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Vibrational analysis of Ni_n clusters

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The vibrational normal frequencies of Ni_n, $n=2$–14, 19, 20, and 55, clusters in their most stable structure are classified using group theory and calculated by direct diagonalization of the dynamical matrix. A Gupta n-body model potential was used to evaluate the second derivatives of the total energy with respect to the cluster atomic coordinates. The symmetry of the lowest-energy structures generate vibrational spectra with strong ($n=13$, and 55), medium ($n=4$ and 6), weak ($n=3$, 5, 7, 8, 10, 12, 14, 19, and 20), and null ($n=9$ and 11) degeneracies. Calculated frequencies for all cluster sizes are lower than the dimer characteristic frequency. The width of the modes distribution and the maximum frequency are independent of the cluster size for $2<n\leqslant 55$. [S0163-1829(96)03739-3]

I. INTRODUCTION

The study of vibrational properties of atomic and molecular clusters is becomig an active field of research in cluster science.[1] This is motivated, in part, by recent developments in experimental techniques that allow the measurement of the vibrational frequency spectrum of size-selected atomic clusters.[2,3] A knowledge of the cluster normal modes spectrum is of crucial importance to discriminate the atomic structure of the system, and to describe its dynamical and thermodynamical behavior. Theoretical calculations of cluster normal frequencies depend on the type of interactions used to mimic the atom-atom bonding. Several studies have been done in this direction using model potentials for van der Waals[4,5] and ionic[6] clusters. Also, first-principles methods have been used to calculate the vibrational spectra of semiconductor[7] and alkali-metal[8] clusters.

In general, vibrational modes are difficult to obtain, especially for clusters with more than a few atoms. The cluster structure associated with a global or local minimum of the multidimensional surface potential should be known in advance. However, the number of minima increases very fast with cluster size, making it a complicated task to determine the global minimum corresponding to the lowest-energy cluster structure. Once the cluster equilibrium configuration is known, symmetry considerations are very useful for a qualitative description of the normal frequencies. A classification of such modes can be done using the irreducible representation of the cluster symmetry group.[9] To have a complete (quantitative) description of the cluster frequency spectrum, a vibrational analysis using second-order derivatives of the total energy with respect to the atomic coordinates is necessary.

In this work, we present results of a vibrational analysis for transition-metal clusters (Ni, in this case) with $n=2$–14, 19, 20, and 55 atoms. First, the normal modes are characterized using cluster symmetry and group theory. Second, cluster frequencies are calculated through a normal-mode analysis by direct diagonalization of the dynamical matrix, which is constructed from the second derivatives of the potential energy with respect to the atomic coordinates. A model n-body Gupta potential was used to describe the metallic bonding in the cluster. In this way, the present study continues a systematic characterization of structural, dynamical, meltinglike,[10–13] and evaporation[14] behavior of transition- and noble-metal clusters. The vibrational properties presented here[15] are expected to motivate spectroscopic measurements of the frequency spectrum for transition-metal clusters. The details of the potential and cluster structures are discussed in Sec. II. In Sec. III we use group theory techniques to classify and give a qualitative description of the cluster vibrational spectrum. The normal frequencies are obtained in Sec. IV by diagonalizing the dynamical matrix. In Sec. V, we conclude with a brief summary.

II. GUPTA POTENTIAL AND CLUSTER STRUCTURES

The metallic bonding of Ni_n clusters is described by an n-body Gupta potential that is based on the Friedel's tight-binding model for the cohesive energy of transition metals.[16,17] Within this model, the attractive part of the interaction is proportional to the square root of the second moment of the electron density of states (d band). The repulsive part is a sum of pairwise Born-Mayer potentials.[18,19] For n-atom clusters, the Gupta model potential is given as a function of the interatomic distances r_{ij} by[10,11]

$$V=\frac{U_n}{2}\sum_{j=1}^{n}\left[A\sum_{i(\neq j)=1}^{n}\exp[-p(r_{ij}/r_{0n}-1)]\right.$$
$$\left.-\left[\sum_{i(\neq j)=1}^{n}\exp[-2q(r_{ij}/r_{0n}-1)]\right]^{1/2}\right],\qquad(1)$$

where the parameters p, q, and A depend on the material. In this work we adopt the values $p=9$ and $q=3$, which have been used for bulk transition metals.[17] The value

