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## DFT normal modes of vibration of the Au<sub>20</sub> cluster

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The vibrational spectrum of the tetrahedral Au<sub>20</sub> cluster was calculated using density functional theory (DFT) with two different approximations: the hybrid-B3LYP and GGA-BP86. The normal modes of vibration obtained were classified according to the irreducible representations of the T<sub>d</sub> group. The calculated vibrational frequencies were tabulated to be compared with experimental data when they became available.

**Keywords:** Au<sub>20</sub>; metallic cluster; normal modes of vibration.

El espectro vibracional del cúmulo tetraédrico Au<sub>20</sub> fue calculado mediante la teoría del funcional de la densidad (DFT) dentro de dos aproximaciones diferentes: la híbrida B3LYP y la GGA-BP86. Los modos normales de vibración obtenidos fueron clasificados de acuerdo a las representaciones irreducibles del grupo T<sub>d</sub>. Las frecuencias vibracionales calculadas fueron tabuladas para su comparación con datos experimentales cuando estén disponibles.

**Descriptor:** Au<sub>20</sub>; cúmulos metálicos; modos normales de vibración.

PACS: 71.15.Md; 33.20.SI; 61.46.Bc

### 1. Introduction

The tetrahedral 20-gold cluster (T<sub>d</sub>-Au<sub>20</sub>) is perhaps the most widely studied gold cluster due to its high symmetry. It was discovered through a combined experimental and theoretical work by Li *et al.* [1]. Its tetrahedral geometry, predicted from a density functional theory (DFT) calculation, has been described as a piece of fcc bulk gold, with the twenty gold atoms on its surface and each of its four faces forming a plane (111). The constructed polyhedra is a tetrahedral pyramid with its four corners being low coordination sites [1,2] (see Au<sup>a</sup> sites in Fig. 1). These kinds of sites are preferred for CO adsorption on gold clusters in the gas phase [3]. Zhang *et al.* [4] synthesized Au<sub>20</sub> in solution, coordinated with eight ligands PH<sub>3</sub>: four located at the apexes of the cluster and the remaining four connected to the face-centered atoms (Au<sup>f</sup> sites in Fig. 1). The new complex molecule definitely shows compatibility with a tetrahedral symmetry. Theoretical studies on T<sub>d</sub>-Au<sub>20</sub> suggest that indeed this cluster presents catalytic characteristics for CO and O<sub>2</sub> at low coordination sites [5]. Experimentally, Neumaier *et al.* [6] report room temperature CO adsorption on isolated gold cluster cations and especially for Au<sub>20</sub><sup>+1</sup> show the existence of four sites with similar adsorption rate constants. However, Veldeman *et al.* [7] do not report a particularly high reactivity for neutral Au<sub>20</sub> towards CO.

The structural stability is another interesting feature of this cluster. Actually, it is well known that the small gold clusters undergo a dynamic structural fluxionality, changing their geometry easily during chemical reactions [8]. Nevertheless, from photoelectron spectroscopy, Li *et al.* showed that T<sub>d</sub>-Au<sub>20</sub> presents a wide HOMO-LUMO gap (1.77 eV), *i.e.* 0.2 eV larger than that of C<sub>60</sub>), which would be a high structural stability indicator.

