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Two Challenges for Experimenters

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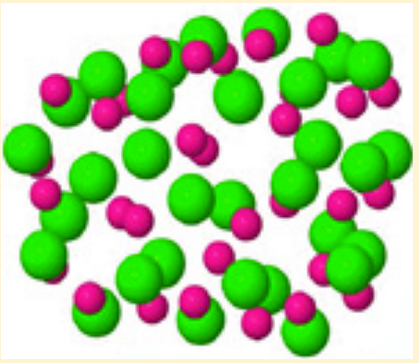
ABSTRACT: In recent years, several theoretical studies have indicated potentially interesting, even perhaps surprising phenomena that could be observed by experiment—but have not yet been studied in the laboratory. Here we give the background and motivation for two of these, with the admitted goal of stimulating those experimental studies. The two topics: (1) the production and study of *amorphous* alkali metal halide clusters; (2) Penning detachment, the analogue of the well-studied Penning ionization, but in which an electron is detached from a negative ion, rather than from a neutral atom, by energy transfer in collision with an excited atom. The latter phenomenon could be particularly relevant for stellar atmospheres where negative ions are abundant. In each case, we indicate the implications and potential of having substantive experimental information about each, in effect explaining the motivation to carry out the experiments.



I. INTRODUCTION

Theoretical studies sometimes yield predictions of phenomena that have not been observed yet, at the time of the prediction. Some of these lead to new processes, some to deeper understanding of observed phenomena, and sometimes, simply because the possibilities of making such observations have gone unnoticed, the scientific community has missed some interesting "low-hanging fruit". Here we present two challenges for experimentalists, covering two rather different phenomena that await observation. In both cases, the theoretical basis is well-developed and in one case, the concepts have developed far enough to spell out just how the experiments could be done.

The more developed of the two cases is the preparation of *amorphous* alkali metal halide clusters. The notion that this might be possible arose from the recognition that the potential surfaces of alkali metal halide clusters typically have orders of magnitude more minima corresponding to locally stable amorphous structures than to rock-salt structures.[1−4] Despite this enormous statistical factor seeming to favor amorphous structures, dynamic simulations indicate that alkali metal halide clusters, cooled from the liquid state, normally find their way to rock-salt structures. Only by extremely rapid cooling can the clusters be caught in amorphous structures. One simulation study seems to reveal a natural way how to carry out an experiment that would produce those amorphous clusters.[5] Of course we can expect them to have properties quite different from clusters with rock-salt structures; therein is the motivation.

The second example, almost as well developed theoretically, is the phenomenon of Penning detachment. Theoretical cross sections for this process, for both atomic[3] and cluster negative ions[4] are available and indicate that the process should be easy to observe. One attempt to observe the process yielded a completely different result, superelastic collisions of photoelectrons with excited atoms,[5] so Penning detachment remains unobserved. This is a process which, because of the very large cross sections expected for it, would be very important in any gaseous medium in which both excited atoms or molecules and negative ions are present, e.g., some stellar atmospheres.

The following sections discuss each of these cases in turn, giving the theoretical background, as much as it exists, and where possible, suggested methods to carry out experiments to observe these phenomena.

II. AMORPHOUS ALKALI METAL HALIDE CLUSTERS

The energy landscapes of alkali metal halide clusters, like those of virtually all atomic clusters, have numbers of local minima that increase terrifyingly rapidly with the number N of atoms in the cluster. The number of geometrically distinct minima increases approximately exponentially, but there are permutational isomers to be considered, which, for a monatomic cluster increases approximately factorially, so, roughly we can expect the number of minima to increase about as $N!e^N$. This kind of increase occurs with the binary alkali metal halide clusters as well. Alkali metal halide clusters, like bulk alkali metal halides, almost all have rock-salt lattice structures as their low-energy structures. A typical lowest-energy structure has as closed, compact a form as possible. Thus, for example, the global minima of $(NaCl)_{32}$ and $(KCl)_{32}$ are $4 \times 4 \times 4$ cubes. However, there are quite a number of other rock-salt structures that such clusters may assume, slabs, cubes with pairs of ions promoted to a surface and other such variants. All of these are low-energy structures. But the number of rock-salt structures is vastly smaller than the total number of locally stable structures on these potential surfaces. For example, though $(KCl)_{32}$ has

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perhaps a few hundred minima corresponding to rock-salt structures, the potential surface of this system has somewhere between 10^{12} and 10^{14} locally stable structures, almost all of which are amorphous.[3] (It is not practical or useful to try to get a more precise estimate of that number, of course.)

