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Dynamic structure of the reaction product of the H–H bond activation by a Ni_2 cluster

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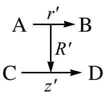
The activated H–H bond was theoretically found to occupy a considerable space characterised by the distances between the centres of mass of H–H and Ni–Ni within the range from –0.5 to +0.5 Å.

The development of catalytic cycles for selective conversion of hydrocarbons is one of the most important chemical problems. Key steps of these cycles are reactions of activation of H–H, C–H and C–C bonds.[1] As a rule, theoretic studies of these reactions are limited by a static quantum-chemical model when the mechanism of a chemical reaction is judged from the calculations of energy and structure geometry of stationary points in potential energy surfaces by solving the Schrödinger electronic equation. On the other hand, the wave nature of not only electrons but also atoms, molecules, and nuclei was clearly demonstrated using a molecular-beam technique.[2] Thus, from the experimental standpoint, wave properties of not only electrons but also nuclei should be taken into account in theoretical studies of the geometry of molecular systems.

In this connection, it is evident that only an optimisation process is insufficient for the analysis of molecular systems. To examine the structure of molecular systems, at the first step, it is necessary to construct a potential energy surface. Next, at the second step, the Schrödinger nuclear equation is solved on the basis of the potential energy surface. This technique for studying the dynamic structure is most popular for three- and four-particle molecular systems.[3]

We examined the dynamic structure of the reaction product of H–H bond activation by a Ni–Ni cluster. The calculations of potential energy surfaces were performed by the density functional technique (DFT).[4] An important advantage of the computer program used was that the Coulomb and exchange-correlation energy components were approximately represented using the expansion of the electron density in an auxiliary basis.[5] The main basis consists of the grouped Gaussian functions {311} for H and {842111/63111/411} for Ni; the auxiliary basis for the representation of electron density, of the ungrouped functions (4*s*1*p*) for H and (7*s*5*p*4*d*4*f*5*g*) for Ni.

The general system of coordinates for the interaction of two diatomic molecules has the following form:[3(*b*),(*c*)]



In our case, C,D ≡ Ni and A,B ≡ H. Here, *z*′, *r*′ and *R*′ are the Jacobi vectors for the four-particle reaction.

The mass-scaled vectors *z*, *r* and *R* are represented as follows:

$$z = z'\sqrt{\frac{(m_C m_D)}{\mu(m_C + m_D)}}$$

$$r = r'\sqrt{\frac{(m_A m_B)}{\mu(m_A + m_B)}}$$

$$R = R'\sqrt{\frac{(m_A + m_B)(m_C + m_D)}{\mu(m_A + m_B + m_C + m_D)}}$$

where m_A, m_B, m_C and m_D are the particle masses.
The equivalent mass μ is expressed as

$$\mu = \sqrt[3]{\frac{m_A m_B m_C m_D}{m_A + m_B + m_C + m_D}}$$

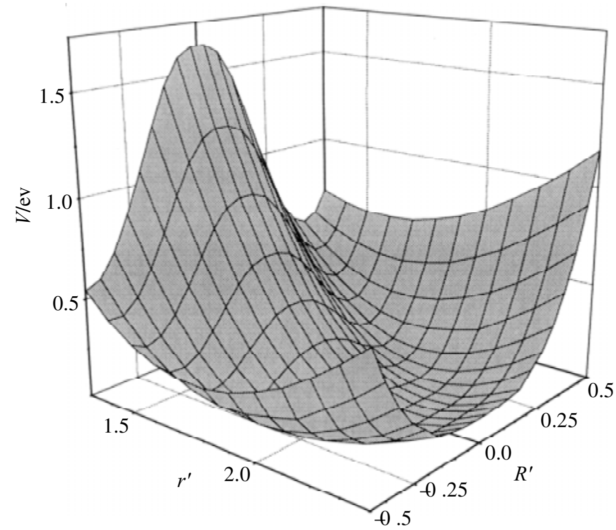
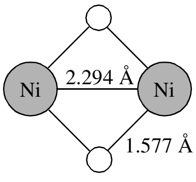


Figure 1 Two-dimensional potential energy surface in the neighbourhood of the reaction product of the H–H bond activation by the Ni_2 cluster as a function *V*(*R*′, *r*′) of the distance (*R*′/Å) between the centres of mass of H–H and Ni–Ni and the H–H distance (*r*′/Å).

The quantum-mechanical Hamiltonian on mass-weighted coordinates results from transformation of classical kinetic energy with the addition of a potential function:

$$H = -\frac{\hbar^2}{2\mu}\;\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial R^2} + V(z, r, R)$$

An analysis of the reaction mechanism of H–H bond activation by the Ni_2 cluster in the reaction-path Hamiltonian approximation[6] demonstrated that the movement along the reaction path is associated with a change in the *R*′ distance between the centres of mass of H–H and Ni–Ni (with the retention of the C_{2v} symmetry). In this case, the barrierless formation of a pseudo-rhombic product with a minimum energy at *R*′ ~ 0.2 Å. Note that the singlet state of the molecular system is lower than the triplet state by 6.6 kcal mol^{-1}. The classical structure of the molecular system is shown below.



