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# MODE SELECTIVITY IN CLUSTER-MOLECULE INTERACTIONS:

# $Ni_{13} + D_2$*

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## DISCLAIMER

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ABSTRACT. Results of a detailed quasiclassical simulation study of the $Ni_{13} + D_2$ collision system are presented. The dissociative adsorption of the molecule as well as its scattering from the cluster are analyzed as functions of the initial rovibrational molecular state, collision energy and structure of the cluster. Mode-specific features of the reactive and nonreactive channels of the cluster-molecule interaction are displayed and discussed. Evidence for resonances and for a strong cluster structure-reactivity correlation is presented.

## 1.  Introduction

Chemical reactivity of atomic and molecular clusters or, more generally, interactions of clusters with individual atoms and molecules, is a research area "at the beginning of the road". The interest in these interactions grew out of the special conceptual role of clusters as a new "bridging" (between atoms/molecules and solids/liquids) phase of matter, and of the recognition of the importance of cluster-molecule interactions in practical applications as well as in natural phenomena (e.g., in the upper atmosphere and in the soil). Heterogeneous catalysis is one of the processes the control over which may be greatly enhanced through the understanding of the mechanisms of cluster-molecule, especially metal cluster-molecule, interactions.

In recent years a variety of experimental studies was performed [1] to probe the kinetics and energetics of metal cluster-molecule reactions. Most of the theoretical work, however, was focused on interactions of molecules with metal surfaces [2]. Although clusters were used in some of these studies to represent the metal surface, their relevance in the context of cluster-molecule interactions is limited by two factors: (1) the clusters were chosen as slabs of a crystal lattice, (2) the slabs were often assumed to be rigid. Only a few theoretical investigations addressed the problem of metal cluster-molecule interaction as the central subject. These can be divided into electronic structure calculations [3] and dynamical treatments [4,5]. The former identify preferred binding sites and yield binding energies as well as (a usually restricted) mapping of the potential energy surface and of the reaction path. The dynamical treatments use model or

semiempirical potentials to characterize the time-evolution of a cluster-atom or a cluster-molecule collision system; they quantify the different processes in terms of probabilities, cross sections, rate constants, etc.

Reactions of $D_2$ with $Ni_n$, n = 4-13, were treated dynamically by Raghavan, Stave and DePristo (RSD) [4] under the assumption that the clusters are rigid [6]. We have performed an extensive quasiclassical simulation study of the $Ni_{13} + D_2$ collision system allowing for all degrees of freedom of the system to participate in the dynamics. A partial account of the results for the reactive channel (dissociative chemisorption of $D_2$ on an icosahedral $Ni_{13}$) has been given [7]. Here we present a more complete account which includes effects of cluster structure as well as state-to-state data for inelastic scattering of the molecule on the cluster. In section 2, the interaction potential and the computational details are outlined. The results, including mode-selective features of the interaction, and their discussion are given in section 3. We conclude with a summary in section 4.

## 2. The Potential and Computational Details

The potential energy surface (PES) V defining the forces acting on each atom in the $Ni_{13} + D_2$ collision system is of the form

$$V = V_{EA} + V_{LEPS},\tag{1}$$

where $V_{EA}$ is a so-called embedded-atom potential describing the interactions between Ni atoms in the cluster, and $V_{LEPS}$ is a LEPS (London-Eyring-Polanyi-Sato) function mimicking the intramolecular (D-D) and molecule-cluster interactions. We have employed Voter and Chen's [8] parameterization of $V_{EA}$ which, in addition to a number of bulk properties of nickel, also correctly reproduces the equilibrium bond length (2.2 Å) and bond energy (~1.95 eV) of $Ni_2$. The so-parameterized embedded-atom potential can be expected to be of relevance for the intermediate size range, i.e., clusters, as well. The LEPS function is the PESII of RSD [4], modified by a smoothing function used by Truong et al. [9] (details will be given elsewhere). We have chosen PESII, rather than PESI employed by RSD, because the former was fitted to reproduce the binding energy and the binding height of an H atom on a threefold site of an icosahedral $Ni_{13}$ as calculated in the framework of the corrected effective medium (CEM) approach [4]; the parameters of PESI, on the other hand, were determined from dynamical simulations of the dissociative chemisorption of $H_2$ on different faces of the bulk (fcc) nickel [10].

The time-evolution of the $Ni_{13} + D_2$ collision system was obtained by solving numerically Hamilton's equations of motion for all 15 atoms. A fourth-order variable step-size predictor-corrector propagator was employed. Choice of the maximal step sizes of $5 \times 10^{-16} - 10^{-15}$ sec assured conservation of the total energy as well as of the total linear and angular momenta within 0.03-0.15%. The initial conditions were specified as follows. Nontranslating and nonrotating $Ni_{13}$ clusters were prepared in an icosahedral (ico), cubooctahedral (cubo) or hexagonal closed-packed (hcp) structure at temperature T defined as

