoms which are farther away from $\mathbf{r}$ and not included in V_{PN}. Note the important difference to clusters of polar molecules such as $(\mathrm{NH}_3)_n$ with a polarization interaction which is much slower than the excess electron.[7] Approximately, the contributions V_R and V_{PH} should be the same in the liquid and in the cluster because of their short range. Note that[1] $V_R + V_{PN} > 0$ and that without $V_{PF} < 0$ the energy of the solvated electrons in the liquid would be positive. Thus V_{PF}, which obviously depends strongly on the cluster size, determines the electron affinity together with the size-dependent kinetic energy of the excess electron. For V_{PF} one can use a simple dielectric-continuum model because the Lorentz relation is a good approximation for the local electric field in liquid rare gases.[1] The effective dielectric constant ϵ_L is obtained from the Clausius-Mossotti relation[8] and given by

$$\epsilon_L = 1 + 3\alpha/(R_{\mathrm{WS}}^3 - \alpha) , \tag{1}$$

where α is the electric dipole polarizability of the atoms and R_{WS} is the radius of a sphere of the atomic volume (Wigner-Seitz radius). The density of the atoms is $\rho = (\frac{4}{3}\pi R_{WS}^3)^{-1}$.

To calculate the electron affinity of a cluster of n rare-gas atoms X_n we approximate the cluster by a sphere of radius $R = n^{1/3} R_{\mathrm{WS}}$. It is now easy to obtain a rough estimate of the minimum size required such that the negatively charged cluster $X_n{}^-$ is stable. We assume that the electron is localized inside the cluster. It should have a high mobility as in the liquid gas.[2,3] Thus we may use the approximate wave function

$$\psi(\mathbf{r}) = |\mathbf{r}|^{-1} \sin(\pi |\mathbf{r}| / R)$$

for the electron. The kinetic energy of the electron is increased by $\Delta E_{\mathrm{kin}} = \hbar^2 \pi^2 R^{-2}/2m$ as compared to the case where the electron is in an infinitely large liquid. Similarly, the attractive polarization interaction V_{PF} is reduced in smaller clusters because there are less atoms, which can be polarized. The energy density of a dielectric in an electric field $\mathbf{E}_0$ with fixed sources is[8] $w = -\frac{1}{2}\mathbf{P}\cdot\mathbf{E}_0$ where $\mathbf{P}$ is the induced polarization. For an electron at the center of a sphere of radius R and dielectric constant ϵ_L we obtain thus the total dielectric energy $W(R) = W_\infty + (1 - \epsilon_L^{-1}) e^2 R^{-1}/2$, where W_∞ is the energy for the infinitely large ($R=\infty$) sphere. Thus the potential energy $V_{PF}\simeq W(R)$ is increased by $\Delta E_{\text{pot}}=(1-\epsilon_L^{-1})e^2R^{-1}/2$ and we obtain an estimate for the energy E of the electron,

$$E(R)\simeq V_0+\frac{\hbar^2}{2m}\frac{\pi^2}{R^2}+\frac{1-\epsilon_L^{-1}}{2}\frac{e^2}{R}\ . \tag{2}$$

Using data on liquid rare gases (Table I) we estimate the critical number of atoms for which an excess electron can be bound inside the cluster from $E(n_e^{1/3}R_{\text{WS}})=0$. We obtain for n_e the following values: 820 for Ar, 210 for Kr, and 73 for Xe. Note that this is only a very rough estimate because the wave function of the excess electron would actually leak out of the cluster surface. This reduces the kinetic energy and bound excess electrons are already expected for smaller sizes.

We shall now examine the electron affinity in more detail requiring extensive numerical work. We have to approximate the effective electron potential at the surface of the cluster. We first consider the liquid which fills the half space $z<0$ and has a plane surface at $z=0$. Sufficiently far away from the surface we can approximate V_{PF} with the electrostatic image-force potential.[8] At the surface this potential diverges and we have to use a suitable cutoff.[10] We set $V_{PF}(\mathbf{r})=\text{const}$ for all points which are less than an appropriate distance d away from the surface. With proper continuity we obtain outside the surface ($\epsilon=1$)

$$V_{PF}(z)=-\frac{e^2}{4z}\frac{\epsilon_L-1}{\epsilon_L+1}\quad(z>d)\ , \tag{3a}$$

near the surface

$$V_{PF}(z)=V_{PF}(d)\quad(-d<z<d)\ , \tag{3b}$$

and in the liquid ($\epsilon=\epsilon_L$)

$$V_{PF}(z)=\frac{e^2}{4z}\frac{\epsilon_L-1}{\epsilon_L(\epsilon_L+1)}-\frac{e^2}{4d}(1-\epsilon_L^{-1})\quad(z<-d)\ . \tag{3c}$$

