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STRUCTURE, MELTING AND REACTIVITY OF NICKEL CLUSTERS FROM NUMERICAL SIMULATIONS*

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STRUCTURE, MELTING, AND REACTIVITY OF NICKEL CLUSTERS FROM NUMERICAL SIMULATIONS*

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1. Introduction

Structure and reactivity are aspects common to surface science, organo- and inorganometallic chemistry, and to the relatively new field of cluster research. Here we use the term *cluster* to designate bare ("naked", "naked") clusters of like atoms (molecules). A broader usage of the term also includes organo- and inorganometallic compounds, i.e., ligated clusters. Although cluster research grew out of studies of bulk and surface properties of materials (clusters were first utilized to inquire about the microscopic origins of these properties), it soon acquired the status of an independent field with its own subjects, objectives, and methodologies. As the field matured, it became clear that the relation between bulk and surface properties, on the one hand, and those of clusters of atoms (molecules) of a given material, on the other, may not be as straightforward as originally thought. One of the reasons is that the finiteness of clusters, especially those of smaller and intermediate sizes, has a major effect on their electronic and energetically favorable geometric structure(s), as well as other properties. Many of these properties turn out to be quite different from the corresponding macroscopic properties of the materials. Another intriguing and complicating issue is that the properties of clusters change and eventually converge to bulk and surface properties, as the clusters grow in size, not necessarily in a monotonic or even unique way.

We shall discuss here properties of metal clusters. These are especially close to organometallic and inorganometallic molecular compounds as they form the skeletal framework of these compounds. Issues such as stability, geometric forms, fluxionality, isomerization transitions, and others are common for both bare and ligated metal clusters. The precise meaning and the details of these issues, as dictated by the nature of the objects studied and as emphasized by the practitioners of the different fields, are not necessarily identical. Thus, for

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example, stable and metastable structures and their possible interconversions are subjects of primary importance and concern in studies of bare metal clusters. One can even talk about a meltinglike transition (loss of structure) in these clusters as their energy is increased. Notions of fluxionality and isomerization as applied to metal-containing molecular compounds, however, often refer to the mobility and bonding rearrangement of the ligands rather than that of the metal framework to which these ligands are attached. Rearrangement of the metal framework may require energies that would cleave the intraligand and metal-ligand bonds and thereby alter the very object of the study. The relationship between the fields of surface science, chemistry of metal-containing molecular compounds, and physics and chemistry of clusters is that of complementarity. Studies of metal clusters and of their interactions with molecules furnish a link between the traditional areas of surface science and the chemistry of metal-based molecular compounds. A comprehensive picture of metal systems and their interactions with ligands that covers the range from a few atoms to the bulk material will emerge as a result of continuing progress in each of the three research areas.

The subject of our discussion is structural and dynamical properties of nickel clusters as derived from numerical simulations. A brief description of the potential energy functions used to represent the intracluster interactions and the interaction of a Ni_{13} cluster with a D_2 molecule is given in Section 2, which also contains a sketch of the theoretical and computational methodologies utilized. A sample of results on structures of nickel clusters of different sizes is presented in Section 3. The evolution of the patterns and peculiarities of the intracluster dynamics with the cluster energy, which leads to structural isomerization and solid-to-liquid-like transitions, is discussed in Section 4. In Section 5 we present and discuss results on the $\text{Ni}_{13} + \text{D}_2$ collision system. In particular, we analyze the dynamics of the reactive channel of the interaction (i.e., dissociative adsorption of the molecule on the cluster) as defined by the initial rovibrational state of D_2 , the system collision energy, and the structure and temperature of Ni_{13} . The calculated data are compared with the available experimental results and a "tuning" of the cluster-molecule interaction potential based on the interplay between theory and experiment is performed. A brief summary is given in Section 6.

2. Theory and Methodology

Ideally one would like to obtain the energies of the interaction and the forces between the atoms in a cluster or in a cluster-molecule system from first principle calculations. Despite the immense recent progress in computational methodologies and computer technology, such calculations for systems containing more than a few transition metal atoms remain beyond the limits of practical feasibility, especially if, as in dynamical simulations, they must be repeated many times. The alternative is to use semiempirical potentials. We employ Voter and Chen's form [1] of an embedded-atom potential V_{EA} to describe the

interatomic interactions in nickel clusters. This potential is fitted to seven properties of bulk nickel (equilibrium lattice constant and cohesive energy, bulk modulus, three cubic elastic constants, and vacancy formation energy), as well as the binding energy and equilibrium bond length of Ni_2 . It is expected to be more adequate for clusters than those potentials that incorporate only properties of bulk matter.