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

where $E_k$ and n are the total kinetic energy and the number of atoms in the cluster, respectively, k is the Boltzmann constant, and $< >$ denotes time averaging. The center of mass of the $D_2$ molecule was placed asymptotically far (8.5 Å) from the center of mass of the cluster, and the initial coordinates and momenta of the D atoms were chosen in accordance with a quasiclassical prescription [11] to define a desired initial quantal vibrational $v_i$ and rotational $j_i$ state of $D_2$. The molecule was sent towards the cluster with a specified initial relative kinetic (collision) energy $E_{tr}^i$ and impact parameter b. The collision event (trajectory) was qualified as reactive when it resulted in a dissociative adsorption of the molecule on the cluster; the molecule was deemed to be dissociated when the D-D bond length exceeded the value of 2.223 Å (three times the equilibrium D-D bond length). The collision could result in a nonreactive scattering of the molecule from the cluster. Upon reaching the asymptotic region, the scattered $D_2$ molecule was characterized by its final relative translational energy $E_{tr}^f$, final vibrational $v_f$ and rotational $j_f$ quantum numbers defined as rounded off to the closest integer

$$v_f = - \frac{1}{2} + \frac{1}{h} \oint p_r dr \tag{3}$$

and

$$j_f = -\frac{1}{2} + \frac{1}{2} \left( 1 + \frac{16\pi^2 J_f^2}{h^2} \right)^{1/2} , \tag{4}$$

where r and $p_r$ are the D-D bond length and its conjugate momentum, respectively; $J_f$ is the magnitude of the classical final rotational angular momentum of the molecule; and h is Planck's constant. We have found that each of the final channels of the interaction (reactive or nonreactive) could be reached through a direct process or via a molecularly adsorbed precursor state. Some of the precursor states had quite long lifetimes. Care was taken to run each trajectory long enough to allow for the molecule to dissociate or, in the case of scattering, to reach the asymptotic region. In the case of dissociative adsorption the trajectory was terminated as soon as the dissociation criterion was met, thus preventing a possible recombination and subsequent desorption of the molecule.

Five hundred trajectories were run for each fixed set of initial conditions. These trajectories differed in the initial orientation of the molecule and of the cluster, and in the initial phase of the $D_2$ oscillator. The $E_{tr}^i$- and b-dependent probabilities $P_{v_i,j_i,T,...}(E_{tr}^i,b)$ of the different processes (dissociative chemisorption, scattering of the molecule) labeled by the initial and, if appropriate, final state parameters were calculated as

$$P_{v_i,j_i,T,...}(E_{tr}^i,b) = \frac{\tilde{N}_{v_i,j_i,T,...}(E_{tr}^i,b)}{N}, \tag{5}$$

where $\tilde{N}...$ is the number of trajectories resulting in the process of interest, and N = 500. The cross sections $\sigma...$ of the processes were determined in accordance with

$$\sigma_{v_i,j_i,T,...}(E_{tr}^i) = 2\pi \int_0^{b_{max}} b P_{v_i,j_i,T,...}(E_{tr}^i,b)db, \tag{6}$$

where $b_{max}$ is (in the reactive case, for which the cross sections are presented in the next section) the lowest value of b at which $P...(E^i_{tr},b) = 0$. The translational temperature $T_{tr}$ dependent state-resolved rate constants $\kappa...(T_{tr})$ were obtained from

$$\kappa_{v_i,j_i,T,...}(T_{tr}) = \pi\mu\left(\frac{2}{\pi\mu kT_{tr}}\right)^{3/2}\int_0^\infty \sigma_{v_i,j_i,T,...}(E^i_{tr})E^i_{tr}\exp\left(-\frac{E^i_{tr}}{kT_{tr}}\right)dE^i_{tr}, \qquad (7)$$

where $\mu$ is the reduced mass of the cluster-molecule system. The low-temperature segments of $\kappa...(T_{tr})$ were fitted to the Arrhenius formula

$$\kappa_{v_i,j_i,T,...}(T_{tr}) = A_{v_i,j_i,T,...}\exp\left(-\frac{E_A^{v_i,j_i,T,...}}{RT_{tr}}\right) \qquad (8)$$

to extract state-specific (translational) activation energies $E_A^{...}$; R in Eq. 8 is the universal gas constant.

## 3. Results and Discussion

Here we display and discuss some representative results for the reactive and nonreactive channels of the interaction of a $D_2$ molecule with a $Ni_{13}$ cluster. It has been predicted by CEM calculations [4] and also using an embedded-atom potential [12] that the icosahedral packing is the lowest-energy, most stable geometry of $Ni_{13}$. The less stable hcp and cubooctahedral structures of $Ni_{13}$ are almost degenerate energetically with the cubooctahedron possibly being just a bit higher in energy. In Fig. 1 the cross sections for dissociative chemisorption of the molecule on an icosahedral $Ni_{13}$, initially at room temperature, are shown as functions of the collision energy for different initial rovibrational states of $D_2$. The $(v_i=0, j_i=3)$ state was considered because it is the most populated at room temperature. The choice of the $(v_i=1, j_i=0)$ and $(v_i=0, j_i=10)$ states was motivated by the fact that they have almost equal energies and thus are appropriate for testing the mode-selectivity of the cluster-molecule interaction. It is seen in the figure that for all the cases considered the cross sections display a small but nonzero threshold value of $E^i_{tr}$ below which they are zero and above which they increase monotonically with $E^i_{tr}$. The higher the initial rovibrational energy of the molecule, the lower the value of the threshold energy and the larger the corresponding cross sections of the dissociative adsorption. While an increase of the probability of breaking the D-D bond with an increase of total energy (higher $E^i_{tr}$ and/or higher initial rovibrational energy of $D_2$) is quite a natural result, a decrease in the threshold value of $E^i_{tr}$ is a more intricate phenomenon. It can be a consequence of (a) a decrease, with an increase of $v_i$ or $j_i$, of an adiabatic-type barrier encountered by the impinging molecule; (b) an enhanced dynamical coupling which channels part of the rovibrational energy into the "reaction coordinate" and thereby helps the molecule to climb the activation barrier; (c) both. Comparison of the cases $(v_i=1, j_i=0)$ and $(v_i=0, j_i=10)$ points clearly to the mode-selectivity of the reaction: an initial vibrational excitation of $D_2$ results in substantially larger cross sections

