Negatively Charged Xenon Atoms and Clusters

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(Received 23 May 1989)

Experimental evidence is presented, for the first time, that Xe_N^-, $N \geq 1$, atoms and clusters have a lifetime of about 10^{-4} s or longer. It is discussed whether the negatively charged xenon atoms and small clusters are in the ground or in an electronically excited, metastable state. Ground-state Xe_N^- clusters are stable if $N \geq 6$ and probably down to $N = 2$. Structure in the mass spectra correlates well with calculated binding energies.

PACS numbers: 35.10.Wb, 35.20.Vf, 35.20.Wg, 36.40.+d

It is generally accepted that ground-state rare-gas atoms cannot bind an electron. For He and Ar, negative-ion states are known, which are metastable against autodetachment.[1,2] For Ne the corresponding negative-ion state is unbound. The authors of Ref. 1 conclude for Kr and Xe that the negative-ion state either has a very low lifetime (< 50 ns) or cannot be formed in their apparatus. We report below the first experimental proof for the existence of a negatively charged Xe atom with a lifetime of about 10^{-4} s or longer.

For solid xenon, on the other hand, it is known that 0.4 eV is necessary to remove an electron from the bottom of the (normally empty) conduction band into the vacuum.[3] For some large enough value of N, a Xe_N^- cluster must therefore be stable. Two groups[4,5] have performed calculations on negatively charged xenon clusters, obtaining minimal cluster sizes in the $N = 6$ to 7 range. For these small cluster sizes the calculated electron affinities are below 1 meV for $N = 6$, but approximately 10 meV for $N = 10$.

In principle, the Xe_N^- clusters could become a model case for an excess electron in a dielectric cluster, a problem which has attracted considerable interest recently.[4-6] The Xe-Xe interaction is known accurately and the electron-Xe interaction is much simpler than that of the much studied electron-H_2O system.[6] We have tried, therefore, to synthesize Xe_N^- clusters and have observed signals corresponding not only to the negatively charged clusters, but also to the supposedly unstable Xe^- atom. To the best of our knowledge no negatively charged Xe atoms or clusters have been experimentally observed before.

The apparatus is shown schematically in Fig. 1. A mixture of 5% to 10% Xe in about equal amounts of Ar and N_2 is expanded from a pulsed supersonic nozzle (diameter 0.8 mm, pressure about 10^5 Pa, ambient temperature). The gas pulse is crossed with a pulsed electron beam (150 eV, 0.1 mA, $\Delta t = 10$ μs). Secondary electrons from ionization processes are slowed down by collisions with Ar and N_2. Slow electrons can attach to the clusters, which grow and cool by collisions. They traverse a skimmer and are detected in a time-of-flight (TOF) mass spectrometer. It is necessary to add N_2; without it no Xe_N^- was ever observed. Nitrogen has a short-lived negative-ion resonance,[7] which slows the electrons down by producing vibrationally excited N_2: $e^- + N_2(v = 0) \rightarrow N_2^- \rightarrow e^- + N_2(v' \neq 0)$. Figure 2 shows two experimental results. Intensity is observed on all Xe_N^- masses, down to the monomer. The flight time from the nozzle to the TOF spectrometer is 10^{-4} s, which gives a lifetime of about 10^{-4} s or longer. The mass scale was calibrated with $(CO_2)_N^-$ clusters, which could be resolved up to $N \approx 150$. At the mass of the Xe atom (≈ 130 amu) this is sufficient to discriminate between Xe^- and H^-Xe. At a laboratory collision energy of 1500 eV the total cross section of Xe_N^-, $N = 5$ to 15, for scattering and destruction by background gas has been measured to be 150 ± 30 Å.[2] This is roughly a factor of 3 larger than the corresponding value for positively charged Xe clusters.[8]

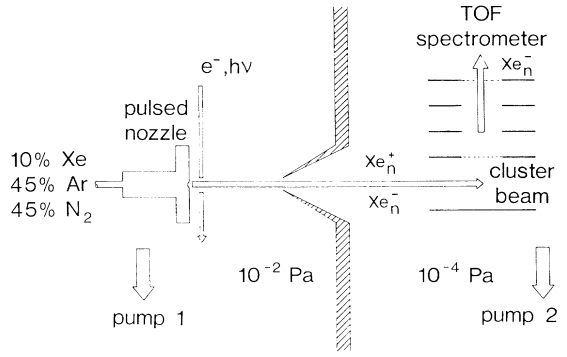

FIG. 1. Schematic of the experimental setup. A pulsed supersonic beam of a Xe-Ar-N_2 mixture is crossed by a pulsed electron beam. Secondary electrons are decelerated by collisions with Ar and N_2. Slow electrons can attach to the growing clusters or to (metastable) xenon atoms. They traverse a skimmer and are detected in a time-of-flight mass spectrometer. Alternatively the electron beam can be replaced by a photon beam and low-energy photoelectrons are ejected from a cathode (not shown) near the expansion in order to avoid the formation of metastable species.