Globally or locally stable structures (isomers) of clusters of different sizes are obtained by simulated thermal quenching from configurations generated along phase space trajectories. These trajectories are produced through constant-energy molecular dynamics simulations. The initial coordinates and momenta of the constituent atoms are defined in such a way as to supply no total linear and angular momenta to the cluster. The forces experienced by the individual atoms are calculated from V_{EA} . The time evolution of the cluster is obtained by solving numerically Hamilton's equations of motion for all atoms. Hamming's modified predictor-corrector propagator is used with a step size of 10^{-15} s. To assure an adequate sampling of the configuration space the trajectories should correspond to sufficiently high values of the internal energy and they have to be run sufficiently long. Even in the longest runs performed ($3 \cdot 10^6$ steps) the total energy is conserved within 0.03%.

The evolution of the dynamics with the cluster energy is analyzed in terms of the following characteristic quantities:

- 1) Short-time averaged (internal) kinetic energy of the cluster per atom $\bar{E}_k$ as a function of time. The goal of the averaging is to suppress the changes in the kinetic energy due to vibrational motion of the atoms. The averaging is performed over intervals of $5 \cdot 10^{-13}$ s. (Note for calibration that the vibrational period of Ni_2 is $1.01 \cdot 10^{-13}$ s, and the period corresponding to the Debye frequency of bulk nickel is $1.18 \cdot 10^{-13}$ s);
- 2) Relative root-mean-square (rms) bond length fluctuation δ ,

$$\delta = \frac{2}{n(n-1)} \sum_{i < j}^n \frac{(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2}}{\langle r_{ij} \rangle}, \quad (1)$$

where n is the number of atoms in a cluster, r_{ij} is the distance between atoms i and j , and $\langle \rangle$ denotes time-averaging over the entire trajectory;

- 3) Mean square displacement $\Delta \bar{r}^2$,

$$\Delta \bar{r}^2(t) = \frac{1}{n \cdot n_t} \sum_{j=1}^{n_t} \sum_{i=1}^n [\bar{r}_i(t_{oj}+t) - \bar{r}_i(t_{oj})]^2, \quad (2)$$

as a function of time t . In Eq. (2), $\bar{r}_i$ is the position vector of atom i and n_t is the number of time origins t_{oj} ;

4) Diffusion coefficient D , which is related to the mean square displacement $\Delta \bar{r}^2$ by the equation

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d(\Delta \bar{r}^2(t))}{dt} . \quad (3)$$

The total interaction energy of the $\text{Ni}_{13} + \text{D}_2$ collision system is described by the potential V ,

$$V = V_{\text{EA}} + V_{\text{LEPS}} , \quad (4)$$

where V_{LEPS} is a London-Eyring-Polanyi-Sato representation of the D-D and D_2 - Ni_{13} interactions. We employ the form of V_{LEPS} suggested by Raghavan et al. [2] and modified by a smoothing function of the form used by Truong et al. [3]. The values of the parameters of V_{LEPS} are those of the potential energy surface (PES) II of Raghavan et al. [2]. These values are chosen to reproduce the binding energy and the binding height of an H atom over a (triangular) face of an icosahedral Ni_{13} as calculated using the so-called corrected effective-medium approach. We examine the adequacy of the PES II by comparing the calculated data on the dissociative adsorption of the molecule on the cluster with the available measured data and suggest a modification of V_{LEPS} that brings the theoretical and experimental results into agreement.

The quasiclassical trajectory approach is used to mimic collisions of D_2 with Ni_{13} . The initial coordinates and momenta of the D atoms are chosen in such a way as to place the center of mass (COM) of the D_2 molecule at a distance 8.5 Å from the COM of the cluster (the energy of interaction of the molecule with the cluster is zero at this distance) and to supply to the molecule amounts of vibrational and rotational energy that correspond to specified vibrational v and rotational j quantum numbers, respectively. The quasiclassical quantization procedure used is described in Ref. [4]. The molecule is propelled toward the cluster with a specified collision (i.e., relative translational) energy E_{tr} and impact parameter b . The initial state of the nontranslating and nonrotating cluster is specified by its geometry and temperature T ,

$$T = \frac{2\langle E_k \rangle}{(3n-6)k} , \quad (5)$$

where E_k is the total internal kinetic energy of the cluster and k is the Boltzmann constant. The time evolution of the collision system is mimicked by solving Hamilton's equations of motion for all fifteen atoms as described above. Upon collision, the molecule either adsorbs on the cluster (dissociatively or nondissociatively) or is scattered by it. The state of molecular adsorption, which we refer to as a *resonance*, is a transient state with a finite lifetime. The cluster-molecule complex is a *reactive* resonance if the adsorbed molecule eventually dissociates on the cluster. The resonance is *nonreactive* if the molecule desorbs from the cluster without ever dissociating. Thus the two ultimate channels of