We approximate V_R and V_{PN} as constant inside the liquid and zero outside. The total electron potential is then $V(z)=V_{PF}(z)$ outside the liquid and $V(z)=V_R+V_{PN}+V_{PF}(z)$ inside (see Fig. 1). Note that $V(z)\to 0$ for $z\to+\infty$, thus deep inside the liquid $V_0=V(z)$ (for $z\to-\infty$) and

$$V_R+V_{PN}=V_0+\frac{e^2}{4d}(1-\epsilon_L^{-1})\ . \tag{4}$$

Springett *et al.*[1] provide an estimate for V_{PF}. From their Eq. (14) we would obtain $d=R_{\text{WS}}/2$ which is rather too small. For the results presented here we have used a larger value $d=R_{\text{WS}}$. Note that the total potential $V(\mathbf{r})$ is independent of d except in a narrow region at the surface.

TABLE I. Parameters used in our calculation: V_0 gives the bottom of the quasifree electron band in the liquid gas (Refs. 2 and 3), ρ is the density of the liquid gas (Refs. 2 and 3), α is the polarizability of the rare gas atoms (Ref. 9). The following results are given: n_c is the smallest number of atoms for which the cluster has a positive electron affinity and n_L is the number of atoms required such that 50% of the density of the excess electron is localized inside the cluster.

	Ar	Kr	Xe
V_0 (eV)	-0.2	-0.4	-0.65
ρ (Å^{-3})	0.021	0.018	0.014
α (Å^3)	1.64	2.485	4.05
n_c	46	16	6–9
n_L	1150	180	43–50

We approximate again the cluster as a sphere of radius R. The electron potential $V(\mathbf{r})$ is then spherically symmetric and using the same model as for the liquid we obtain

$$V(\mathbf{r})=\begin{cases}V_R+V_{PN}+V_{PF}(|\mathbf{r}|), & |\mathbf{r}|<R\\ V_{PF}(|\mathbf{r}|), & |\mathbf{r}|>R\end{cases} \tag{5}$$

where V_R+V_{PN} are given by Eq. (4). $V_{PF}(\mathbf{r})$ is calculated similarly as for the planar surface of the liquid. If the excess electron is at a position $\mathbf{r}$ its charge $-e$ induces a polarization $\mathbf{P}$ in the dielectric sphere. This polarization gives rise to an electrostatic potential ϕ at the position of the electron. Using the same cutoff procedure as for the planar surface we obtain

$$V_{PF}(\mathbf{r})=\begin{cases}-\frac{1}{2}e\phi_>(r), & r>R+d\\ -\frac{1}{2}e\phi_>(R+d), & R-d<r<R+d\\ -\frac{1}{2}e[\phi_<(r)-\phi_<(R-d)+\phi_>(R+d)]\ , & \\ & r<R-d\end{cases} \tag{6}$$

where the factor $\frac{1}{2}$ arises because we consider image forces.[8] $\phi(r)$ can be obtained from a multipole expansion.[11] One obtains outside the surface ($r>R$)

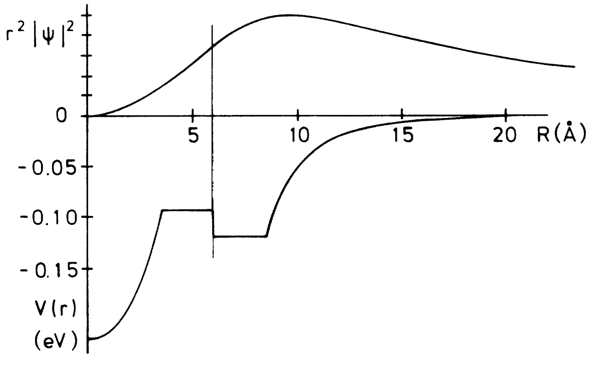

FIG. 1. Radial density distribution $r^2|\psi(r)|^2$ and effective model potential $V(r)$ for an excess electron at a Xe_{13} cluster. The energy eigenvalue is $E=-5$ meV. The reduced dielectric constant ϵ_s has been used for the calculation. The surface of the cluster at $R\simeq 6$ Å is indicated by the vertical line. Note that the discontinuities of $V(r)$ are an artifact of our model and have only a small influence on $\psi(r)$ and the electron affinity.