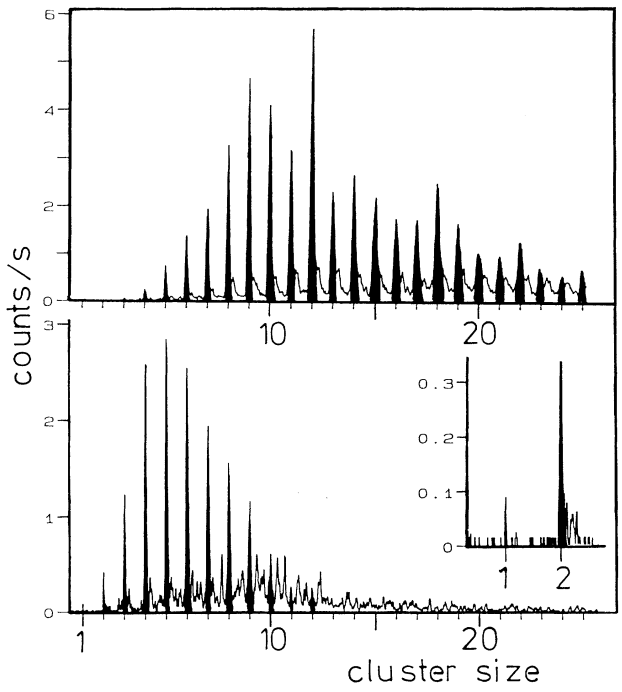

FIG. 2. Two negative-ion mass spectra taken under different expansion conditions. For the lower spectrum the electron beam intersects the gas beam as close to the nozzle as possible; for the upper spectrum about 5 mm further downstream. The Xe_N^- peaks are marked black. An expanded part of the lower spectrum is shown in the inset. Note the low signal intensity, and the higher intensity on $N=12$ and 18, which is discussed in the text. The other peaks correspond mainly to Cl^- or CO_2^- attached to xenon clusters.

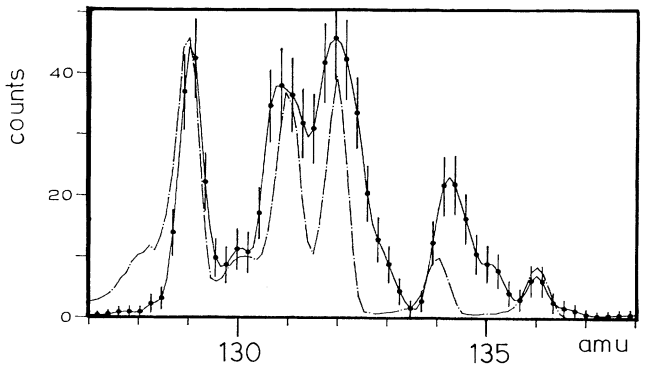

FIG. 3. Comparison of the experimental Xe^- (solid line joining points with error bars) and Xe^+ (dot-dashed line) mass spectra, showing the resolved Xe isotope distribution. The total number of counts accumulated in 10 min is given on the ordinate. For the positive mass spectrum the count rate is many orders of magnitude higher, but suffers from similar impurity problems.

Figure 3 compares the signals on the Xe^+ and the Xe^- atomic isotopes. Because of the very low signal level for Xe^- (at the maximum about 1 count per channel and 15 s) some averaging was necessary, which accounts for the lower resolution of the negative-ion spectrum. The agreement is good for the isotopes 129, 130, 131, 132, and 136. The positive-ion spectrum shows an unidentified peak at 128, and the negative one shows additional intensity between 134 and 135. As four of the five dominant Xe isotopes agree within 1 standard deviation, we deduce from Fig. 3 that Xe^- was indeed observed. There is a small possibility of an error in this conclusion, as we have never succeeded in generating a Xe^- mass spectrum which shows no impurity peaks at all. The reduction of the impurities has been a major experimental problem. Troublesome have been traces of CO_2 used to calibrate the negative-ion mass spectrum or freons from the ambient air, which reach the heatable inlet system, when changing gas bottles. No suspicious peaks have been observed around 130 amu for Ar-N_2 expansions. But if the Xe gas used contained a molecular impurity with (1) high electron affinity, (2) concentration at the ppm level, (3) a negative-ion mass spectrum compatible with that of Fig. 3, and (4) no electron-impact-induced fragments with high electron affinity, this could invalidate our conclusion of the existence of Xe^-. The joint occurrence of these four conditions is thought to be unlikely. Note that the ions are not formed under single-collision conditions. They experience many charge-exchange and/or ion-molecule reactions before traversing the skimmer. Any impurity with high electron affinity or low ionization potential will become ionized. This behavior has been encountered earlier with this type of source, but xenon has been the most difficult case so far.[6,9]