the cluster-molecule interaction (both may proceed via direct and resonance-mediated pathways) are the reactive one (dissociative adsorption of the molecule) and the nonreactive one (scattering of the molecule). We ran $N=500$ to 10000 trajectories for each fixed set of initial conditions to calculate the probabilities of the two channels. The trajectories for a given set of initial conditions differ by the initial phase of the D_2 oscillator and by the initial relative orientation of the molecule and of the cluster. Each trajectory is propagated until either the D-D separation reaches the value of 2.223 Å (three times the equilibrium bond length of the D_2 molecule), in which case the trajectory is counted as reactive, or the molecule after collision with the cluster returns into the asymptotic region, in which case the trajectory is qualified as nonreactive. The state-specific probability $P_{v,j,T,\dots}(E_{tr},b)$ of a channel is defined as

$$P_{v,j,T,\dots}(E_{tr},b) = \frac{\tilde{N}_{v,j,T,\dots}(E_{tr},b)}{N} , \quad (6)$$

where $\tilde{N}_{v,j,T,\dots}(E_{tr},b)$ is the number of trajectories resulting in the channel of interest. The nonreactive channel probabilities are resolved also with respect to the final states of the molecule and of the cluster (for details see Ref. [5]). Here we consider only the reactive channel. The detailed probabilities are calculated on a grid of energies and impact parameters with increments of $\Delta E_{tr}=0.05$ eV and $\Delta b=0.25$ Å, respectively. The state-resolved reaction cross sections $\sigma_{v,j,T,\dots}(E_{tr})$ are obtained as

$$\sigma_{v,j,T,\dots}(E_{tr}) = 2\pi \int_0^{b_{\max}} b P_{v,j,T,\dots}(E_{tr},b) db , \quad (7)$$

where $b_{\max}$ is the largest impact parameter contributing to the dissociative adsorption of the molecule. The translational-temperature T_{tr} dependent state-specific reaction rate constants $\kappa_{v,j,T,\dots}(T_{tr})$ are calculated using the formula

$$\kappa_{v,j,T,\dots}(T_{tr}) = \pi\mu \left(\frac{2}{\pi\mu k T_{tr}} \right)^{3/2} \int_0^{\infty} \sigma_{v,j,T,\dots}(E_{tr}) E_{tr} \exp\left(-\frac{E_{tr}}{k T_{tr}}\right) dE_{tr} , \quad (8)$$

where μ is the reduced mass of the cluster-molecule collision system.

3. Structures

In Fig. 1 we present the lowest energy structures, as obtained from V_{EA} , for a variety of small nickel clusters [6,7]. The major feature to notice is that these structures, for the cluster sizes shown, are either complete icosahedra (Ni_{13} , Ni_{55}) or icosahedra-based geometries with missing (Ni_9 , Ni_{12} , Ni_{18}) or added (Ni_{14} , Ni_{15} , Ni_{20}) atoms. Ni_{19} is a so-called double icosahedron. Most of these

Figure 1. Most stable structures of Ni_n clusters as obtained from V_{EA} . Their energies in eV are: $n=9$: -25.29; $n=12$: -36.48; $n=13$: -41.12; $n=14$: -44.09; $n=15$: -47.70; $n=18$: -58.52; $n=19$: -63.01; $n=20$: -65.98; $n=55$: -203.02.

structures are in agreement with those calculated using alternative approaches [2,8-11], as well as with the ones inferred from experiments on the reactivity of nickel clusters [12]. Under normal conditions bulk nickel assumes the face-centered cubic (fcc) lattice structure. It emerges as a general rule that the energetically most favorable geometries of small [tens of atoms (molecules)] and intermediate [hundreds to a few thousands of atoms (molecules)] size clusters are different from the corresponding bulk structures of the materials, irrespective of the fact that the nature of the interatomic forces in these materials may be very different. One of the tantalizing questions is what are the critical sizes for clusters of different materials at which they prefer to assume the bulk structure, and how do these sizes depend on the nature (e.g., anisotropy and range) of the interatomic forces [13-15]. A related issue is the pathways of the evolution of the preferred geometries with the cluster size. There are indications that these pathways may be quite intricate in that they may involve polycrystalline states [16].

Another morphological property of clusters is that for fixed sizes they form hierarchies of structural isomers. These isomers correspond to different minima of the $(3n-6)$ -dimensional potential energy surfaces (we abstract ourselves from minima related by permutational symmetry). In Fig. 2 five isomers of Ni_9 obtained from V_{EA} are shown. The energies of some of these isomers are indeed very close.

Figure 2. Isomers of Ni_9 . Their energies in eV are: I: -25.29; II: -25.20; III: -24.86; IV: -24.84; V: -24.65.

Figure 3 displays three highly symmetrical structures of Ni_{13} . The icosahedral (ico) isomer of the cluster is separated from its hexagonal close-packed (hcp) and cuboctahedral (cubo) forms by a relatively large energy gap, whereas the energies of the hcp and the cubo structures are again very close. The cubo structure can be viewed as a fragment of the fcc lattice. The two lowest energy structures of Ni_{14} , as defined by V_{EA} , are obtained by placing an extra atom over a face (threefold hollow site) and over an edge (twofold site), respectively, of the ico Ni_{13} and allowing for a small relaxation. The energy difference between the thus obtained two isomers of Ni_{14} is 0.19 eV. The fact that both have an ico-based structure has a profound effect on the way the dynamics of Ni_{14} responds to an increase of the internal energy of this cluster (see section 4).