$A = 0.101\,036$ was determined by minimizing the cohesive energy of the fcc metal at the equilibrium value of its nearest-neighbor distance.[10] The remaining two parameters U_n and r_{0n} are not only material dependent but also cluster size dependent, which is indicated by attaching the subscript n to them. They can be fitted using experimental or *ab initio* data of the cluster binding energy and nearest-neighbor distance. Instead of performing a fitting procedure for each cluster size, we work in reduced units: $r_{ij}^* = r_{ij}/r_{0n}$, $V^* = V/U_n$.[10–13] This unit transformation allows the calculation of cluster properties of arbitrary size without the explicit knowledge of U_n and r_{0n}. To recover absolute units, a fitting procedure of these parameters is necessary.

The Gupta potential given in Eq. (1) has been used to study structural and thermodynamical properties of fcc [Refs. 18 and 19] and hcp transition metals and alloys.[19] Structural, dynamical, meltinglike,[10–13] and fragmentation[14] properties of metal clusters have been extensively studied using the Gupta n-body potential in molecular-dynamics simulations. In this work, we extend the range of applications of this potential to describe vibrational properties of Ni_n clusters.

Lowest-energy structures of the nickel clusters have been obtained before,[10,12,14] combining molecular-dynamics and simulated quenching techniques. Figure 1 shows the cluster most stable structures, their energies, and symmetry groups. It is observed that Ni_n clusters grow following a close-packing pattern in which the number of nearest-neighbor distances is maximum. Pentagonal symmetry starts at $n=7$ (except for $n=8$). The 13-atom cluster has an icosahedral lowest-energy structure, whereas the $n=12$ and 14 cluster structures are obtained from the icosahedron by removing one surface atom and adding one to a threefold symmetry surface site, respectively. The two-overlapping icosahedra is the most stable geometry for $n=19$. The corresponding configuration for $n=20$ is the 19-atom structure with an additional atom placed over an edge of the central five-atom ring. The two-shell icosahedron is the lowest-energy configuration for $n=55$.

Although the most stable cluster structures discussed above are similar to those obtained with pairwise potentials (Lennard-Jones or Morse), other structural and dynamical properties can be distinct, due to n-body interactions included through the Gupta potential. Differences in the relative stability of cluster isomers[13] and a more complex melting behavior[10,12] (premelting for $n=14$ and 20), are examples of n-body effects present in the bonding of transition- and noble-metal clusters.

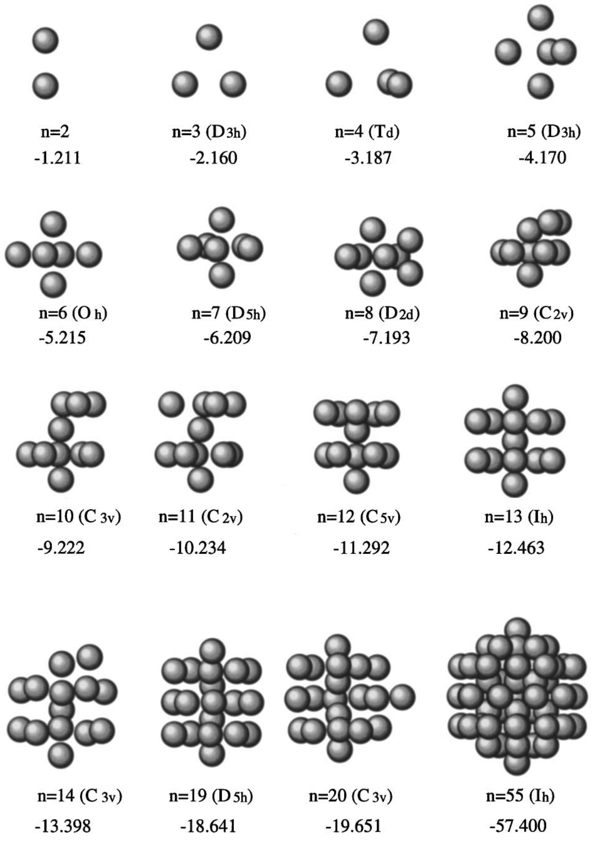

FIG. 1. The most stable structures, their energies in reduced units, and the associated symmetry group for Ni_n, $n=2$–14, 19, 20, and 55, clusters.