$$\phi_>(r)=e(\epsilon_L-1)\sum_{k=1}^{\infty}\frac{k}{k\epsilon_L+k+1}\frac{R^{2k+1}}{r^{2k+2}}$$

and inside ($r<R$)

$$\phi_<(r)=-e\frac{\epsilon_L-1}{\epsilon_L}\sum_{k=0}^{\infty}\frac{k+1}{k\epsilon_L+k+1}\frac{r^{2k}}{R^{2k+1}} .$$

The dominant part of these sums can be performed exactly to obtain better converging forms,

$$\begin{aligned}\phi_>(r)&=e\frac{\epsilon_L-1}{\epsilon_L+1}\frac{R}{r^2}\left[\frac{R^2}{r^2-R^2}-S\left[\frac{R^2}{r^2}\right]\right] ,\\ \phi_<(r)&=-\frac{\epsilon_L-1}{\epsilon_L+1}\frac{1}{R}\left[\frac{1}{\epsilon_L}\frac{R^2}{R^2-r^2}+S\left[\frac{r^2}{R^2}\right]\right] ,\end{aligned}\tag{7}$$

where

$$S(x)=\sum_{k=1}^{\infty}\frac{1}{k\epsilon_L+k+1}x^k .$$

The resulting V_{PF} is negative everywhere. In the limit $\epsilon_L\rightarrow\infty$ we obtain for V_{PF} the usual image potential at a neutral metal sphere.[8]

The excess electron is bound in the spherically symmetric potential in a state with zero angular momentum. Its wave function is then of the form $\psi(\mathbf{r})=u(|\mathbf{r}|)/|\mathbf{r}|$ and the Schrödinger equation reduces to the radial equation[12]

$$\left[\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+V(r)\right]u(r)=Eu(r) .\tag{8}$$

The appropriate boundary conditions are $u(0)=0$ and $u(\infty)=0$. If the lowest-lying eigenvalue E is negative then the electron affinity is positive and equal to $-E$. Otherwise, E is zero and the electron affinity vanishes. Far away from the surface of the cluster the potential is asymptotically $V(r)\sim r^{-4}$. Thus we put in our numerical analysis of Eq. (8) $V(r)=0$ for $r>R+\Delta$ in a good approximation for a sufficiently large Δ. We are using $\Delta=50$ Å, which is large enough because $|V(R+\Delta)|<0.1$ meV in all our calculations. The wave function is then $u(r)\sim\exp(-\chi r)$ for $r>R+\Delta$ and $\chi=(-2mE/\hbar^2)^{1/2}$ for $E\leq 0$. The outer boundary condition is thus $(d/dr)\ln u(R)=-\chi$. This eigenvalue problem is then solved numerically. To examine how the electron is localized in the cluster we calculate the fraction P_L of its density inside the surface of the cluster

$$P_L=\int_{|r|<R}d^3r\,|\psi(r)|^2\Big/\int d^3r\,|\psi(r)|^2 .\tag{9}$$

This is essentially the probability[12] to find the electron in the cluster and characterizes together with the energy eigenvalue E how strongly the excess electron is bound.

The parameters used in our calculation are presented in Table I. For the results shown here we use the cutoff parameter $d=R_{\mathrm{WS}}$. Our results for the Xe$_n$ clusters depend only weakly on this parameter and remain nearly constant if the value for d is chosen between $0.5R_{\mathrm{WS}}$ and $2R_{\mathrm{WS}}$. The results for the other rare gases are more sensitive on d and the electron affinity decreases slightly if d is increased. As an effective dielectric constant in Eq. (7) we use Eq. (1) which estimates the dielectric constant of the liquid. It contains contributions to the polarization due to interactions between dipole moments of the atoms themselves. This is quite reasonable for the larger clusters but probably overestimates the polarization for the very small Xe clusters. Thus we did another set of calculations using in Eq. (7) a reduced dielectric constant