Figure 3. Highly symmetrical structures of Ni_{13} .
Their energies in eV are: ico: -41.12; hcp: -39.53; cubo: -39.51.

Figure 4 shows three isomers of Ni_{55} . A 55-atom cluster is the smallest one in which a complete closure of two spherical atomic shells can be achieved. The lowest energy ico form of Ni_{55} is just such a structure. The next isomer in the figure, labeled as "defico", is especially interesting in that its structure is that of an ico with a defect: one of the edge atoms is missing and an extra atom appears on the opposite side of the cluster causing a small relaxation away from the ideal ico geometry. The cubo structure - a fragment of the fcc lattice - is a metastable form of the cluster. A more complete description of the structures of nickel clusters of various sizes, as determined from V_{EA} , will be given elsewhere.

Figure 4. Isomers of Ni_{55} . Their energies in eV are: ico: -203.02; defico: -201.68; cubo: -199.63. The shade-coding is used to establish a correspondence between the structures rather than between the individual atoms of the ico and defico isomers.

4. Isomerization and Melting

In this section we present evidence for isomerization and solid-to-liquid-like transitions in small nickel clusters caused by an increase of their internal energy. In particular, we illustrate the important role of the cluster size and the associated with it structures in determining the particular mechanisms and stages of the meltinglike transition. Bulk melting is usually viewed and treated as a thermodynamic phenomenon. The essence of this phenomenon can, however, be expressed and understood in dynamical terms as a transition from a limited and correlated (periodic) motion of atoms, which is typical for solids, to an essentially uncorrelated motion, which is typical for liquids. More precisely, melting is characterized by a drastic reduction in the characteristic correlation

time and length. Clusters, as systems with a relatively small number of atoms (molecules), afford us the opportunity to carry out detailed dynamical investigations of the analog of the bulk melting in finite systems.

In earlier studies of the meltinglike phenomenon in van der Waals and ionic clusters [17-22] the solid-to-liquid-like transition has been characterized as a change in the cluster dynamics from being confined to a part of configuration space ("catchment area", "basin of attraction") associated with a single, e.g., lowest energy, structure of a cluster to exploring all its possible configurations. We exclude from consideration here those parts of configuration space that correspond to fragmentation of the cluster (cf. Ref. 11). The change in the pattern of dynamics is caused by an increase of the cluster energy. (As specified above, we consider nontranslating and nonrotating clusters, and therefore the total energy of a cluster is its internal energy. In general, the energy may be partitioned between the vibrational modes and the overall rotation; the translational motion is of no consequence for phenomena considered here. For a discussion of the effects of the rotational motion in clusters see Refs. [23-25]). As the cluster energy increases, it reaches the value of the lowest barrier separating the catchment area of the initial geometry from the rest of the configuration space. Then, unless the initial conditions specify a so-called trapped trajectory, the cluster dynamics finds its way out of the basin of attraction of the initial structure, i.e., the cluster undergoes an isomerization transition. As the cluster energy continues to increase so does the number of isomers sampled. Extensive numerical simulations [17-22] confirm the prediction derived from an analytical model [26] that there is a range of energy (or temperature, if temperature is the control parameter) of finite size that separates the solidlike and the liquidlike forms of a cluster. This range represents the isomerization stage in the meltinglike transition. The dynamics carries the cluster through the basins of its different isomeric forms, but between successive isomerization transitions it gets trapped in the catchment areas of the individual isomers for relatively long times (as measured by the characteristic vibrational period of the cluster) so that these isomers can be identified. This stage is called also the "coexistence" stage, and the energy (temperature) range corresponding to it is called the "coexistence" range. Different isomers of the cluster sequentially appear, and in this sense coexist, along the same phase space trajectory. The term acquires a more direct meaning when one considers the ensemble counterparts of the dynamics - microcanonical for constant energy dynamics and canonical for constant temperature dynamics (cf., e.g., Refs. [17,18]). At any energy (temperature) from the coexistence range solidlike and liquidlike clusters coexist within the same corresponding ensemble. With an increase of the energy, not only the number of isomeric forms visited, but also the frequency of isomerization transitions increases. The dwell times between these transitions decrease. A cluster is qualified as liquidlike when its dwell times in the basins of the individual isomers become comparable to or less than its characteristic vibrational period. Numerical simulations [6-9,27-29] confirm that this general picture applies to metal clusters as well. However, these simulations also reveal

that metal clusters may possess new elements in the mechanisms of their meltinglike transition.