Since direct experimental information on the lowest-energy structure of nickel clusters is not yet available, it is

TABLE I. Symmetry structures of Ni_n clusters.

n	Group	Symmetry structure
2		$\Gamma = 1A_g$
3	D_{3h}	$\Gamma = 1A'_1 + 1E'$
4	T_d	$\Gamma = 1A_1 + 1E + 1T_2$
5	D_{3h}	$\Gamma = 2A'_1 + 1A''_2 + 2E' + 1E''$
6	O_h	$\Gamma = 1A_{1g} + 1E_g + 1T_{2g} + 1T_{1u} + 1T_{2u}$
7	D_{5h}	$\Gamma = 2A'_1 + 2E'_1 + 2E'_2 + 1A''_2 + 1E''_1 + 1E''_2$
8	D_{2d}	$\Gamma = 4A_1 + 1A_2 + 2B_1 + 3B_2 + 4E$
9	C_{2v}	$\Gamma = 7A_1 + 4A_2 + 5B_1 + 5B_2$
10	C_{3v}	$\Gamma = 6A_1 + 2A_2 + 8E$
11	C_{2v}	$\Gamma = 9A_1 + 4A_2 + 7B_1 + 7B_2$
12	C_{5v}	$\Gamma = 5A_1 + 1A_2 + 6E_1 + 6E_2$
13	I_h	$\Gamma = 1A_g + 1G_g + 2H_g + 2T_{1u} + 1T_{2u} + 1G_u + 1H_u$
14	C_{3v}	$\Gamma = 9A_1 + 3A_2 + 12E$
19	D_{5h}	$\Gamma = 5A'_1 + 1A'_2 + 6E'_1 + 5E'_2 + 1A''_1 + 4A''_2 + 5E''_1 + 4E''_2$
20	C_{3v}	$\Gamma = 13A_1 + 5A_2 + 18E$
55	I_h	$\Gamma = 2A_g + 4T_{1g} + 3T_{2g} + 5G_g + 7H_g + 6T_{1u} + 4T_{2u} + 5G_u + 6H_u + 1A_u$