We interpret all the familiar properties of solid alkali metal halides in terms of their rock-salt structures. We attribute colors to the defects we call "F-centers,", for example, to vacant sites in the regular lattice. The two regular lattices are the only forms of solid alkali metal halides known to us. When alkali metal halides melt incompletely, so that part of the system remains crystalline and part is liquid, the two phases segregate because liquid alkali metal halides do not wet the solid—as a consequence of their ionic nature and the difference in the densities of the two phases.[3,6]

A small historical note: when it became apparent that locally stable amorphous structures of alkali metal halide clusters vastly outnumber the rock-salt structures, it seemed plausible that amorphous alkali metal halide clusters might be observable, if they were cooled fairly rapidly from the liquid state. However, simulations of such cooling, specifically with $(KCl)_{32}$, at rates first of 10^{11} K/s and then at 10^{12} K/s, yielded only rock-salt structures![4] Only if the cooling rate in the simulations was faster than 10^{13} K/s did the clusters "get trapped" in amorphous structures. This corresponds to removing virtually all the heat of fusion in fewer than 10 vibrational periods. It hardly seemed feasible at that time to carry out such experiments.

Soon after that work appeared, Cheng and Landman[5] conducted simulations of deposition of fast-moving $(NaCl)_{32}$ clusters onto several different surfaces: a solid NaCl (001) surface, liquid neon, and liquid argon. At a speed of 3 km/s, the cluster fragments when it hits the solid; it makes a soft landing on the neon by transferring its kinetic energy to atoms as deep as about 10 Å, but on striking liquid argon, that energy is dissipated very close to the surface, to a depth of only about 4 Å.

In that specific process, the cluster melts on impact as a consequence of the very effective momentum transfer to the argon, heating at ca. 5×10^{15} K/s; the argon atoms in the vicinity of the impact become very hot and evaporate about ten times faster, and effectively chill the sodium chloride cluster at about 10^{14} K/s, fast enough to trap it in an amorphous structure.

The simulations of deposition of fast alkali metal halide clusters onto a suitable rare gas surface lead directly to revealing the kind of experiment that would allow the study of amorphous alkali metal halide clusters. Specifically, if the clusters were prepared in a high-velocity beam and were then *codeposited* with the rare gas onto a solid rare gas matrix, presumably argon if sodium chloride clusters were used, and either argon or krypton with potassium chloride, the amorphous clusters would form extremely fast on impact, and then would become embedded in the matrix, isolated enough to retain their identity and structure. First experiments might well be done with no special effort to achieve size selection. A natural next stage would of course be to restrict the clusters either to a narrow range of sizes, e.g., by selective timing of passage through an inert gas, or to a single size, perhaps by size-selecting from a beam of negatively charged clusters and then photodetaching the extra electrons. Of course, such methods would require very sensitive means to probe the small samples that such methods would produce.

What behavior might we expect these amorphous clusters to exhibit? They might, for example, be colored, by analogy with F-centers. They might have dielectric response functions unlike any we have known, because the electrons responding to an external field would be in a polar but random environment. But the very environment of the solid matrix provides a well-established medium to carry out such studies. The natural probes: optical and IR spectroscopy, dielectric relaxation, possibly magnetic resonance.

If the cluster beam were to begin as accelerated negative ions, then of course it would be straightforward to do mass selection and then photodetach only the clusters of the single desired size. This would immediately make possible the study of the behavior of the amorphous salt clusters as a function of their size. We know from simulations that the very small alkali metal halide clusters differ significantly in their properties from those containing about 50 or more particles, so it may be possible to observe such changes in behavior with cluster size, in such experiments.

III. PENNING DETACHMENT

The phenomenon of Penning ionization—ionization of neutral atoms or molecules by energy transfer from electronically excited collision partners—has been a subject of investigation for decades. It is an efficient process, with typical cross sections of the magnitude of atomic collision cross sections. Surprisingly, the closely related analogue in which the excited species collides with a negative ion, transferring energy and releasing the "extra" electron has remained almost uninvestigated. We have been referring to this as "Penning detachment".

The first reported instance of detachment of an electron from a negative ion by collision with an excited species[7] was not really Penning detachment, although closely related to it. This was the observation of associative detachment of electrons from O^- and O_2^- by collision with excited oxygen molecules, $O_2(^1\Delta_g)$ to form ozone, O_3. The one reported observation of Penning detachment was that of detachment of electrons from Cl^- ions by collision with optically excited sodium atoms; this was presented at a conference and no subsequent follow-up can be found.[8] That observation was made some time after the first theoretical estimates of the cross sections for several detachment collisions.[9] The theoretical treatment assumed that the excited neutral atoms were in metastable—and hence long-lived—states, and the cross sections were estimated for both the Penning detachment process and for collision-induced radiative de-excitation of the neutrals. The intent of that study was estimating the magnitude of the cross sections, and the results were not intended to be very precise. The smallest estimated cross section, for H(2s) colliding with an H^- ion at 1 eV was 1.7×10^{-15} cm^2, and next was He(2^1S) with H^-, 2.7×10^{-15} cm^2. All the others fell between 4×10^{-15} and 2×10^{-14} cm^2.