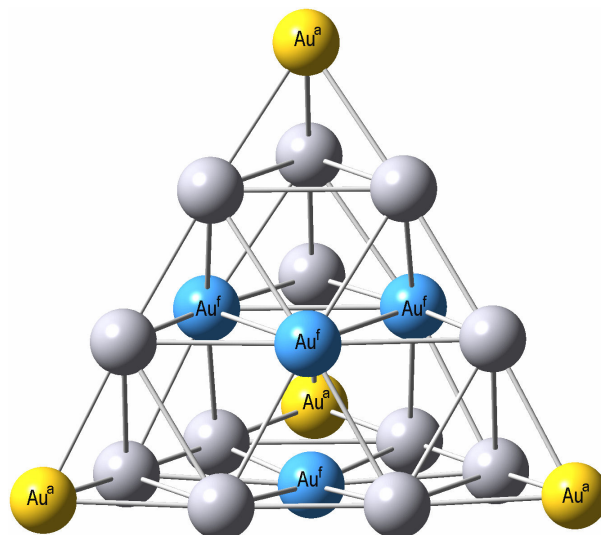


FIGURE 1. Tetrahedral structure of Au<sub>20</sub> showing its three non-equivalent sites: Au<sup>a</sup>, Au<sup>f</sup> and Au<sup>e</sup> corresponding to apexes, face centers and edges respectively (the last ones corresponding to the empty spheres in figure).

On the other hand, it can be seen that the spectrum of theoretical and experimental studies around T<sub>d</sub>-Au<sub>20</sub> is broad; for instance, the T<sub>d</sub>-Au<sub>20</sub> cluster has been studied theoretically associated with surface-enhanced Raman scattering by pyridine [9]. Furthermore, this cluster has also been proposed for application in molecular opto-electronic devices and monolayer film materials because theoretically it has a remarkably large static first hyperpolarizability [10]. In addition, several of its ions have been obtained (Au<sub>20</sub><sup>±γ</sup>, γ=1,2,3) [11], but there are few theoretical studies on them.

Recently, in Au<sub>n</sub> clusters, the use of vibrational spectra has been proposed as an efficient tool to resolve between dif-

ferent isomers [12]. About the T<sub>d</sub>-Au<sub>20</sub> cluster, Kryachko and Remacle [13] have reported its lowest and highest vibrational frequencies using different approximations. Before, Carnalla *et al.* [14] provided the frequency spectrum for the unsymmetrical Au<sub>20</sub> cluster. The experimental frequency spectrum of the T<sub>d</sub>-Au<sub>20</sub> cluster is not yet available because it must be obtained through infrared or Raman optical spectroscopies, or using inelastic neutron dispersion carried out when the material is in solid-phase. However, there are many experimental efforts to achieve the self-assembly of gold nanoparticles in periodic arrangements through interligand interaction [15]. Thus, the self-assembly of ordered T<sub>d</sub>-Au<sub>20</sub> and therefore, the experimental frequency spectrum for T<sub>d</sub>-Au<sub>20</sub>, is only a question of time.

Briefly, we can mention some features concerning the vibrational spectrum of the T<sub>d</sub>-Au<sub>20</sub> cluster. The normal modes of vibration of this cluster may be classified according to their symmetry using group theoretical techniques. There are 60 degrees of freedom for the Au<sub>20</sub> cluster. Three of these degrees correspond to translations and three to rotations, leaving 54 vibrational degrees of freedom. Since tetrahedral symmetry gives rise to a large number of degenerate modes, only 23 distinct mode frequencies are expected for the T<sub>d</sub>-Au<sub>20</sub> cluster:

$$\Gamma_{vib} = 4A_1 + A_2 + 5E + 5T_1 + 8T_2. \quad (1)$$

The symmetry labels (*e.g.* T<sub>1</sub>, E) refer to irreducible representations (IR's) of the tetrahedral point group T<sub>d</sub>.

Group theory, furthermore, indicates that nine of the 23 normal modes of vibration are Raman-active (4A<sub>1</sub> + 5E) in the first order, eight are both infrared and Raman-active (8T<sub>2</sub>) in the first order, and the remaining six are optically silent.

In this work, we present the results of DFT calculations for the normal modes of vibration and the respective frequencies of the T<sub>d</sub>-Au<sub>20</sub> cluster, classified according to their symmetry group.

