Correspondence between Electron Binding Energy and Chemisorption Reactivity of Iron Clusters

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New experiments in a fast-flow reactor have uncovered a strong correlation between the reactivity of free iron clusters and cluster ionization thresholds: Clusters with low thresholds efficiently add molecular hydrogen, and the relative rates of this reaction closely follow variations in cluster-electron binding energy. This correspondence can be understood in terms of a requirement for metal-to-hydrogen charge transfer in the activation of the H_2 bond.

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A multidisciplinary effort has evolved to investigate the unexplored realm of matter involving clusters of from several up to a few hundred atoms.[1-4] A new technique of synthesizing isolated clusters of any material,[5] that of sudden condensation of laser-produced vapor, has made it possible to perform a growing range of experiments aimed at elucidating the nature of metallic clusters. From such physical and chemical measurements it is hoped to correlate observed properties for a given type of cluster, and thereby to obtain at the experimental level an understanding of the interplay of physical factors in the behavior of these complex systems. This Letter reports the first observation of a strong correlation, a striking parallel between the measured ionization thresholds of small iron clusters and the reactivity of the same toward the hydrogen molecule.

Since the development of the metal-cluster synthetic technique, we have taken several steps to explore the cluster-size dependence of transition-metal cluster properties, with Fe serving as a particularly important case. In early experiments[6] the abundances and rough ionization thresholds of clusters of up to 25 Fe atoms were determined. We have also performed magnetic-moment measurements by the Stern-Gerlach technique on iron clusters and their oxides,[7] and found evidence for monotonically increasing moments, which are expected for incipient ferromagnetism, with increasing cluster size.[8,9] In a more recent development we and others have constructed fast-flow chemical reactors to measure the elementary chemical properties of transition-metal clusters,[10-12] and studied the reactions of Fe clusters with O_2, H_2S, and methane, only to see relatively smooth variations in reactivity with cluster size.[13]

Finally, the first precise determination of the ionization thresholds (hereafter denoted IP, as is customary) of transition-metal clusters was carried out with use of tunable ultraviolet lasers to measure Fe-cluster photoion yields.[14] The unexpected result of this work was a very sharp drop in IP toward the bulk work function, accompanied by oscillations, i.e., definite regions where the IP *increased* with cluster size. Perhaps the most pronounced feature is a distinct IP minimum near 5.4 eV in the Fe_9–Fe_{12} region. We show here that a strong correlation exists between this IP dependence on cluster size and the reactivity of clusters toward H_2 and D_2, such that those clusters with lowest IP are most reactive toward chemisorption of molecular hydrogen.

Because our techniques follow closely those described in a recent article,[13] we give only a brief summary here. Metal clusters are synthesized by synchronizing the intense He flow from a pulsed nozzle with pulsed-laser (10^8 W/cm^2) vaporization of a rotating-translating Fe rod. The hot metal vapor partially condenses to form clusters, and cools toward the He gas temperature during flow through a 4.5-cm-long by 0.2-cm-diam channel. In ionization-potential and magnetic-moment experiments the resulting cluster mixture expands directly into vacuum (10^{-6} Torr) and is collimated into a cluster beam for subsequent measurements. In the reaction experiments, however, we append to the channel a reactor cylinder 6 cm long by 1 cm diameter, into which is fired a secondary He pulse containing the reactant gas. This secondary flow is much weaker than the primary flow, but is sufficient to produce a zone of turbulent mixing extending downstream from the secondary nozzle. It is in this zone that cluster-molecule reactions take place, mediated by 50–500-Torr flowing He. The important experimental parameters at our control are the reactant concentration and time length of the secondary pulse and the temporal overlap between primary and secondary pulses. All detection is accomplished by photoionization time-of-flight mass spectrometry using the F^2 excimer-laser line (158 nm, 7.9 eV), whose photon energy is well above the threshold of all clusters yet soft with respect to fragmentation (completely unfocused, 2×10^{-4}-J/cm^2 fluence incident on the cluster beam).[15]

When the secondary gas pulse has a D_2:He density ratio greater than 1:10 and is temporally overlapped with the Fe cluster-source pulse, clusters of certain sizes deplete preferentially, and products having masses corresponding to $Fe_x(D_2)_y$ are detected, as shown for small clusters by Fig. 1. All detected products have an even number of D atoms, although the Fe cluster isotopic dispersion increasingly limits this distinction for $x > 20$. Increasing either the time length of the secondary pulse or its D_2 concentration increases these effects, so that certain sizes of clusters can be completely depleted in favor of new products. By contrast, when the secondary pulse is an equivalent pure He pulse, a uniform depletion of up to 50% in cluster signal intensity is observed, with negligible change in the cluster abundance distribution.

Our essential results on the reactivity of clusters of up to 45 Fe atoms can then be summarized as follows:

(i) All Fe_x clusters with $x < 23$ are at least 10^2 times less reactive toward D_2 than toward H_2S or O_2, with the Fe atom unreactive toward all three.[13] In particular, whereas we estimated 10^1–10^2 collisions between clusters and O_2 in the previous experiments,[13] here 10^4 D_2-cluster collisions during the 200-μsec residence time are required to achieve comparable depletion of reactive clusters.