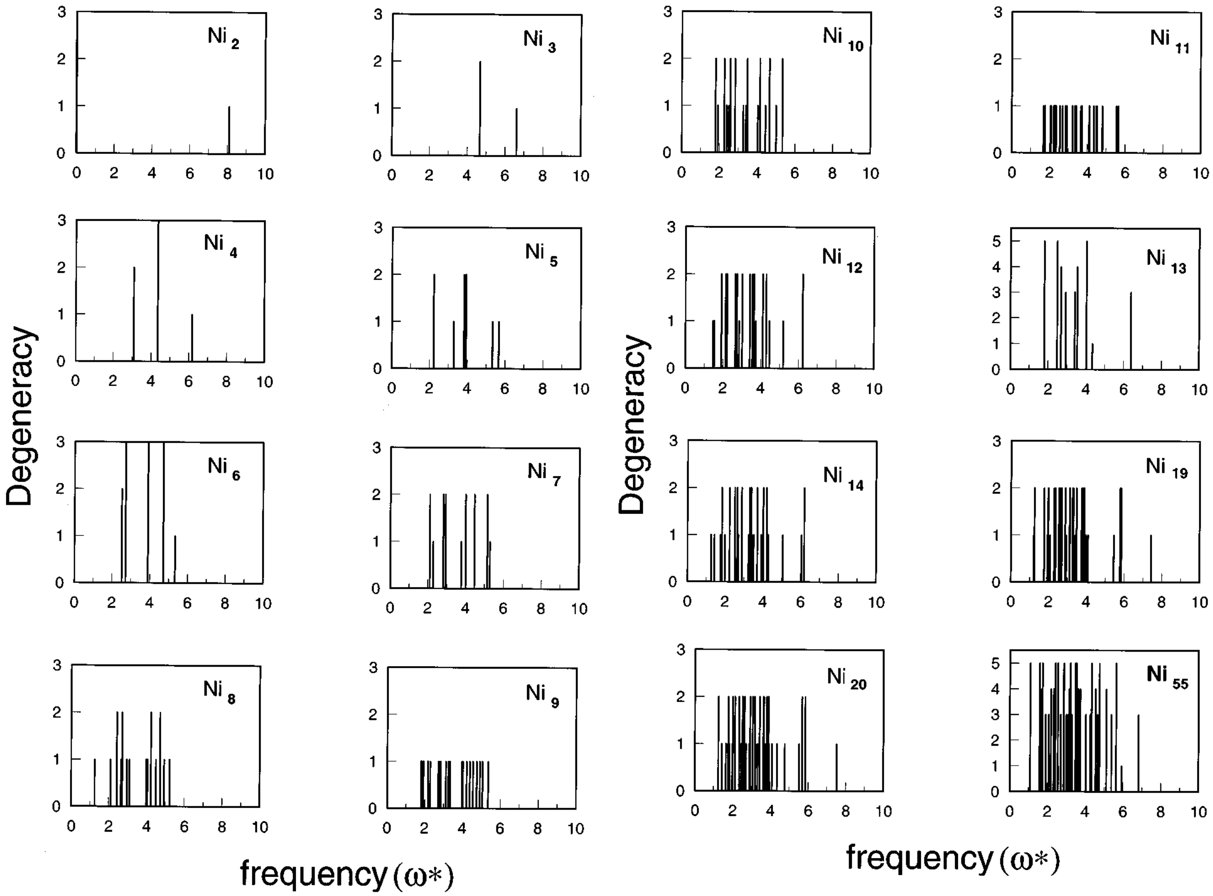

FIG. 2. Normal mode distributions of Ni_n, $n=2$–14, 19, 20, and 55, clusters. The vertical axis shows the degree of degeneracy. Frequency values are in reduced units. To set up an approximated absolute scale of frequencies, one can use the dimer frequency value of 262 cm^{-1} (see text).

not possible to test the above predictions given by the n-body Gupta potential. However, experiments on the chemical reactivity of molecular adsorbates on nickel clusters[20] suggest that close packing and icosahedral symmetry are present in the structure of these clusters. On the other hand, accurate *ab initio* methods are not easily applicable to nickel clusters, and comparison with them is difficult since their results fail to agree among themselves.[21] Other semiempirical studies on the lowest-energy structures of Ni_n clusters show good[22–24] and partial,[21,25] agreement with the above results.

III. GROUP THEORY ANALYSIS

The cluster configurations and the associated point group shown in Fig. 1 are used to do a group theory analysis,[9] and classify the cluster normal frequencies. To obtain the total number of normal modes, symmetry operations of the corresponding point group are applied to each cluster under consideration. Using the number of atoms that remain fixed after such transformation, and the trace of the transformation matrix associated to the symmetry operation, the characters of the reducible representation for the cluster symmetry group are obtained. The reducible representation gives the normal modes once the number of times each irreducible representation appears in the reducible one is calculated. Table I shows the vibrational symmetry structure of the nickel clusters. The degeneracy of the frequency modes will be discussed in Sec. IV in conjunction with their numerical values obtained from the diagonalization of the dynamical matrix.