## 2. Methodology

Density functional theory calculations were carried out to optimize the geometry of the T<sub>d</sub>-Au<sub>20</sub> cluster. The exchange and correlation interactions were treated through GGA-BP86

and hybrid-B3LYP approximations. The GGA-BP86 approximation uses the gradient-corrected exchange-energy functional proposed by Becke [16] and the gradient-corrected correlation-energy functional proposed by Perdew [17]. The hybrid-B3LYP approximation was formulated by Becke [18] and includes a mixture of Hartree-Fock and DFT exchange energy functionals. We have used the relativistic effective core potential LANL2DZ basis set [19] to describe the gold atom. This basis set models the gold atom as being composed of 19 valence electrons plus a relativistic core potential centered at the gold nucleus. In order to improve the SCF convergence, an accuracy of 10<sup>-4</sup> Hartrees was selected for energy and, for the optimization process, a gradient maximum limit of 10<sup>-5</sup> Hartrees/Bohr. Analytical second derivatives were performed in order to obtain the Hessian of T<sub>d</sub>-Au<sub>20</sub>. Gaussian 03 [20] was employed for all the calculations.

## 3. Results and discussion

The geometry of the tetrahedral Au<sub>20</sub> cluster is characterized by five distinct Au-Au distances between the three non-equivalent sites (Au<sup>a</sup>, Au<sup>f</sup>, and Au<sup>e</sup>, with the last of these corresponding to the empty spheres in Fig. 1). For Au<sub>20</sub>, the highest occupied molecular orbital (HOMO) is two-fold degenerate with *e* IR, while the lowest unoccupied molecular orbital (LUMO) is three-fold degenerate with *t*<sub>2</sub> IR. The corresponding closed-shell total electronic state symmetry is the completely symmetrical A<sub>1</sub> IR with a large HOMO-LUMO gap. If we compare our HOMO-LUMO energy gap and bond length results in T<sub>d</sub>-Au<sub>20</sub> with those reported by Li *et al.* (see Table I, third row), it can be concluded that the BP86 functional obtains good agreement with the experiment and gives us better predictions than the B3LYP functional. In fact, recently Kryachko and Remacle carried out density functional calculations using BP86, PW91, PBE and B3LYP functionals with two basis (LANL2DZ and SSD) on T<sub>d</sub>-Au<sub>20</sub>. Table I includes their results for BP86/LANL2DZ and B3LYP/LANL2DZ and can be compared respectively with the results of this work. The power of prediction of BP86 and B3LYP functionals has been tested before in diatomic molecules formed from alkali metals (Li, Na, K) and noble transition metals (Ag, Cu, Au) [21], and BP86 was better than B3LYP.

TABLE I. HOMO-LUMO energy gap ( $\Delta E_{HL}$ ), HOMO energy, electronic configuration, and Au-Au distances for T<sub>d</sub>-Au<sub>20</sub> employing different DFT approximations as compared with Ref. 13 and experiment [1].

Method	$\Delta E_{HL}$ (eV)	HOMO (eV)	configuration	Au-Au distances (Å)
BP86	1.92	-6.03	(t <sub>2</sub> ) <sup>6</sup> (e) <sup>4</sup> (t <sub>2</sub> ) <sup>0</sup>	2.71, 2.76, 2.87, 3.01, 3.13
B3LYP	2.96	-6.41	(t <sub>2</sub> ) <sup>6</sup> (e) <sup>4</sup> (t <sub>2</sub> ) <sup>0</sup>	2.73, 2.79, 2.91, 3.08, 3.21
KR-BP86 [13]		-6.02		2.71, 2.76, 2.86, 3.01
KR-B3LYP [13]		-6.40		2.73, 2.80, 2.91, 3.08
Theo/Exp. [1]	1.77		(t <sub>2</sub> ) <sup>6</sup> (e) <sup>4</sup> (t <sub>2</sub> ) <sup>0</sup>	2.68, 2.71, 2.83, 2.97, 3.12

TABLE II. The  $Au_{20}$  vibrational spectra in  $cm^{-1}$  calculated in the present work using the DFT-BP86 and B3LYP approximations. The irreducible representation (IR) of each mode is given in the first column. The KR1 y KR2 columns correspond to the BP86/LANL2DZ and B3LYP/LANL2DZ respectively of Ref. 13.