for dissociative adsorption than an energetically equal (in fact, by 0.023 eV even higher) initial rotational excitation. Although the threshold values of the collision energy are very close for these two cases, the reactive cross section grows initially much faster for $(v_i=1, j_i=0)$. At large $E_{tr}^i$'s the cross sections grow almost linearly and with the same rate for both cases.
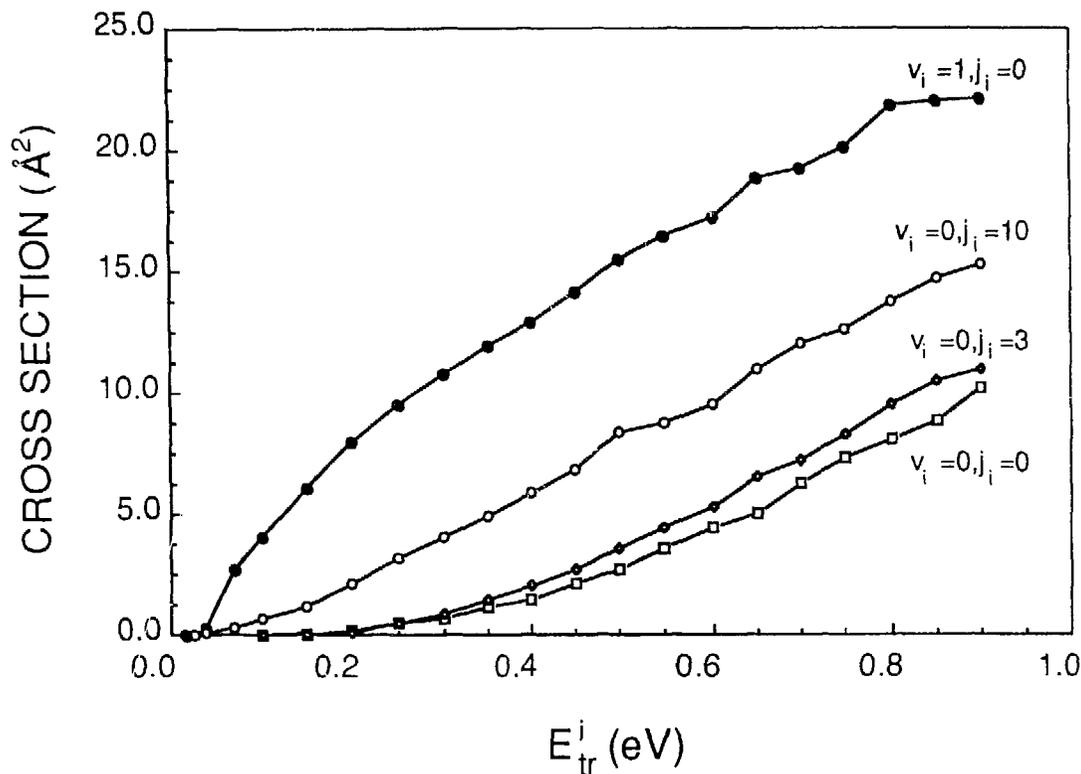


Figure 1. Cross sections of dissociative adsorption of $D_2(v_i, j_i)$ on a room-temperature icosahedral $Ni_{13}$ as functions of the collision energy.

Fig. 2 displays the calculated rate constants (circles) for the dissociative adsorption of $D_2(v_i=1, j_i=0)$ and $D_2(v_i=0, j_i=10)$ on a room-temperature icosahedral $Ni_{13}$. The rate constants clearly behave in a non-Arrhenius fashion. Their low-translational-temperature segments can, however, be fitted to straight lines. The activation energies extracted from the fits are 0.027 eV for the $(v_i=1, j_i=0)$ case and 0.031 eV for the $(v_i=0, j_i=10)$ case. These values are in excellent agreement with the corresponding threshold energies (cf. Fig. 1). An agreement between the threshold energies and the activation energies extracted from the fits of the low-temperature segments of the corresponding rate constants has been found for all the $(v_i, j_i)$ cases considered. This suggests that the state-specified threshold energies can be interpreted as measures of the heights of the state-dependent *dynamical* barriers for dissociative adsorption of the molecule on the cluster.