In Fig. 5 the time dependence of the short-time averaged kinetic energy (per atom) $\bar{E}_k$ is shown for Ni_{13} at different values of the total energy (per atom) [6]. Graphs a) and b) display an essentially constant $\bar{E}_k$, which, taking into account the constancy of the total energy of the cluster, means constancy of its short-time averaged potential energy. The reason for this constancy is that at energies corresponding to graphs a) and b) the cluster dynamics explores the catchment area of a single isomer - in this case of the lowest energy ico isomer. Thermal quenches from configurations traced out by the trajectories that generate graphs a) and b) confirm this assertion. Graph c), which corresponds to a higher energy of the cluster, displays well-identifiable branches that persist for appreciable times and that are intermittently revisited by the dynamics. These branches represent different averaged potential energies, i.e., different structures of the cluster. The highest- $\bar{E}_k$ branch corresponds to dynamics trapped in the basin(s) of the ico isomer. The lower- $\bar{E}_k$ branches represent sampling of the catchment areas of the higher energy metastable isomers. The pattern of graph c) is typical of the coexistence stage. As the energy of the cluster increases further, the pattern of $\bar{E}_k$ becomes that of graph d). Large fluctuations and the almost complete disappearance of resolvable individual branches indicate frequent interbasin transitions - the cluster becomes liquidlike.

Figure 5. Short-time averaged kinetic energy per atom as a function of time for Ni_{13} . The graphs correspond to the following total energies (in eV) per atom: a) -3.05; b) -2.92; c) -2.73; d) -2.49.

The above assignment of the solidlike and liquidlike states of Ni_{13} is corroborated by Fig. 6. It shows the graphs of the mean square displacement for two energies considered in Fig. 5 (graphs corresponding to the same energy are labeled by the same letter in the two figures). The long-time tale of graph b) has a zero slope indicating no diffusion in the cluster at the energy corresponding to this graph [cf. Eq. (3)]. The cluster is solidlike despite the fact that its temperature exceeds 1000 K (cf. Fig. 7). In contrast, the large slope of graph d), Fig. 6, signifies a well-developed diffusive motion, which is a signature of a liquidlike state. Further corroboration of the meltinglike transition in the cluster is given by Fig. 7. The abrupt increase in the rms bond length fluctuation with the temperature is analogous to the Lindemann criterion of bulk melting [30]. The transition starts only when the temperature of Ni_{13} reaches the value of approximately 1300 K, which indicates a high degree of stability of this cluster. (The melting temperature of bulk nickel is 1726 K). The general qualitative features of the meltinglike transition in Ni_{13} , with a possible exception of its extra stability, are shared by nickel clusters of other sizes, such, for example, as $n=12, 15, 18, 19$, etc. The double-icosahedral Ni_{19} also shows a considerable resistivity to melting. The mechanism of the solid-to-liquid-like transition in these clusters is similar to that in van der Waals and ionic clusters [17-22].

Figure 6. Mean square displacement as a function of time for Ni_{13} . Graphs b) and d) correspond respectively to the same total energies as graphs b) and d) of Fig. 5.

Figure 7. Relative rms bond length fluctuation as a function of cluster temperature for Ni_{13} . Arrows indicate points of the graph that correspond to the total energies considered in Fig. 5.

The picture is quite different for Ni_{14} . The rms bond length fluctuation as a function of temperature is shown for this cluster in Fig. 8. The graph clearly displays two abrupt increases. Such a pattern of δ has not been obtained for nonmetallic clusters. The first increase starts at $T \approx 300$ K and is associated with the so-called premelting phenomenon [6,8,9]. This phenomenon involves only the two lowest energy structures of Ni_{14} mentioned above. It includes a coexistence (isomerization) stage, when the 14-th atom intermittently changes its position from a threefold to a twofold site and back, followed, as the energy increases, by a local melting of the cluster. The local melting involves frequent migrations of the 14-th atom between its threefold and twofold sites and occasional insertion of this atom into the framework of the icosahedral 13-mer. The insertion is accompanied by one of the neighboring atoms of the 13-mer moving outward and becoming the "extra" 14-th atom. The relatively large amplitude motions are localized to the vicinity of the 14-th atom. The rest of the cluster preserves its overall icosahedral symmetry. Premelting is a consequence of the local destabilizing effect of the 14-th atom on the otherwise stable structure of the underlying icosahedral 13-mer. The second abrupt increase of δ takes place at considerably higher temperatures. It signifies complete melting of Ni_{14} . This complete melting requires melting of the underlying icosahedral 13-mer and it includes all the stages described above for Ni_{13} [6]. Inspection of Figs. 7 and 8 shows that, indeed, the second abrupt increase of δ for Ni_{14} takes place over a temperature range that is part of the transition range of Ni_{13} . We have used visualization techniques to disentangle the different elements in the quite intricate melting mechanism of Ni_{14} . The Ni_{20} cluster, which is similar to

Figure 8. Relative rms bond length fluctuation as a function of cluster temperature for Ni_{14} .