IR	BP86	KR1	BLYP	KR2	IR	BP86	KR1	BLYP	KR2
1T <sub>1</sub>	29.13	28	26.42	26	5T <sub>2</sub>	72.94		65.21	
1T <sub>2</sub>	33.29		29.94		2A <sub>1</sub>	81.24		74.70	
1E	35.44		32.52		4T <sub>1</sub>	89.36		80.22	
2T <sub>2</sub>	43.46		39.47		3A <sub>1</sub>	97.37		88.97	
2E	44.51		41.34		5T <sub>1</sub>	106.61		93.74	
1A <sub>2</sub>	47.14		44.66		4E	109.59		97.45	
2T <sub>1</sub>	50.05		44.94		6T <sub>2</sub>	114.61		102.94	
3T <sub>2</sub>	55.04		51.47		7T <sub>2</sub>	129.75		119.01	
3E	55.40		51.95		5E	159.18		149.67	
1A <sub>1</sub>	57.33		47.81		8T <sub>2</sub>	165.68		155.69	
3T <sub>1</sub>	59.73		54.79		4A <sub>1</sub>	172.35	172	162.22	161
4T <sub>2</sub>	66.56		58.90						

The calculated values for all of the 23 mode frequencies are displayed in Table II for both approximations (BP86 and B3LYP) where each frequency level is identified according to

its appropriate irreducible representation. We can see that the frequencies predicted by BP86 are slightly greater than those predicted by B3LYP (the maximum and minimum difference

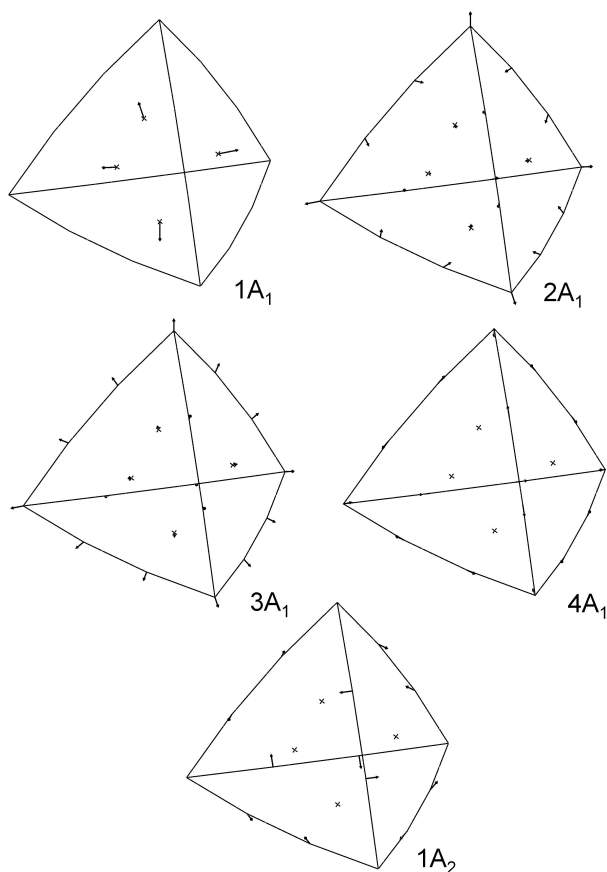


FIGURE 2. Schematic diagram of normal mode displacements for the four nondegenerate modes  $A_1$  and  $A_2$  in  $Au_{20}$ .