$10^{-9}$

$10^{-10}$

$10^{-11}$

$10^{-12}$

$10^{-13}$

$10^{-14}$

$10^{-15}$

$10^{-16}$

$10^{-17}$

$10^{-18}$

$\kappa (cm^3 /sec)$

$E_A^{\bullet} = 0.654$ kcal / mol (0.027 eV)

$E_A^{\circ} = 0.731$ kcal / mol (0.031 eV)

$v_i = 1, j_i = 0$

$v_i = 0, j_i = 10$

0     10     20     30     40
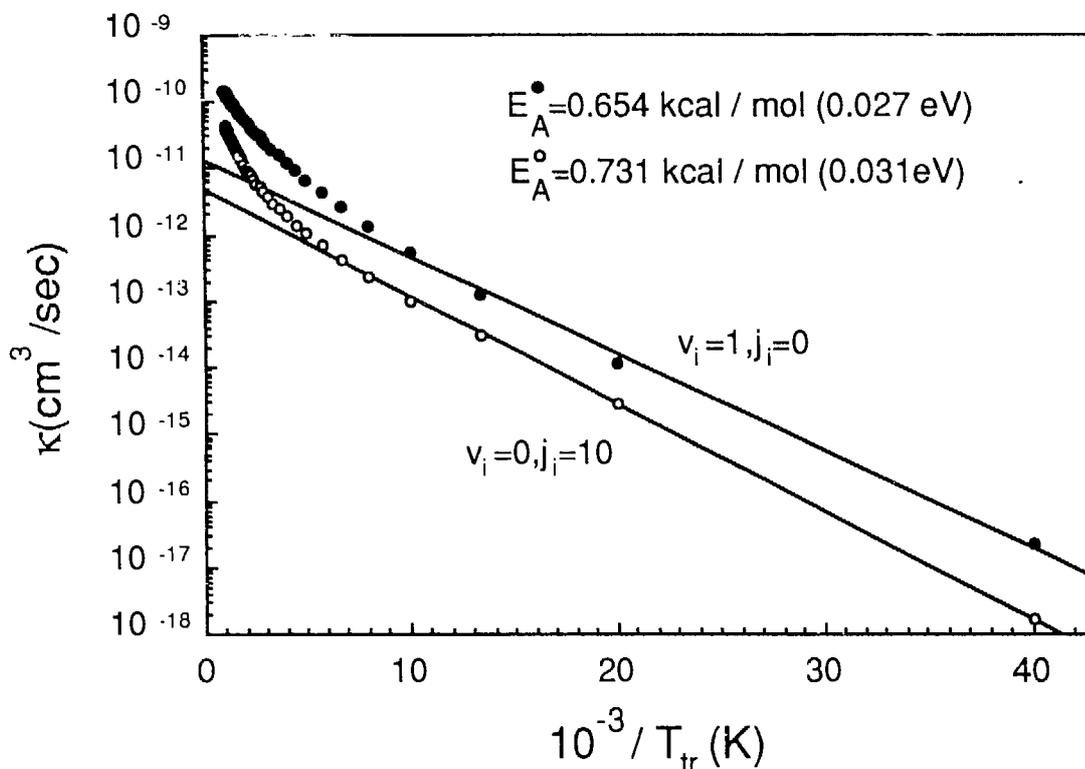
$10^{-3} / T_{tr}$ (K)

Figure 2. Rate constants of dissociative adsorption of $D_2(v_i, j_i)$ on a room-temperature icosahedral $Ni_{13}$ as functions of the translational ("collision") temperature. The circles are the calculated results, the lines are the Arrhenius fits in the low-temperature regime. $E_A$ are the activation energies extracted from the fits.