Ni_{14} in that its lowest energy structure is obtained by adding an extra atom to an especially stable network - the 19-atom double icosahedron - also exhibits the premelting stage in its meltinglike transition. We conjecture that the premelting phenomenon is a feature of nickel clusters of those sizes that form complete icosahedra with one (or, possibly, more than one for clusters of larger sizes) extra atom. The n-body character of metallic cohesion certainly plays a role in emergence of the premelting phenomenon (cf. Refs. [8,9]). Not all 14-atom metal clusters, however, exhibit it. The reason is that the lowest energy structure of these clusters may be different from that of Ni_{14} . Au_{14} is one example, and it does not exhibit premelting [29]. An important factor in defining the lowest energy structures of metal clusters is the range of the attractive and repulsive components in the n-body interactions.

Yet another possible melting scenario is shown in Fig. 9, which displays the rms bond length fluctuation for Ni_{55} . The ico isomer of the cluster is chosen as its solid form. As mentioned, this isomer contains two complete spherical shells of atoms, and its core is a 13-atom icosahedron. The graphs show the temperature dependence of δ calculated for the surface, core, and all atoms of the cluster. Whereas the network of the 42 surface atoms that form the external shell begins to undergo a meltinglike transition at $T \approx 850$ K, the core remains solidlike up to $T \approx 1100$ K. Thus, there is a finite temperature range for which Ni_{55} can be viewed as a liquidlike mantle encapsulating a solidlike core. At $T \approx 1200$ K the entire cluster becomes liquidlike. Analysis of other physical quantities, for example of the diffusion coefficients, confirms the phenomenon

of surface melting in Ni_{55} (the details are given in Ref. [7]). Surface melting has also been predicted for Cu_{55} and noble gas clusters of a variety of sizes [31], as well as gold clusters of larger sizes [32].

Figure 9. Relative rms bond length fluctuation as a function of cluster temperature for Ni_{55} (see text).

5. Reactivity

In this section we present results on the reaction $\text{Ni}_{13} + \text{D}_2 \rightarrow \text{Ni}_{13} \cdot 2\text{D}$ [5,33-36]. First we consider results obtained with the PES II (see section 2) parameters of V_{LEPS} . The cross sections of the dissociative adsorption as a function of the collision energy are shown for the room-temperature ico Ni_{13} and different initial rovibrational states of D_2 in Fig. 10. The $(v=0, j=10)$ and $(v=1, j=0)$ states of the molecule are energetically almost degenerate. They are chosen to test the mode-selectivity of the reaction, i.e., its sensitivity to the initial partitioning of the energy between the vibration and rotation of the molecule. The major features displayed by Fig. 10 are: 1) the reactivity of the cluster increases monotonically with an increase of the system collision energy; 2) in order to initiate the reaction the collision energy has to be larger than a (small) (v, j) -dependent threshold value; 3) larger initial rovibrational energy of the molecule results in larger reaction cross sections; 4) the reaction is mode-selective - an initial vibrational excitation of the molecule leads to considerably larger reaction cross sections than an energetically equal initial rotational

excitation. We have determined that change of the initial cluster temperature in the range $T=0$ -300 K has no effect on the graphs of Fig. 10 (cf. also below).

Figure 10. Reaction cross sections as functions of the collision energy for a room-temperature ico Ni_{13} . The different graphs correspond to different initial rovibrational states of D_2 .

Because the cubo and hcp structures of Ni_{13} are metastable, the reactivity of these forms is studied at zero initial temperature of the cluster. The reaction cross sections for the cubo and hcp geometries are shown in separate panels of Fig. 11. The qualitative features of the corresponding graphs in the two panels are strikingly similar, with the cubo structure being slightly more reactive. As in the case of the ico isomer, higher initial rovibrational energies of D_2 result in larger cross sections, and the reaction remains mode-selective. In all other respects the features of the graphs in Fig. 11 are different from those in Fig. 10. Overall, the cubo and hcp forms of Ni_{13} are more reactive than its ico isomer. The molecule dissociates on the cubo and hcp clusters at any collision energy. But more importantly, the graphs of Fig. 11 show a nonmonotonic change of the reaction cross section with the collision energy. Especially intriguing are the peaks in the graphs at very low collision energies. We have used time-dependent reaction probabilities and cross sections to differentiate between the direct and the precursor-mediated reaction pathways [33,34,36] and determined that these peaks are almost entirely due to formation of reactive resonances. At very low collision energies the probability of molecular adsorption ("sticking") on the cluster is high. This is true for all three structures of Ni_{13} considered here. A large fraction of the adsorbed D_2 molecules then proceeds to dissociate on the cubo and hcp forms of the cluster. In contrast, the precursor states

Figure 11. The same as Fig. 10 but for zero-temperature cubo and hcp forms of Ni_{13} .