IV. NUMERICAL RESULTS AND DISCUSSION

To construct the dynamical matrix, the Gupta potential second derivatives with respect to the atomic coordinates were calculated analytically using Eq. (1). The cluster most-stable structures were used to evaluate the second derivatives in the equilibrium configurations. These values generate the elements of the dynamical matrix. A numerical diagonalization of this matrix was performed to obtain the normal frequencies and eigenvectors. Six of the calculated $3n$ eigenvalues are equal to zero, corresponding to translational and rotational motions. The remaining $3n-6$ frequencies are the vibrational normal modes. Figure 2 displays the frequency distribution of the nickel clusters under study. The vertical axis indicates the degeneracy of the modes. Frequencies are given in reduced units, $\omega^{*}=\omega/(U_n/mr_{0n}^2)^{1/2}$, where m is the nickel atomic mass.

From Fig. 2 it is observed that Ni_{13} and Ni_{55}, with a highly symmetric icosahedral lowest-energy structure, have normal modes with fivefold, fourfold, and threefold degeneracy. In addition, they have a single nondegenerate breathing mode and, in the case of Ni_{55}, other radial nondegenerate vibrations. Ni_4 and Ni_6 also have their lowest-energy structures with high symmetry, the tetrahedron and octahedron, respectively. These structures cause normal modes with threefold and twofold degeneracy, plus a single nondegenerate breathing mode. All other cluster sizes, except Ni$_9$ and Ni$_{11}$, present frequency distributions with twofold degeneracy and nondegenerate modes. Ni$_9$ and Ni$_{11}$, with C_{2v} symmetry, have a nondegenerate frequency spectrum. In sum, the normal modes of nickel clusters can be classified, according to degeneracy, as strong for Ni$_{13}$ and Ni$_{55}$, medium for Ni$_4$ and Ni$_6$, and weak for Ni$_n$, $n=3$, 5, 7, 8, 10, 12, 14, 19, and 20. Null degeneracy is obtained for Ni$_9$ and Ni$_{11}$. As expected, the degeneracy of the cluster normal modes calculated from the diagonalization of the dynamical matrix agree with that obtained from a group theory analysis. The advantage of the numerical analysis is that the frequency values can be calculated.

There are other interesting features in the normal modes spectrum of nickel clusters: First, assuming that the U_n and r_{0n} parameters are similar for the cluster sizes under study, all cluster frequencies are lower than the characteristic dimer frequency. This effect has also been found in the vibrational spectrum of ionic clusters.[6] It is attributed to the small interatomic distance in the dimer and the nearest-neighbor distance relaxation as the cluster size increases toward the bulk phase.[6] Experimental[2] and first-principles theoretical studies[7] of the vibrational spectrum of silicon clusters as a function of size also show that the dimer frequency is higher than the frequencies of larger cluster sizes. Second, taking out the dimer value, the width of the bands and the maximum frequencies are independent of the cluster size in the range of sizes studied here. Some size effects in the maximum frequency are expected for $n > 55$, as was found for argon clusters in He-atom scattering experiments.[3] Third, low-frequency modes and special repetitive patterns are absent from the frequency distribution for all cluster sizes investigated.

Experimental or *ab initio* data of the cluster binding energy and nearest-neighbor distances can be used to calculate the cluster normal frequencies in absolute units. Such information is not yet available, except for Ni$_2$.[21] As an example, using experimental data[26] for the nickel dimer, we fit the U_2 and r_{02} parameters and obtain a value of 262 cm^{-1} for the vibrational frequency. This number compares well with the measured value[26] (329 cm^{-1}), and is within the range of theoretical *ab initio* values (between 190 and 289 cm^{-1}, reported in Refs. 21 and 27). A closer agreement is expected if nickel dimer properties are included in the fitting of the p and q parameters of the Gupta potential.

V. SUMMARY

The vibrational frequencies of Ni$_n$, $n=2$–14, 19, 20, and 55, clusters in their most stable configurations, were obtained through a normal-mode analysis using an n-body Gupta potential to model the interatomic interactions in the cluster. Nickel clusters have a frequency spectrum with strong, medium, weak, and null degeneracies, according to the degree of symmetry in their lowest-energy configurations. The cluster frequencies are lower than the dimer characteristic frequency for all cluster sizes, whereas the width of modes distribution and the maximum frequency are independent of the cluster size.

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