In Fig. 3 the cross sections of dissociative adsorption on a zero-temperature cubooctahedral $Ni_{13}$ are shown for different $(v_i, j_i)$ states of $D_2$. The large differences in the cross sections for the $(v_i=1, j_i=0)$ and $(v_i=0, j_i=10)$ cases indicate again a pronounced mode-selectivity of the reaction. However, the most striking feature of Fig. 3 is the nonmonotonic behavior of the cross sections. Particularly intriguing are the peaks for the $(v_i=1, j_i=0)$ and $(v_i=0, j_i=10)$ cases at very low collision energies. We have found that at these energies the predominant pathway for the reaction is the one involving molecularly adsorbed precursor states. The peaks thus can be identified with reaction resonances. Other distinctive features of reactivity of the cubooctahedral $Ni_{13}$ are that the cross sections do not indicate any thresholds (barriers) for the reaction and they are larger than the corresponding cross sections for the icosahedral $Ni_{13}$.
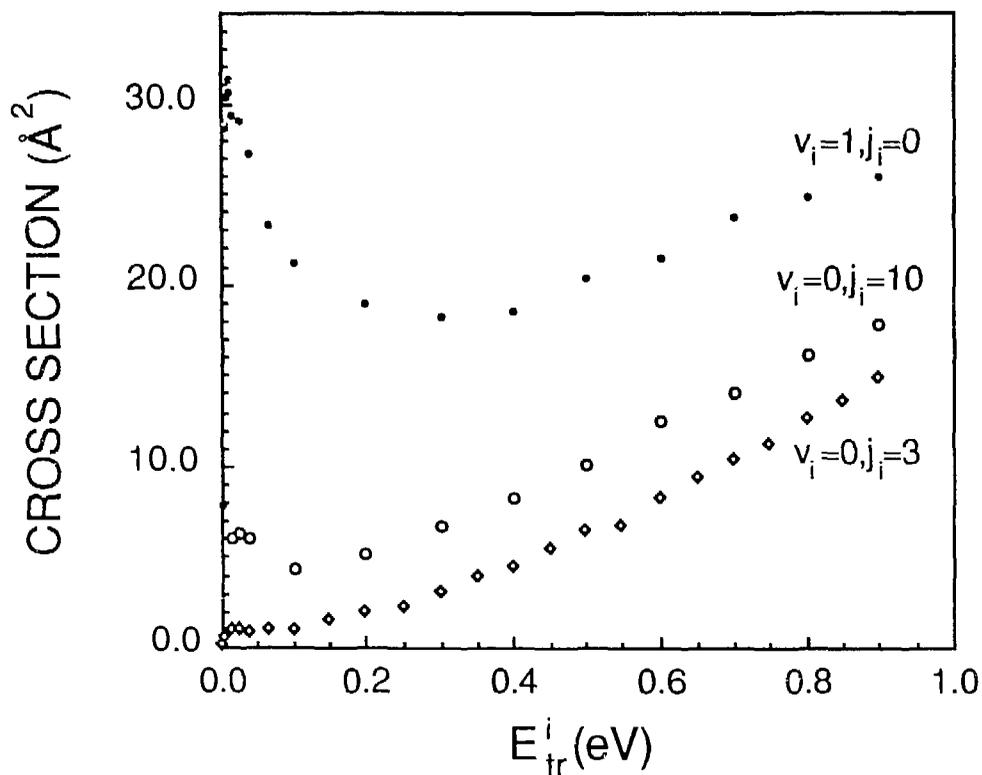
Figure 3. Cross sections of dissociative adsorption of $D_2(v_i, j_i)$ on a zero-temperature cubooctahedral $Ni_{13}$ as functions of the collision energy.

The features of dissociative adsorption of $D_2$ on a zero-temperature hcp $Ni_{13}$ are essentially the same as those for the cubooctahedral $Ni_{13}$. The only difference is that for most $E_{tr}^i$'s the magnitudes of the cross sections for the hcp cluster are slightly lower than the corresponding values for the cubooctahedral cluster. Figs. 4 and 5 show the reactive cross sections for the ($v_i=0$, $j_i=3$) and ($v_i=1$, $j_i=0$) initial molecular states, respectively, and each of the three isomers of the cluster. The cluster structure-reactivity correlation is apparent. Its features can be summarized as follows. The reactivity of $Ni_{13}$ changes inversely with the stability of its structure; this is in agreement with what has been found by RSD [4] for rigid isomers of $Ni_{13}$ interacting with a $D_2(v_i=0$, $j_i=0)$. The qualitative features of the $E_{tr}^i$-dependence of the reaction cross sections for the hcp and cubooctahedral geometries are drastically different from those for the icosahedral structure. The qualitative dissimilarities (e.g., presence or absence of thresholds and of resonance peaks) are particularly pronounced at low collision energies, at which the molecule stays a longer time in the vicinity of the cluster surface. Taking, in addition, into account that the reactivity properties of the hcp and of the cubooctahedral structures closely resemble each other even in details and that the surface topologies of these two structures are very similar (for example, both have threefold and fourfold faces, while the icosahedron has only threefold faces), one is led to the conclusion that the topology of the cluster surface (or its structure) is another "initial condition" or "mode" which affects its
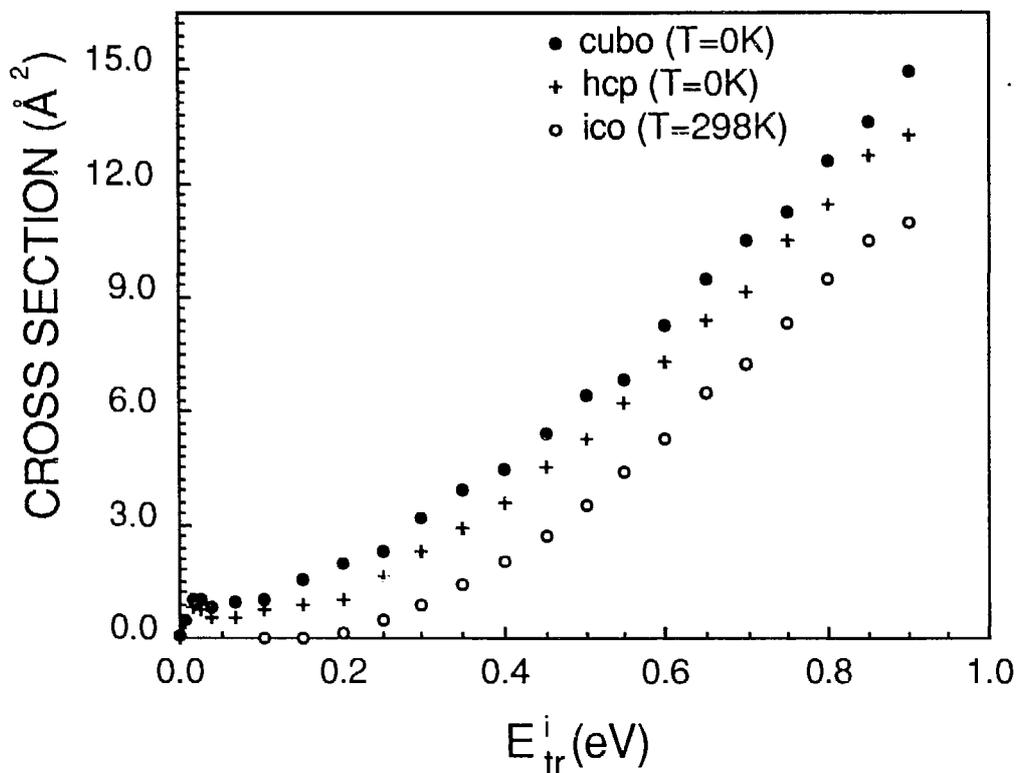
**Figure 4.** Cross sections of dissociative adsorption of $D_2(v_i=0, j_i=3)$ on three isomers (ico, hcp and cubo) of $Ni_{13}$ as functions of the collision energy.