There is clear experimental and theoretical evidence that a ground-state Xe atom cannot bind an electron with angular momentum $l=0$. This can be deduced from the calculated and observed Ramsauer minimum in the cross section for low-energy electron–Xe-atom collisions,[10,11] from the pressure shift of the alkali Rydberg spectra,[11] and from field-detachment experiments[9] with $Xe(H_2O)_2^-$. These independent data all point to a negative scattering length for the low-energy e^--Xe interaction. The negative sign of the scattering length is proof that no bound e^--Xe state with $l=0$ exists,[11,12] provided the Xe atom remains in its $5s^25p^6$ electronic ground state. But a bound state with $l>0$ is still possible. An unexpected bound p state has been observed[13,14] recently for Ca^-, and calculated for the heavy alkaline-earth atoms.[15,16] For Xe the corresponding p state is unbound.[17] This is not surprising, as the electron has to move to the next higher principal quantum number, $n=6$. This state can be expected to have a higher energy. But a higher angular momentum state might still be possible. In the next-higher-Z elements, after adding the $6s$ electrons in Cs and Ba, the next electrons go into the $5d$ (La) and then the $4f$ (Ce) shell. Perhaps the $5d$ or

$4f$ electrons could interact in a correlated way with the $5p$ orbitals and the correlation energy could provide the binding, similar to the $4p$-$4s$ interaction in Ca^-. An indication of a stable electronic state of Xe^- is also the unusual long lifetime observed.

The Xe^- atoms and clusters experience electric fields up to 250 V/cm in the TOF spectrometer. Using the theory of Demkov and Drukarev[18] this puts a lower limit of about 1 meV on the electron affinity. The intensity is presently not high enough to perform a field-detachment experiment similar to that reported for $(H_2O)_2^-$. A photodetachment experiment would need an even higher intensity.

According to the calculation of Bunge *et al.*[19] Ar^- is in a $3s^23p^54s4p, {}^4S$ state, and has an electron affinity of 135 meV with respect to the metastable $3s^23p^54s, {}^3P_0$ state. Its short lifetime of 260 ± 25 ns makes it unobservable in our apparatus. The Ar^- autodetaches due to a relativistic interaction, which one would naively expect to be stronger for Xe.

If the Xe^- atoms are in a metastable state they are probably formed by a two-step process. Metastable Xe atoms are produced by electron impact and attach an electron subsequently. The following experiment was performed to avoid the first step. Low-energy photoelectrons were generated on an Al cathode next to the expansion. The photoelectrons have a kinetic energy below 1 eV, insufficient to excite the metastable Xe states. The mass spectra measured this way are less intense and show more impurity peaks. The smallest cluster identified unambiguously was Xe_6^-. For smaller clusters this was not possible due to interfering background. One has to conclude that stable Xe_n^- clusters, $N \geq 6$, do exist. Because of the very small intensity this experiment does not provide evidence against the existence of ground-state Xe^- atoms and small clusters.

Is Xe_2^- in a stable or in an electronically excited, metastable state? The He_2^- molecule has been observed to be metastable against autoionization with lifetimes of 10^{-4} s and less.[20] This state consists of a $2p$ electron added to the lowest $^3\Sigma_u$ state of He_2, which has a lifetime of 0.05 s or longer.[21] The lifetimes of the molecular excimer states of Xe_2 are 10^{-5} or shorter.[22,23] It seems unlikely that an added electron would increase the lifetime by 2 orders of magnitude for Xe, whereas it decreases the lifetime by 2 to 3 orders of magnitude for He. Therefore, we conclude, tentatively, that Xe_2^- is not in an electronically excited, metastable state. The same argument applies also to Xe_N^-, $N=3$, 4, and 5.

We now focus our attention on the clusters. Two calculations have appeared for Xe_N^-. Stampfli and Bennemann used an effective-medium approach.[4] They calculate that clusters having six to nine atoms start to have a positive electron affinity. According to the theory of Martyna and Berne[5] the electrons are delocalized over the Xe_N clusters, which also retain, more or less, their natural geometries. The electron can move in channels between the xenon atoms and outside the cluster. If there are more, or deeper or wider, channels for the electron to move in, its binding energy increases. For $N=13$ the clusters have the shape of an icosahedron, which has a central atom with two caps of six atoms each, displaying a fivefold symmetry. For $N=19$ one has an icosahedron with an additional pentagonal cap. These icosahedral shapes are more compact than their neighboring clusters, with narrower channels between the atoms and consequently a lower electron affinity. If the binding energy for the electron is smaller, it is plausible that an electron is less often attached and more easily detached in the expanding jet. This yields a lower intensity on masses $N=13$ and 19. Similarly, the open structure of $N=12$ and 18 leads to a higher electron affinity, and consequently to a higher intensity on these masses. This has always been observed independently of the expansion conditions.

In summary, it cannot be decided at present if the observed Xe^- atom is in the ground or electronically excited, metastable state. The lifetime is about 10^{-4} s or longer. The Xe_N^- are stable for $N \geq 6$, and probably down to $N=2$. Structure in the mass spectra correlates well with calculated electron affinities for $N=12$, 13, 18, and 19.

This research was supported by the Deutsche Forschungsgemeinschaft. We thank J. R. Peterson of SRI International for several very interesting comments on this manuscript.

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