We examined the displacement of the molecular system within the range *R*′ = 0–1.5 Å with the retention of the C_{2v} symmetry (the D_{2h} symmetry at *R* = 0). In this case, only the two coordinates *z*′ and *r*′ (the Ni–Ni and H–H distances) are changed (except for *R*′). Because *z*′ changed insignificantly (to within 4%), we plotted the two-dimensional potential function *V*(*r*′, *R*′) at the fixed coordinate *z*′ = 2.294 Å with the retention of the C_{2v} symmetry (Figure 1). In this case, the *r*′ and *R*′

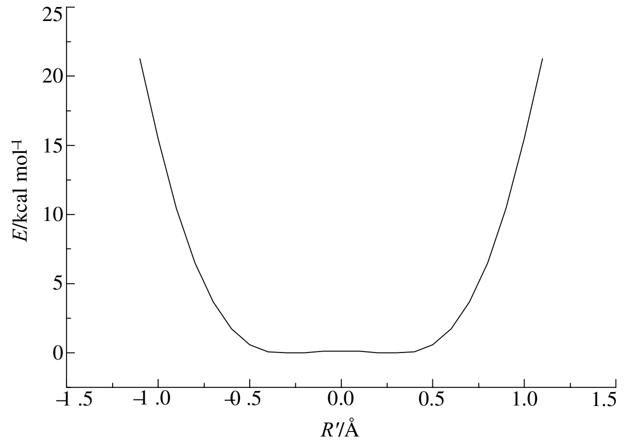


Figure 2 Minimum energy path in the neighbourhood of the reaction product of the H–H bond activation by the Ni_2 cluster as a function of the distance ($R'/\text{Å}$) between the centres of mass of H–H and Ni–Ni.

coordinates varied from 1.0 to 2.9 and from 0 to 1.5 Å, respectively, at a step of 0.1 Å. The 300 points obtained in this manner were used as nodes in the interpolation of the final function $V(r', R')$ by cubic spline functions. Note that the energy of the molecular system varied to within 0.6 kcal mol^{-1} as the R' coordinate along the reaction path changed within the range from −0.5 to +0.5 Å (Figure 2).

In our case, the equivalent mass is equal to $3.0725m_\text{H}$, and the mass-scaled coordinates are $R = 0.800R'$ and $r = 0.403r'$. The wave functions ψ_i(r, R) were obtained by solving the two-dimensional Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{\partial^2}{\partial R^2}\right)+V(r,R)\right]\psi(r,R)=E\psi(r,R)$$

The two-dimensional Schrödinger equation was solved by the Rietz method on the basis of 100×100 trigonometric functions with an accuracy of 10^{-5} cm^{-1} or better[7] in the calculations of eigenvalues.

Table 1 summarises the vibrational energy levels and their population at $T = 300$ K according to the Maxwell–Boltzmann statistics. It can be seen that only the first three vibrational levels are occupied.

Figure 3 demonstrates the probability densities of the spatial distribution of an activated H–H bond at a temperature of 300 K.

Table 1 Energies (E) of vibrational levels (n) of the product of oxidative addition of a hydrogen molecule to a Ni_2 cluster and their Maxwell–Boltzmann populations (MB) at $T = 300$ K.

n	E/eV	MB (%)
0	0.140	74.2
1	0.171	22.4
2	0.222	3.0
3	0.279	0.3
4	0.342	0.03
5	0.395	~0.0

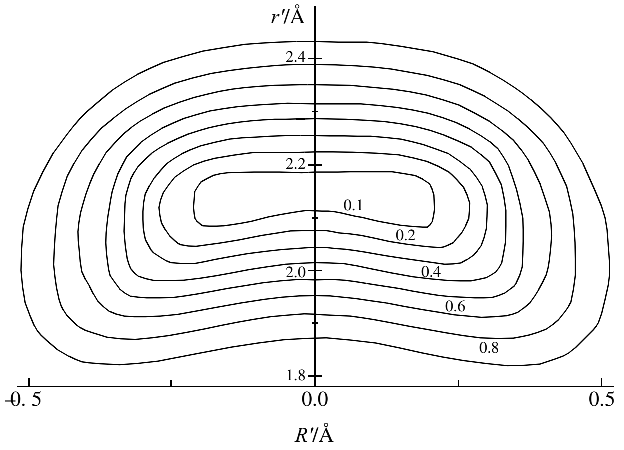


Figure 3 Dynamic structure of the reaction product of the H–H bond activation by the Ni_2 cluster, represented by the probability density distribution. The figures at each of the contour lines represent the total probability of the molecular structure occurring within the given contour.

The probability densities were obtained after considering the population of the vibrational energy levels E_n according to Maxwell–Boltzmann. A significant difference between the dynamic (quantum) and classical structures of the product is obvious. In the classical approach, the activated H–H bond is located at the fixed distance $R' \sim 0.2$ Å from the Ni–Ni cluster. The results of the dynamic study allowed us to conclude that, with a considerable probability density (~0.8), the activated H–H bond occupies a great deal of space within the R' and r' ranges from −0.5 to +0.5 and from 1.9 to 2.4 Å, respectively.

These data are of paramount importance for the development of catalytic cycles of hydrocarbon conversion, for example, olefin hydrogenation, by not only transition metal clusters but also bimetallic complexes.

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