reactivity. As seen in the figures, the effect of this "mode" diminishes at high collision energies. (It should be remarked that the hcp and cubooctahedral geometries of $Ni_{13}$, as defined by the embedded-atom potential, are metastable minimum energy structures in that they are not separated by a computationally detectable barrier from the icosahedral structure. This was the reason for "preparing" them initially at T=0K. Interaction with a $D_2$ molecule, either reactive or nonreactive, triggers a structural "fluctuation" to the icosahedral geometry. The induction time for the structural change is, however, much longer than the collision or reaction time. The fact that the results are compared to those for an icosahedral $Ni_{13}$ at room temperature is of no consequence since the reactivity features of the latter are insensitive to temperature changes in the range 0-298K [7]). The dependence of the reactivity of a cluster on its structure has been utilized recently [13] to measure the ionization potentials for different isomers of niobium clusters.
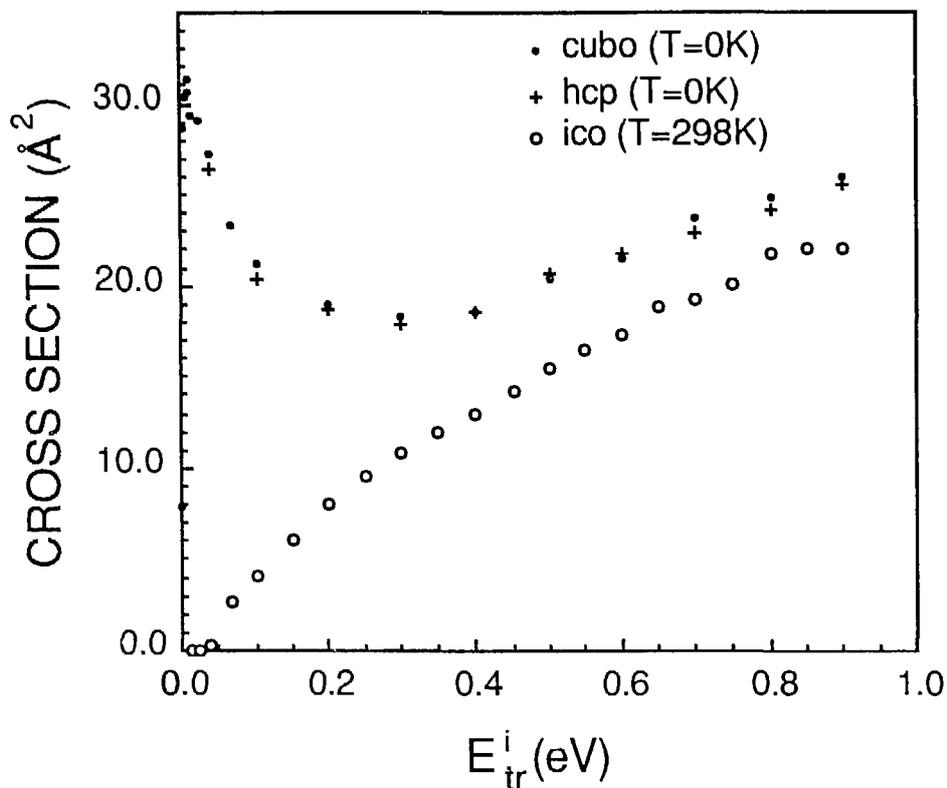
Figure 5. The same as Figure 4 but for $D_2(v_i=1, j_i=0)$.