formed on the ico Ni_{13} at low collision energies turn out to be nonreactive resonances, i.e., the adsorbed D_2 molecules eventually desorb from the cluster without ever dissociating. As a consequence, the graphs of Fig. 10 do not possess the low- E_{tr} peaks. Upon increase of the collision energy the probability of molecular adsorption and, consequently, of the indirect reaction, decreases. This is the reason for the decrease of the cross sections over a finite range of E_{tr} exhibited by the graphs of Fig. 11. As the collision energy continues to increase, the direct reaction begins to play a more important role. Its probability increases with E_{tr} , and eventually the cross sections become increasing functions with values that are less sensitive to the cluster structure. It is clearly the difference in the surface topology of the ico isomer, on the one hand, and of the cubo and hcp forms, on the other, that is responsible for the difference in the low- E_{tr} parts of the graphs in Figs. 10 and 11. The ico isomer has only threefold faces whereas the cubo and hcp structures possess threefold and fourfold faces. (An energy argument regarding the difference in the reactivity of the different structures of Ni_{13} at low collision energies is given below). Characteristic results on the reactive resonance formation probabilities and lifetimes, as well as the branching ratio between the direct and indirect reaction pathways are given in Table 1 (for details see Refs. [33,34,36]). With increase of the collision energy, the lifetime of the reactive resonances decreases and the relative contribution of the direct reaction into the process of dissociative adsorption of the molecule increases. Experimental evidence corroborating the important role of reactive resonances in reaction of D_2 with nickel clusters has been obtained recently [37,38].

For the ico isomer one can examine the effect of the cluster temperature on its reactivity. Results covering a broad temperature range are shown in Fig. 12.

TABLE 1. Probabilities $P_{...}^{DR}$ and $P_{...}^{IR}$ of the direct and indirect reaction, respectively, fractional contribution $f_{...}^{DR}$ of the direct reaction, and reactive resonance lifetime $\tau_{...}$ for a cubo Ni_{13} ($T=0K$), $D_2(v=1, j=0)$, $b=0.25$ Å and different values of E_{tr} .

E_{tr} (eV)	0.038	0.30	0.50	0.90
$P_{...}^{DR}$	0.06	0.11	0.13	0.20
$P_{...}^{IR}$	0.44	0.39	0.52	0.57
$f_{...}^{DR}$ (%)	12	22	19	26
$\tau_{...}(ps)$	0.07	0.03	0.02	0.01

As mentioned, the reactivity of the cluster does not change in the range $T=0$ -300 K. This has been confirmed experimentally [37]. Because of the relatively large mass of nickel atoms, heating from 0 to 300 K causes only slow motions in the cluster and only small departures in its structure from the ideal

Figure 12. Reaction cross sections as functions of the collision energy for dissociative adsorption of $D_2(v=0, j=3)$ on an ico Ni_{13} at different initial temperatures T of the cluster.

icosahedral geometry. It is somewhat surprising, however, that further heating and even melting of the cluster has only a minor effect on its reactivity.

Whereas a number of predictions [5,33-36] derived using the PES II parameterization of V_{LEPS} has been confirmed experimentally, the computed value of the reaction rate constant at room temperature turns out to be orders of magnitude lower than that inferred from the experiments [37]. This indicates that the original PES II parameterization has to be modified. As a guidance for "tuning" of V_{LEPS} we used the following considerations. The binding energy of a D atom in a threefold hollow site of an ico Ni_{13} calculated using the original V_{LEPS} is 2.43 eV. This value is about 10% lower than the measured energy of binding of a D atom to the (111) and (100) faces of bulk nickel. No experimental or ab initio results on the D- Ni_{13} binding energy are available at present. Arguments have, however, been put forward [39] that this energy may be close to or even exceed the corresponding value for the atom-surface binding. We modified the PES II parameters [35,36] so that the "tuned" V_{LEPS} gives a 10% larger D- $Ni_{13}(ico)$ binding energy than the original one. The reaction cross section calculated with the modified V_{LEPS} for the case of a room-temperature ico isomer of the cluster and ($v=0, j=3$) initial rovibrational state of D_2 is shown in Fig. 13.

Figure 13. Reaction cross sections for room-temperature ico (full squares) and zero-temperature cubo (empty squares) forms of Ni_{13} obtained using the "tuned" V_{LEPS} . The graphs correspond to $D_2(v=0, j=3)$.

Comparison with the corresponding graph of Fig. 10 shows that the modified V_{LEPS} results in a much higher reactivity of the ico cluster. The reaction rate constant at room temperature computed using the cross sections of Fig. 13 is $3 \cdot 10^{-10} \text{ cm}^3/\text{s}$. This value is in good agreement with the experimentally derived estimate of $(8 \pm 4) \cdot 10^{-10} \text{ cm}^3/\text{s}$ [37].