$$\epsilon_s=1+3\alpha/R_{\mathrm{WS}}^3 ,\tag{10}$$

which only includes the direct interaction of the atoms with the electric field of the electron. This reduces the dielectric constant by about 20% but the change in the electron affinity is small. Results are given in Table I. For Xe clusters the smaller numbers are obtained using the larger dielectric constant ϵ_L of Eq. (1) and the larger numbers using the smaller ϵ_s of Eq. (7). The difference between these results is small and indicates that our calculations should be reliable. For small clusters just larger than n_c the electron is bound in a very diffuse orbital. The electron is localized inside the cluster only for much larger cluster sizes ($n_L\gg n_c$). For these sizes strong binding is achieved. Note that the estimate n_e obtained from Eq. (2) agrees well with n_L. Our results indicate the Xe$_n{}^-$ clusters should be easier to produce and detect than the other clusters considered here because they are smaller. In Fig. 2 we show the size dependence of the energy E of the bound excess electron and the probability P_L of localization for Xe$_n$ clusters. Just above the critical size $n_c=6-9$ the electron affinity is small and in-

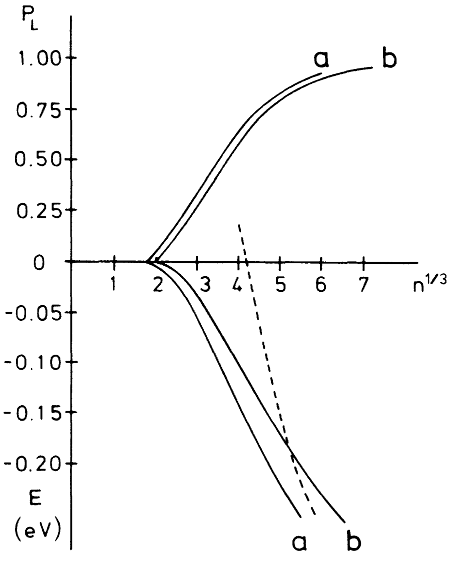

FIG. 2. Energy E of the bound excess electron at a Xe$_n$ cluster and the fraction P_L of its density localized inside the cluster. Curve a is obtained using for the cluster the dielectric constant ϵ_L [Eq. (1)] of the liquid and b using a reduced dielectric constant ϵ_s [Eq. (10)] which might be more appropriate for small clusters. The dashed line shows the estimate for E according to Eq. (2).

creases only slowly with increasing cluster size. The electron is bound in a very diffuse orbital and the density of the electron inside the cluster is small, see Fig. 1. For much larger clusters (approximately $n > 25$) the electron is strongly bound and localized inside the cluster. The same qualitative behavior is found for the other rare-gas clusters and for a spherical square-well potential.[13]

We conclude from our calculation of the electron affinity of rare-gas clusters that Xe_n^- might be stable for approximately $n > 10$. The excess electron is only weakly bound for smaller cluster sizes and the marginally stable Xe_n^- clusters are probably difficult to produce and detect. Larger clusters ($n > 25$) with a strongly bound excess electron should be observable more easily. Note that we include the screening of the interaction between the electron and the rare-gas atoms due to the polarizable atoms which lie in between[14]. This will be increasingly important for larger clusters.

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[13] The spherical square well potential is $V(|\mathbf{r}|) = -v < 0$ if $|\mathbf{r}| < R$ and $V(|\mathbf{r}|) = 0$ otherwise. Its dimensionless strength is $S = mR^2 v\hbar^{-2}$. A bound state appears first in this potential if $S > \pi^2/8$. For a slightly stronger potential the energy eigenvalue is $E = -vS^{-1}(S - \pi^2/8)^2/8$ with quadratic critical behavior and the electron density inside the well is $P_L = S - \pi^2/8$ with linear behavior. This agrees qualitatively with our numerical results and has a formal similarity with second-order phase transitions.

[14] After the first submission of our paper similar studies for Xe_n clusters were published by G. J. Martyna and B. J. Berne, J. Chem. Phys. **88**, 4516 (1988), using a diffusion Monte Carlo method. In this study the screening of the electron-Xe interaction due to the Xe atoms which lie in between has been neglected. Our theory includes this screening and uses an alternative model, somewhat simpler, for calculating the electron affinity.