We turn now to a brief discussion of the nonreactive interaction of $D_2$ with $Ni_{13}$. In Fig. 6 the probability distributions of the final vibrationally ($v_f$) and rotationally ($j_f$) resolved states of $D_2$ scattered from a room-temperature icosahedral $Ni_{13}$ are shown. The collision energy is 0.9eV. Three panels, corresponding to different impact parameters, are displayed for each of the ($v_i=0, j_i=0$), ($v_i=1, j_i=0$) and ($v_i=0, j_i=10$) cases. Each $P_{v_f}$ is the (summed over the final rotational states) total probability of a specified final vibrational state. By adding up all the $P_{v_f}$'s, one arrives at the initial-state-resolved total probability of the nonreactive scattering. One easily verifies that this latter is an increasing function of the impact parameter b for all three ($v_i, j_i$) cases (cf. Ref. [7]). At large impact parameters the molecule samples only the peripheral parts of the potential where the weak dynamical couplings channel less energy into the D-D bond. This makes the probability of the dissociative adsorption lower and, consequently, of the nonreactive scattering higher. The same reasoning applies to the b-dependence of the probability distributions of the final rovibrational states of the molecule for the ($v_i=0, j_i=0$) and ($v_i=0, j_i=10$) cases. At low impact parameters and high collision energies, as in this case, the molecule penetrates deeply into the core part of the potential where the strong translational-vibrational and rotational-vibrational couplings result not only in bond breaking but also in populating the initially unoccupied $v_f = 1,2$ and possibly even $v_f = 3$ states. As the impact parameter increases, $v_f = 0$ becomes by far the most probable state. The pattern of the probability distributions of the final rovibrational states is very different for the
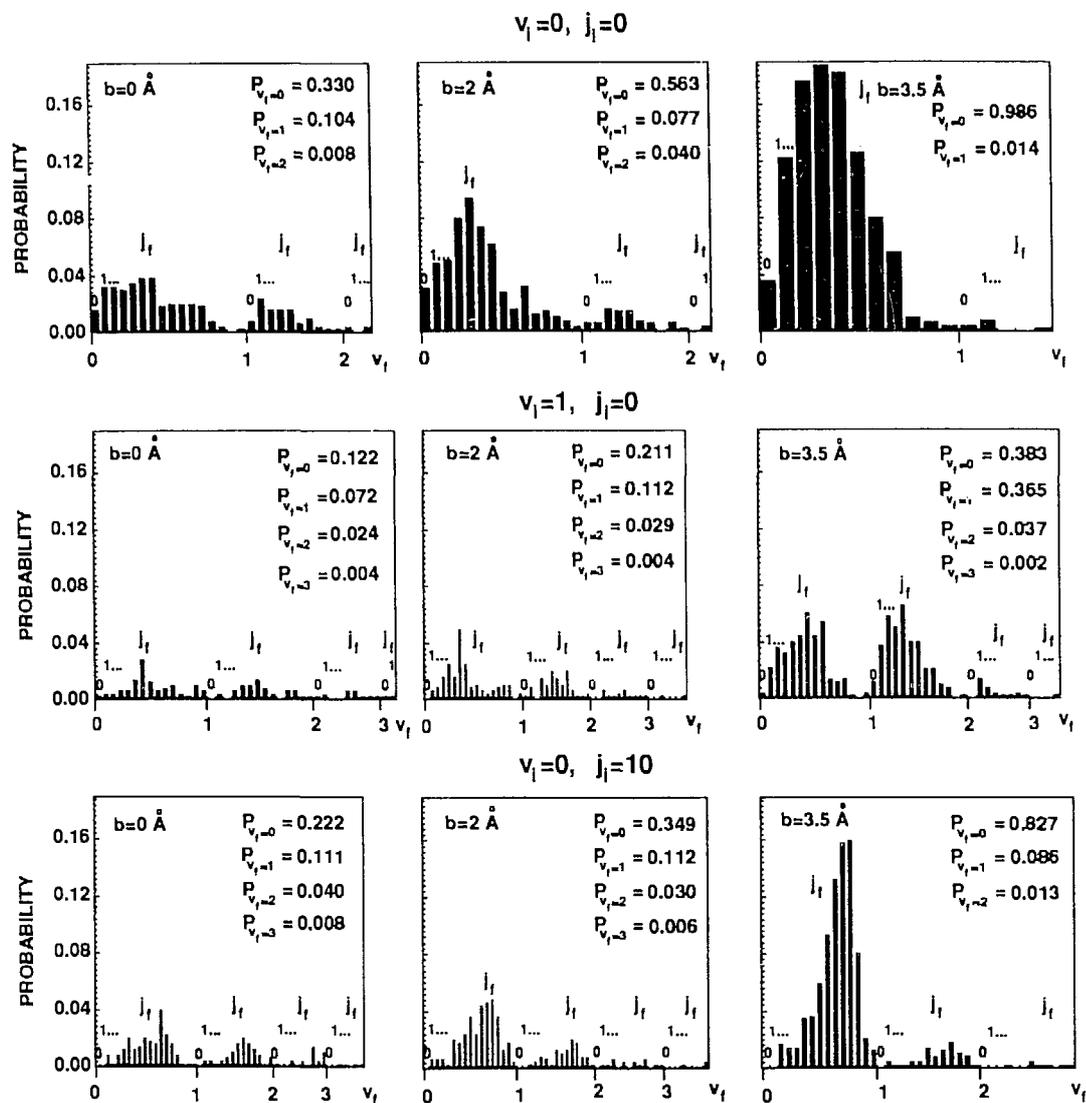
$v_i = 0, \; j_i = 0$

