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Comment on "Binding of Hydrogen Molecules by a Transition-Metal Ion"

In a recent Letter Niu, Rao, and Jena [1] showed that a positively charged nickel ion (Ni^+) can bind several hydrogen molecules in its vicinity. This result and the consequent conclusions are based on self-consistent field molecular-orbital calculations, with correlation effects included through standard techniques. Essentially, the aim of Ref. [1] has been to look for the ground-state geometry of the (classical) atoms in the small cluster consisting of a Ni ion and a number of H_2 molecules.

Niu, Rao, and Jena extrapolate from their numerical binding-energy results that the ion can bind up to ten hydrogen molecules. The purpose of this Comment is to point out that this is not the correct asymptotic limit. In fact, at zero temperature the ion can bind arbitrarily many molecules.

The results of Niu, Rao, and Jena demonstrate the power of up-to-date quantum chemistry methods in calculating small energy differences and predicting associated new phenomena. However, the binding of inert molecules to ions is an old and well-known phenomenon [2], the physics of which can be understood by simple physical arguments without extensive computations.

The clustering of neutral atoms and molecules around ions was first observed in the context of measuring ion mobilities in gases. The mobility of ions is radically reduced due to the cluster of molecules stuck on the ion. Atkins [2] explained this using the so-called snowball model: A "solid" ball of molecules is formed around the ion. The binding is caused by the long-range van der Waals forces between the ion and the polarizable molecules. The size of the snowball depends on the pressure and the temperature of the ambient gas. A similar dense cluster of molecules is also observed around a free positron in many inert gases [3].

The long-range interaction between a molecule and an ion is caused by the polarization of the molecule in the electric field of the ion

$$V(r) = -\frac{\alpha}{2\epsilon^2 r^4}, \quad (1)$$

where α is the polarizability of the molecule and ϵ the (static) dielectric constant of the medium. This equation gives an estimate for the binding energy of a molecule at a distance r from the cluster center. It is clear that this long-range attractive potential will attract all the available gas molecules to the ion at zero temperature. At

finite temperatures, the size of the condensed droplet is determined by straightforward free energy considerations, as shown in Ref. [2].

The binding energy of the last molecules on the surface of the zero-temperature droplet is proportional to $N^{-4/3}$, N being the total number of molecules in the cluster. The binding energy of the first molecule, using Eq. (1) and the bond distance obtained by Niu, Rao, and Jena, is approximately 0.5 eV, in complete agreement with the result of the exact calculation in Table II of Ref. [1]. However, this binding energy is about a factor of 2 smaller than the quantum chemical calculation when more extended basis functions were used (see Ref. [15] in [1]). Assuming a constant density for the gas in the cluster, the average binding energy of the molecules is proportional to N^{-1} .

The binding of molecules on ions is due to polarization forces as has been pointed out by Niu, Rao, and Jena. In this Comment we have pointed out that their results can be understood from a simple picture in Eq. (1). In this picture the binding is similar for all ions, only the binding energies of the first molecule depend upon the chemical identity of the ion. The asymptotic binding is independent of the ion in question. The important quantities determining the number of bound molecules are the ambient gas pressure and temperature. The cluster phase diagram can be determined using mean-field theory. Interesting open questions remain as regards the dynamics of the droplet formation.

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