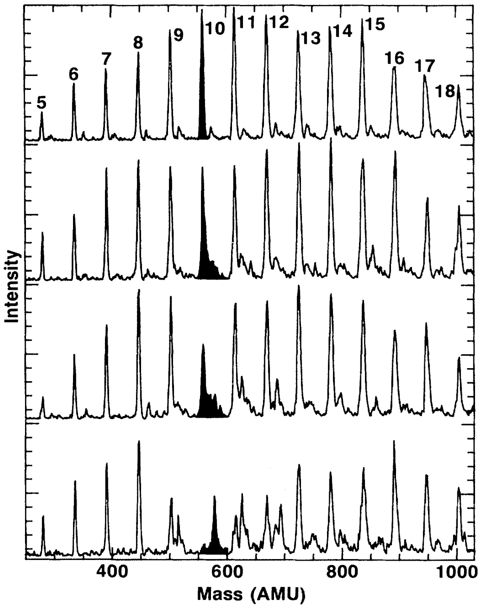

FIG. 1. Chemisorption of D_2 on certain small Fe clusters is seen from these photoionization time-of-flight mass spectra in the preferential depletion of bare clusters Fe_x, accompanied by appearance of products of masses corresponding to $Fe_x(D_2)_y$. The three lower frames correspond to different time lengths (nominally 100, 250, and 600 μsec) of the secondary gas pulse, which is a 25% mixture of D_2 in He. The top frame shows the bare-cluster distribution (Fe_x and small impurity Fe_xO peaks) obtained when the secondary pulse does not overlap the cluster pulse, while lower frames correspond to successively longer overlapping pulses. The darkened peaks emphasize the evolution of one of the most reactive small clusters, Fe_{10}.

(ii) Among small clusters, at successively higher D_2 pressure, extensive reaction is observed first for Fe_{10}, then Fe_{11} and Fe_{12}, and finally Fe_9, with only marginal reaction detected for Fe_{13} and Fe_{14} at the highest D_2 pressure.

(iii) Under highest pressure conditions these reactive clusters appear to "saturate" at a maximum D_2 uptake, $y_{\max}$, with $y_{\max} = 5$ D_2 molecules for Fe_{10}, 4 for Fe_{11}, and 6 for Fe_{12}, as seen by the highest-mass peak to the right of each Fe_x peak.

(iv) Among larger clusters, another sharp onset of relatively high reactivity is seen for Fe_{19-22}, which react as rapidly as Fe_{12}. A final change to even higher reactivity is observed between Fe_{22} and Fe_{23}.

Quite similar results, although with poorer product mass resolution, are observed with H_2, except that depletion of reactive clusters comparable to that with D_2 is obtained with one-fourth the hydrogen concentration. Just such an isotope effect is expected for a process involving the breaking of the hydrogen molecular bond.[16]

These combined results give a conclusive picture of the reactive processes in terms of the following elementary events:

$$Fe_x + D_2 \longrightarrow Fe_xD_2, \tag{1}$$

$$Fe_x(D_2)_y + D_2 \longrightarrow Fe_x(D_2)_{y+1}, \tag{2}$$

with all products stabilized through collisions with the He buffer. This process is almost certainly the cluster analog of dissociative adsorption, in which the hydrogen molecular bond is broken and two metal-H bonds are formed. We thus conclude that the Fe cluster activation of molecular hydrogen depends strongly on the nature of the cluster, with an observed propensity among the most active small clusters: $Fe_{10} > Fe_{11}$, $Fe_{12} > Fe_9 >> Fe_{13,14}$. Note that this scale is based on a *depletion* of Fe_x clusters, which is necessarily the consequence of the primary step (1).

A striking correlation is found when the reactivity is compared with ionization threshold measurements.[14] Figure 2 shows this detailed correspondence, which links low ionization thresholds to high reactivity. To obtain the quantitative estimate of the relative reactivity of Fe_x clusters used in Fig. 2, we define a phenomenological rate constant k_x proportional to $-\ln(s_x)$, where s_x is the observed fractional survival of cluster Fe_x signal. Comparison of k_x among clusters for different conditions (and for both D_2 and H_2) removes the proportionality to give a self-consistent set of relative rates spanning over two orders of magnitude.