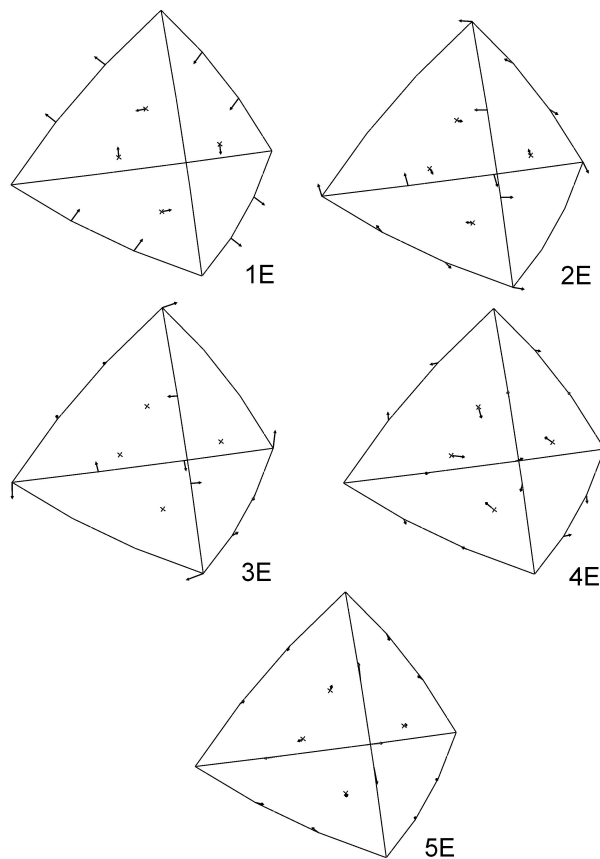


FIGURE 3. Schematic diagram of normal mode displacements for the five E modes in  $Au_{20}$ .

are 12.87 and 2.48 cm<sup>-1</sup> respectively) and the increasing order of the frequencies is only broken in the 1A<sub>1</sub> representation for B3LYP with respect to BP86 results. Our BP86 and B3LYP lowest and highest vibrational frequencies are very close to the corresponding frequencies calculated by Kryachko and Remacle with their respective functionals, as can be seen also in Table II.

In Fig. 2 we display eigenvectors for the four A<sub>1</sub> and one A<sub>2</sub> modes. These non-degenerate modes, because of their higher symmetry, are easier to visualize. In the 1A<sub>1</sub> mode only the face-centered atoms are displaced perpendicularly to the face planes. The lower non-degenerate mode (1A<sub>2</sub>) displaces atoms only at the edges, not at the vertices or face centers. The 3A<sub>1</sub> Raman breathing mode with a frequency of approximately 97 cm<sup>-1</sup> (BP86) or 89 cm<sup>-1</sup> (B3LYP) involves identical radial displacements for all 20 gold atoms, whereas the higher frequency 4A<sub>1</sub> mode involves only tangential displacements of the atoms at the edges.

In Figs. 3-5 we show some representative modes of each degenerate IR from the DFT-BP86 approximation. There is a general tendency of the higher frequency modes to have displacements that are more tangential in character than those at lower frequencies, except for two intermediate-frequency modes (2T<sub>1</sub> and 4T<sub>1</sub>). There is at least one mode of each

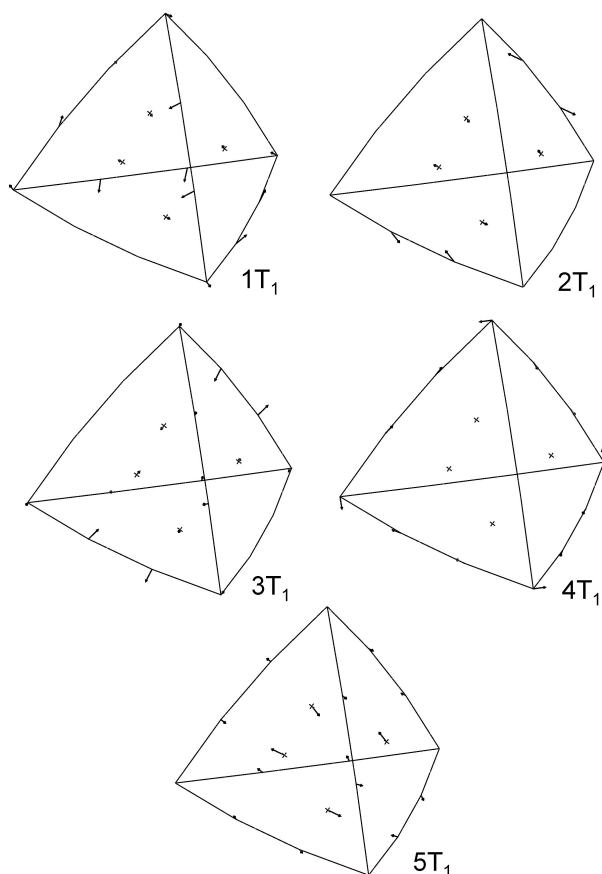


FIGURE 4. Schematic diagram of normal mode displacements for the five T<sub>1</sub> modes in Au<sub>20</sub>.