The subject lay dormant until 1997, when much more accurate calculations showed that the cross sections for Penning detachment in collisions of H^- with He($1s2s^1$S) or with any of several excited states of Li (the 2p, 3s, 3p, and 3d states).[10] These were carried out for collision energies from 25 meV to 20 eV. The calculated cross sections from this work, based on the assumption that the products are left in their ground states, were significantly larger than those of the 1971 estimates. At collision energies below 1 eV, all the cross sections except that of H^- with Li(3d) were above 10^{-14} cm^2, and some, with Li(3s) and Li(3p), were well above 10^{-13} cm^2 at energies below 0.1

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eV. The physical basis for such large cross sections is easy to rationalize: the collisions involve the long-range interaction of a charged particle with a highly polarizable neutral partner. Hence the cross sections are expected to be much larger than gas-kinetic cross sections and, for that matter, much larger than those of the analogous Penning ionization.

Those calculations were refined to take into account the possibility that the target excited atom could be left in an excited state after the collision.[11,12] With excited channels included, the cross sections for collisions at energies of up to 20 eV or more remained well above 10^{-14} cm^2. This was the case with excited Calcium atoms as well as with Lithium.

The last of the theoretical calculations of Penning detachment cross sections dealt with negatively charged atomic clusters of sodium, namely Na_7^- and Na_{19}^-. The excited species, the energy donor, for this analysis was excited sodium, Na*(3p); this could be compared with H^- and the corresponding Li*(2p). These atoms have enough energy to detach the extra electron from the negative clusters, but not enough to excite the lowest plasmon resonances of the clusters. The cross section for H^- with excited lithium is about 3×10^{-14} cm^2 for the entire energy range from 25 meV to 20 eV, whereas the cross sections for excited sodium with the sodium clusters is approximately 10^{-13} cm^2. Though somewhat larger, this is still of the same magnitude as the cross sections for atomic Penning detachment. In short, the process is a result of a long-range interaction, and does not depend on the detailed structure of the colliding species.

The phenomenon has remained at that stage for the past 14 years. Yet, with cross sections of the magnitude predicted for this process, it must play a very important role in any gaseous system containing both negative ions and excited atoms. For example, we can expect Penning detachment to destroy negative ions in all but the coldest plasmas. Any simulation of a discharge in which negative ions are likely to be produced must include Penning detachment if it is to be at all realistic. But these cross sections are just theoretical; to describe ionized gases accurately, we will need experimental values of the detachment cross sections. Even the conditions for fusion will inevitably involve negative ions, even if transiently, and there, because the concentrations of excited species must be high, Penning detachment probably plays a significant role in neutralizing those negative ions. And naturally, we can expect Penning detachment to play a significant role in the kinetics of the species in the outer parts of stellar atmospheres, where conditions allow negative atomic ions and excited atoms to exist in significant concentrations.[13]

There are many ways that one could conduct experiments to observe this process. One of the most obvious is to pass a slow beam of the desired (presumably mass-selected) negative ions through a region containing excited atoms, perhaps directly optically excited, although it might be preferable to have metastable excited energy donors, which might be prepared by optical excitation to a higher state that decays to a metastable form. The electrons would most easily be collected in a magnetic bottle spectrometer[14] to allow energy analysis, which would allow identification of the final state of the energy donor. It might even be possible to observe the neutralized target species in an excited state, something the electron energy spectrum would reveal.

IV. CONCLUSION

The goal of this presentation is, quite frankly, to try to stimulate new experiments to observe and study certain phenomena that we can expect to display novel characteristics, in the first case of a kind totally unexplored, and in the second, a kind that must necessarily play an important but heretofore neglected role in plasmas and other gases containing negative ions. There are other examples of phenomena that await experimental observation, such as the capture of an electron by the large quadrupole moment produced by the correlated valence electrons of certain atoms,[15] or the possible symmetry-breaking in very cold solid molecular hydrogen, where the intermolecular quadrupole−quadrupole interaction may spoil the "good quantum number" designating the (J = 0) rotational state of each individual molecule, leaving only a collective constant for some aggregation of molecules. These are simply examples to remind us that our science always offers us new frontiers, and that so long as we can keep our minds open to recognize new questions, we will remain at the frontier, where science is most exciting.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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