Tuning of V_{LEPS} also has a profound effect on the qualitative characteristics of the reactivity of ico Ni_{13} . The low- E_{tr} peak in the graph of Fig. 13 corresponding to this isomer indicates that with the modified V_{LEPS} the ico form of the cluster also supports reactive resonances. The figure displays the reaction cross section obtained with the modified V_{LEPS} for the cubo isomer as well. The ico and cubo forms of the cluster show now almost identical reactivities, except at very low collision energies where the cubo isomer is slightly more reactive. Regarding the temperature dependence of the reactivity, the modified V_{LEPS} gives essentially the same result as the original one. Except at low E_{tr} , the reactivity of the ico isomer is practically independent of its temperature. The only noticeable effect is the gradual disappearance of the low- E_{tr} peak in the graph as the cluster temperature increases [40]. The reason for this is that the resonance formation probabilities (cross sections) are decreasing functions of the cluster temperature.

In order to understand the profound effects of a relatively minor modification of the cluster-molecule interaction potential (the modification performed is within the limits of uncertainty of the original PES II parameters) we have mapped out the original and the tuned V_{LEPS} functions (for details see Refs. [35,36]). The minimum energy paths (MEPs) defined by these functions for ico Ni_{13} are shown together with the Morse potential (and the zero-point energy) of D_2 as functions of the D-D distance in Fig. 14. The minima in the MEPs with the smallest D-D separation are the molecular adsorption wells. The next five minima that correspond to larger D-D distances are the dissociative adsorption wells. They represent the five topologically different possible pairs of threefold faces of the ico isomer as preferred sites for adsorption of two D atoms. The maxima between the dissociative adsorption wells are the diffusion barriers. They correspond to one of the D atoms being over a threefold site (face) and the other over a twofold site (edge) of the cluster. The maxima separating the molecular adsorption wells are the dissociation barriers. The zero-point energy of D_2 is below the dissociation barrier defined by the original V_{LEPS} . This explains the collision energy thresholds in Fig. 10 and the fact that the low- E_{tr} resonances are nonreactive. The dissociation barriers defined by the original V_{LEPS} for the cubo and hcp forms of the cluster are lower than the zero-point energy of D_2 (not shown) [40], which explains the qualitative and quantitative differences between the graphs of Figs. 10 and 11. As seen in Fig. 14, apart from a 10% downward shift, the performed modification of V_{LEPS} does not change the "topology" of the exit channel part of the original MEP. It does, however, have a considerable effect on the transition state. The dissociation barrier gets reduced quite substantially, and its value becomes lower than the zero-point energy of D_2 . Figure 13 reflects the consequences of this change. Further discussion on tuning of V_{LEPS} and its implications can be found in

Refs. [35,36]. Here we remark only that use of parameterized potentials appears to be at present (and will, probably, remain for quite some time) the only feasible way for carrying out comprehensive simulation studies of systems as complex as clusters interacting with molecules. An adequate representation of the cluster-molecule interaction is of paramount importance. It can be achieved only through an intimate interplay between theoretical dynamics, ab initio calculations, and experiment.

Figure 14. The minimum energy paths corresponding to the PES II and the "tuned" parameterizations of V_{LEPS} as functions of the D-D separation for the case when the cluster is frozen in its ico geometry. The Morse potential and the zero-point energy of D_2 are also shown.

6. Summary

We have presented here a sample of results on the structural and dynamical properties of nickel clusters derived from numerical simulations. These properties are exhibited through the response of the clusters to an increase of their internal energy and through their chemical reactivity.

The interatomic interactions in the clusters are mimicked by a many-body embedded-atom potential. The most stable isomers of small nickel clusters obtained from this potential tend to favor icosahedra-based structures. The clusters exhibit a characteristic meltinglike transition as their internal energy is increased. Distinct stages in this transition can be identified, which depend on

the cluster size. A novel feature exhibited by Ni_{14} (Ni_{20} , etc.) is premelting or, alternatively, local melting. It is quite remarkable that in a system containing only 14-atoms a liquidlike part can coexist with a solidlike. This coexistence within the same cluster is different from the "canonical" coexistence between liquidlike and solidlike clusters of the same energy (or temperature). The meltinglike transition in the Ni_{55} cluster includes the stage of surface melting - a phenomenon that has been found to be more generic and shared not only by metal clusters.

Cluster-molecule interactions, more specifically reactions, can be characterized at the same level of detail as the more extensively studied atom-molecule, molecule-molecule, and gas-surface interactions. We have presented here results on the dissociative adsorption of D_2 on Ni_{13} and described the dependence of this reaction on the system collision energy, initial rovibrational state of the molecule and the structure and temperature of the cluster. The reaction may be direct or resonance-mediated. The resonances are characterized in terms of their formation probabilities and lifetimes, both of which depend on the collision energy. An important issue is the correlation and agreement (or lack of it) between the computed and measured data. We have used the experimental value of the D-nickel-surface binding energy to modify ("tune") the D_2 - Ni_{13} interaction potential and have shown that this modification brings the computed and the measured rate constants of the dissociative adsorption of the molecule on the cluster into agreement.

7. References

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