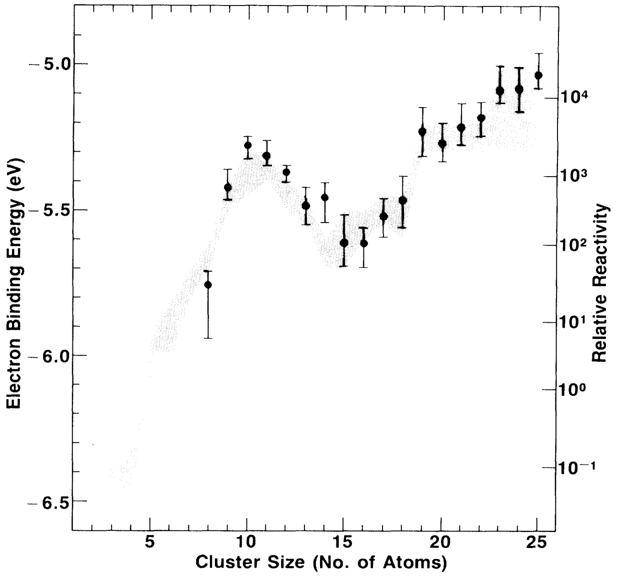

FIG. 2. Comparison of measured ionization thresholds (left-hand scale and Ref. 14) with intrinsic relative reactivities of Fe clusters (right-hand scale, see text). The grey band reflects the uncertainty in ionization threshold measurements, while the vertical lines indicate uncertainties in reactivity results, taken from measurements of Fe_x depletion by reaction with D_2 and H_2.

To understand the source of this correspondence, first note that the IP, which is related indirectly to the Fermi or highest-occupid orbital energy, measures directly the adiabatic *binding energy* to be overcome in removing the most weakly bound electron from the cluster. The simplest explanation of this correspondence therefore is that hydrogen chemisorption requires charge transfer from the metal cluster, i.e., an ability to give up the most weakly bound electron. If we then adopt a purely charge-transfer model for cluster activation of hydrogen, the energy barrier will depend directly on the energy required to transfer this electron from the cluster. If it is furthermore assumed that the electrostatic bonding changes slowly with cluster size, then one immediately obtains the desired exponential form (used in Fig. 2) relating relative reactivity to differences in IP:

$$k_x/k_{x'} = \exp[\epsilon(I_{x'} - I_x)/k_B T], \tag{3}$$

where I_n is the IP of a cluster of size n and the dimensionless parameter ϵ, which translates electron binding-energy differences into reaction-barrier differences, is unity within the simple charge-transfer model (see below). As seen in Fig. 2, this direct correspondence provides a fairly successful initial explanation, although it requires $\epsilon = 0.2$ when $T = 298$ K, the temperature of the reactor walls and gases.

Of course, it is unlikely that the activation of hydrogen by metal clusters is based solely on charge transfer, just as the bonding of H atoms to metal surfaces or transition-metal complexes is not purely ionic, although the "metal-hydride" M^+H^- convention persists. In the past year Saillard and Hoffmann[17] have given a comprehensive treatment in molecular-orbital and solid-state languages describing the activation of H_2 both by organometallic complexes and on surfaces. In this work several interactions inherent in metal-hydride bond formation are delineated, and it is of interest to note that, in the empirical reasoning used there, the critical factor in surface activation of hydrogen is electron transfer from the metal, while for complexes it is the reverse. Within this more complete model, the results of Fig. 2 are explained in terms of an enhanced ability of clusters with a higher Fermi level (lower IP) to give electron density to the antibonding σ^* orbital of the hydrogen molecule. The stabilization of the barrier to dissociative adsorption can then be calculated within a perturbative molecular orbital formulation. The same relation (3) holds, except that now ϵ has meaning as the square of the ratio of the interaction matrix element to the difference (6–8 eV) between the cluster's Fermi energy and the hydrogen σ^* orbital. Because the interaction energy is approximately that of the forming bonds (~ 3–5 eV), this very likely places ϵ as slowly varying with cluster size and less than unity, in agreement with experiment.

Thus, within this picture, reactive Fe clusters are more surfacelike in their propensity for H_2 activation. The adsorption of hydrogen on iron surfaces has been repeatedly studied in the past decade,[18] with results that are additionally not at odds with those described here: (i) Initial sticking probabilities are 0.03 to 0.16 depending on crystal surface, and (ii) metal-hydride bonds are reasonably strong (desorption activation energy of roughly 90 kJ/mol for the strong-binding site), so that the reverse of Eq. (1) would not occur under our experimental conditions.

Finally, it should be stated that no source for the oscillations in IP has yet been found,[19] although calculations on some Fe clusters have been done[8] and are currently underway in several laboratories. In particular, whereas the calculated Fe cluster electronic structure, as indicated by band formation and cumulative density of states, appears quite similar to that of the bulk metal for clusters as small as Fe_9, important differences exist in the charge and spin density of surface relative to central atoms.[8,20] Further, no correct understanding of Fe-cluster electronic structure can be reached without consideration of magnetic ordering effects[8]; local spin-density functional calculations, which include these effects, show very large spin polarization shifts and give an ionization energy of 5.2 eV for Fe_9,[20] in reasonable agreement with the 5.4–5.5-eV measured value.

This potential relationship between cluster magnetism, ionization threshold variations, and activation of hydrogen is now open to further investigation. Geusic, Morse, and Smalley[12] have recently measured the chemisorption of D_2 on clusters of cobalt, another spin-polarized bulk ferromagnet, and found oscillations in reactivity for small Co clusters. We are currenty carrying out experiments to measure magnetic moments and ionization thresholds of these clusters.

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