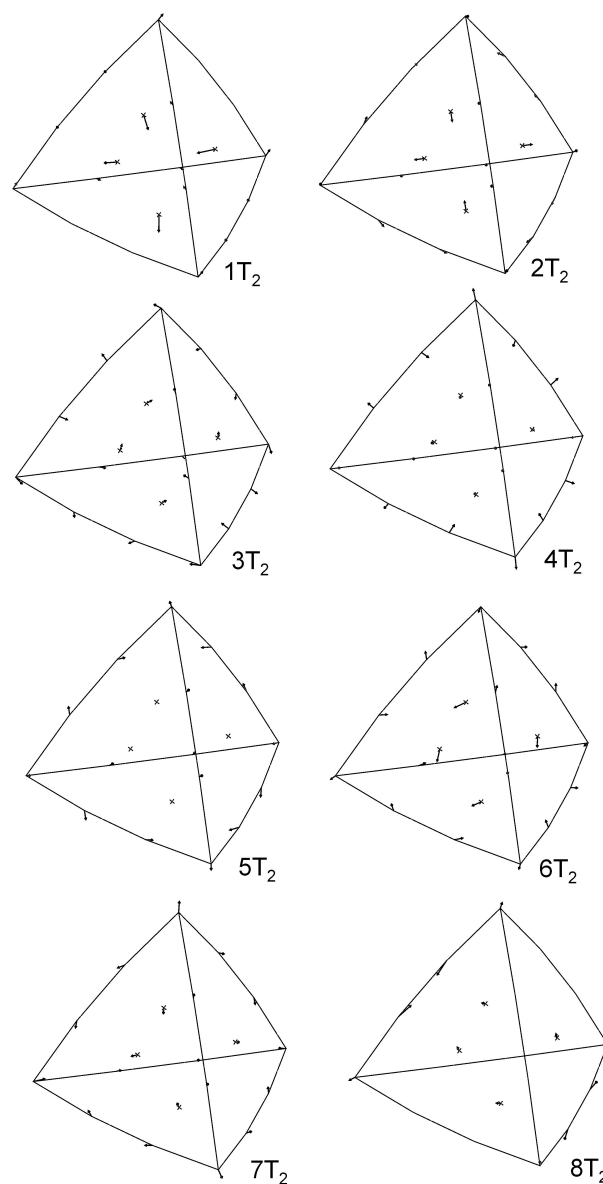


FIGURE 5. Schematic diagram of normal mode displacements for the eight T<sub>2</sub> modes in Au<sub>20</sub>.

IR whose eigenvectors are nulls at the face-centered atoms (4A<sub>1</sub>, 3E, 5T<sub>2</sub>, 1A<sub>2</sub>, and 4T<sub>1</sub>) and with the exception of T<sub>2</sub> IR, there is at least one mode of each IR whose eigenvectors are nulls at the triangle vertices (1A<sub>1</sub>, 4E, 5E, 1A<sub>2</sub>, and 5T<sub>1</sub>).

#### 4. Conclusions

We use DFT with restricted B3LYP and BP86 to optimize the T<sub>d</sub>-Au<sub>20</sub> structure and to obtain its frequency spectrum. The resulting geometric and electronic structures are in agreement with other first principle calculations. The lowest and highest frequency values, as we mentioned previously, are very close to other similar calculations recently reported. The present calculation of the frequency spectrum is a prediction to be confirmed when the experimental data become available.

The Hessian matrix, calculated to obtain the normal modes of vibration in this work, can be useful in molecular dynamics simulations which can find a dependency of the gold-cluster-assisted catalytic processes on temperature.

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