$b=0$ Å $\quad P_{v_f=0} = 0.330$

$P_{v_f=1} = 0.104$

$P_{v_f=2} = 0.008$

$b=2$ Å $\quad P_{v_f=0} = 0.563$

$P_{v_f=1} = 0.077$

$P_{v_f=2} = 0.040$

$j_f \; b=3.5$ Å $\quad P_{v_f=0} = 0.986$

$P_{v_f=1} = 0.014$

$v_i = 1, \; j_i = 0$

$b=0$ Å $\quad P_{v_f=0} = 0.122$

$P_{v_f=1} = 0.072$

$P_{v_f=2} = 0.024$

$P_{v_f=3} = 0.004$

$b=2$ Å $\quad P_{v_f=0} = 0.211$

$P_{v_f=1} = 0.112$

$P_{v_f=2} = 0.029$

$P_{v_f=3} = 0.004$

$b=3.5$ Å $\quad P_{v_f=0} = 0.383$

$P_{v_f=1} = 0.365$

$P_{v_f=2} = 0.037$

$P_{v_f=3} = 0.002$

$v_i = 0, \; j_i = 10$

$b=0$ Å $\quad P_{v_f=0} = 0.222$

$P_{v_f=1} = 0.111$

$P_{v_f=2} = 0.040$

$P_{v_f=3} = 0.008$

$b=2$ Å $\quad P_{v_f=0} = 0.349$

$P_{v_f=1} = 0.112$

$P_{v_f=2} = 0.030$

$P_{v_f=3} = 0.006$

$b=3.5$ Å $\quad P_{v_f=0} = 0.827$

$P_{v_f=1} = 0.086$

$P_{v_f=2} = 0.013$

PROBABILITY

Figure 6. Probability distributions of the final rovibrational states of $D_2$ scattered from a room-temperature icosahedral $Ni_{13}$. Each bar is the probability of a specified $(v_f, j_f)$ state. The $P_{v_f}$'s are the probabilities of the final vibrational states $v_f$. Three panels, corresponding to different values of the impact parameter b, are presented for each of the $(v_i = 0, j_i = 0)$, $(v_i=1, j_i=0)$ and $(v_i=0, j_i=10)$ initial states of the molecule.

$(v_i=1, j_i=0)$ case, where it appears to be, at least qualitatively, independent of b. The b-dependent population of the different $v_f$ states by the translational-vibrational coupling is masked by the partial depopulation of the $v_i=1$ state primarily into the $v_f=0$ state. The difference in the distribution patterns of the final rovibrational states for the $v_i=0$ and $v_i=1$ cases, respectively, indicates and illustrates a (vibrational) mode-selectivity (or specificity) in a nonreactive cluster-molecule interaction. One notices the non-Boltzmann character of the distribution of the final rotational states for all the $v_f$'s. Work is in progress on

investigation of the scattering of $D_2$ from the hcp and cubooctahedral $Ni_{13}$. Based on reactivity properties of these isomers, one may expect interesting structural effects also in the nonreactive interaction of the molecule with the cluster, especially at low collision energies.

## 4. Summary

We have reported here results of a quasiclassical simulation study of the interaction of a $D_2$ molecule with a $Ni_{13}$ cluster. Both channels, the reactive (dissociative adsorption of the molecule on the cluster) and the nonreactive (scattering of the molecule from the cluster), were considered. The processes were examined as functions of the initial quantal rovibrational state of the molecule, collision energy and structure of the cluster.

The main findings can be summarized as follows. Energizing the system (increasing either the collision energy or the rovibrational energy of the molecule) results in larger cross section of the dissociative adsorption. The reaction is mode-selective: initial vibrational excitation of the molecule leads to a more efficient bond breaking than an energetically equal initial rotational excitation. The structure of the cluster is an important factor in the specification of its reactivity features. It appears that the topology of the cluster surface plays a crucial role, especially at low collision energies. The topologically similar hcp and cubooctahedral structures of $Ni_{13}$ are not only more reactive than the icosahedral $Ni_{13}$, but the dynamical details of the interaction of the molecule with these isomers are also very different. While the reaction cross sections for the icosahedral geometry display thresholds (dynamical activation barriers) and increase monotonically with the collision energy, there are no barriers for the reaction with the hcp and cubooctahedral isomers and the reactive cross sections change nonmonotonically, exhibiting possible resonance features. The resonance features (heights and widths of the peaks) depend on the initial vibrational and rotational state of the molecule.

The distribution of the final vibrational states $v_f$ of the $D_2$ scattered from a room-temperature icosahedral $Ni_{13}$ depends strongly on the initial vibrational state $v_i$ of the molecule. With increase of the impact parameter the distribution shifts almost exclusively towards $v_f=0$ for the $v_i=0$ cases. On the contrary, the probabilities for the $v_f=0$ and $v_f=1$ final states of the $D_2$ remain of the same order of magnitude at all impact parameters when the molecule impinges with $v_i=1$. We expect to find particularly interesting features in the nonreactive interaction of $D_2$ with the hcp and cubooctahedral isomers of $Ni_{13}$. Work in this direction is in progress.

## Acknowledgments

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