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On excited states of the Au_3 cluster: an *ab initio* study

Research Article

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Abstract: Excited electronic states of the Au_3 cluster are studied within the shape-consistent small-core relativistic pseudopotential model using many-body multipartitioning perturbation theory. Vertical transition energies and dipole moments are evaluated. For highly symmetric isomer, these theoretical results are in reasonable agreement with spectroscopic data from experiments.

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1. Introduction

Quantitative theoretical modeling of the electronic structure and spectra of small gold clusters is a challenging task because it necessarily requires a proper description both of relativistic effects and the correlation of a large number of electrons. Our recent theoretical study of the ground state and isomerism of the Au_3 cluster has employed various reliable methods of relativistic quantum chemistry [1]. We have found that an appropriate description of the electronic states of Au_3 is attained only if the outer-core electrons of Au atoms are correlated and only if spin-dependent relativistic effects are taken into account. These requirements are readily satisfied simultaneously in two-component relativistic density functional theory calculations for the ground state. However, the situation becomes more complicated for excited states. This problem inspired several theoretical investigations aimed at assigning the observed vibronic spectra to the modeled Au_3 excited states.

Only a few electronic transitions are detected in experimental spectra in the region from 0.25 eV to 5.32 eV [2–5]. The information available is limited to transition energies and relative intensities. In addition, a lifetime of 28 μs is known for an excited state responsible for the 1.66 eV transition.

Theoretical modeling of the excited states and attempts to assign the transitions are reported in Refs. [5–9]. Early publications by Balasubramanian and co-workers [6–8] are focused on the electron-correlation problem in the scalar relativistic approximation. The effects of correlations are considered at the multiconfigurational SCF (MCSCF) and configuration interaction (CI, singles + doubles) level of the theory within the relativistic core-potential model with 5*d* and 6*s* valence electrons of the gold atoms. The basis set employed in the calculations is limited to *d* functions. The importance of spin-dependent relativistic effects is discussed in Ref. [8] where relativistic (double group) CI

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calculations are performed. According to the authors, the spin–orbit coupling results in the splitting of the degenerate E state (in terms of irreducible representations of the D_{3h} point group), thereby quenching the Jahn–Teller distortion of the symmetric D_{3h} configuration. Despite the qualitative significance of this result, the situation with excited states remains tentative. In Ref. [9], the results obtained in Refs. [6, 7] are argued to be incorrect due to the use of insufficiently extensive basis sets and the fact that *d*-shell contributions to the correlation energy were neglected.

The recent work [5] presents a study of the Au_3 electronic states within the relativistic (double group) CI approach. To the best of our knowledge, it has been thus far the sole investigation that has systematically treated spin–orbit effects, which are well-known to be of significant importance for the correct description of the properties of gold compounds. Although employing a small basis set and neglecting of the correlation of the outermost 5*s* and 5*p* core electrons does not ensure the reliability of the quantitative estimates, the qualitative conclusions are of actual importance. The spin–orbit coupling of scalar relativistic states elucidates the nature of the transitions that cannot be referred to as other than spin-forbidden. In standard spectroscopic notation, these transitions can be designated as $A^2E' \leftarrow X^4E'$. For the two lowest-lying excited states, the calculated transition energies, according to the authors, agree with the experimental values. It is noteworthy that both transitions occur between the states that are related to the highly symmetric equilateral triangle configuration which does not undergo Jahn–Teller distortion.

In this paper, we report on our studies of the excited states of Au_3 with many-body multipartitioning perturbation theory (MPPT) [10] for quasirelativistic intermediate effective Hamiltonians. As opposed to previous investigations, we invoke a superior relativistic pseudopotential model and use an extensive basis set. Both energies and dipole moments are evaluated for vertical transitions.

2. Computational details

We employ the same shape-consistent semilocal pseudopotentials for the 60-electron cores of Au atoms [11] and the same generally contracted [5*s*5*p*4*d*3*f*2*g*] Gaussian basis set as in our previous paper [1]. Quasirelativistic multipartitioning second-order perturbation theory [10] is invoked in our calculations. A state-selective effective Hamiltonian is built in a model space spanned by Slater determinants following the procedure reported in Ref. [12]. The spin–orbit interactions between the model and outer spaces are completely neglected. Therefore, additional requirements on the model space and a procedure for its composition are imposed [12]. The procedure employed is based on the spin–orbit-free iterative perturbative configuration selection against a threshold [13]. To improve the description of spin–orbit effects associated with the one-body spin–orbit pseudopotential operator, a lower selection threshold is set for configurations evolving from single excitations of the leading determinants. The details of the procedure are reported elsewhere [1, 12]. Since the energies and wavefunctions of the ground state with a filled 5*d* shell and excited states with 5*d* holes are calculated simultaneously, it is highly desirable that the common set of molecular orbitals be well-balanced for $5d^9$- and $5d^{10}$-like occupancies. This is achieved through generating the orbitals by the fractional-occupancy Nesbet–Fock technique [14] with fixed MO occupancies corresponding to the formal atomic population scheme $5d^{9.5}6s^{1.5}$ at the dissociation limit. It is worth noting that relativistic symmetry is ignored in constructing and diagonalizing the effective Hamiltonian, and that the symmetry types of the resulting states are determined *a posteriori*.

Along with the energies obtained via effective Hamiltonian diagonalization, the components of dipole transition moments for the excitations from the ground state are evaluated by computing the spin-free one-body transition density matrices at first MPPT order.

The computations are carried out for the two stable isomers described in Ref. [1]. Our previous studies revealed the D_{3h} isomer (an equilateral triangle with the 2.640 Å bond length) to be of higher stability than the C_{2v} one (an open triangle with Au–Au bond of 2.539 Å and Au–Au–Au angle of 141.9°). For these reasons, our primary attention is focused on the first one of the above isomers.

3. Results and discussion

The relativistic electronic states of Au_3 for a nuclear configuration of an equilateral triangle bear one of the three types of symmetry normally denoted as $E_{1/2}$, $E_{3/2}$, and $E_{5/2}$ according to irreducible representations of the double group $\overline{D_{3h}}$. As shown by Guo *et al.* in Ref. [5], the only dipole-allowed transitions are $E_{1/2} \leftrightarrow E_{3/2}$, $E_{1/2} \leftrightarrow E_{5/2}$, $E_{3/2} \leftrightarrow E_{3/2}$, and $E_{3/2} \leftrightarrow E_{5/2}$.

Information on the vertical transitions of the D_{3h} isomer is collected in Table 1. Two points are noteworthy regarding these data. As Au_3 has an odd number of electrons, each state is doubly degenerate (a Kramers pair). Therefore we should explicitly define what a squared transition moment ($|\mu|^2$) implies. In this paper, we use the sum of patterns $|\mu_x|^2 + |\mu_y|^2 + |\mu_z|^2$ for transitions from each component

of one Kramers pair to one of the components of another pair. Only the strongest transitions are highlighted in Table 1, although the energy range studied has a rather high density of states (16 Kramers pairs). The corresponding

Table 1. Au_3 excited states: energies of the strongest transitions, symmetry types, and squared transition dipole moments

Transition energy [eV]	Symmetry type	$\|\mu\|^2$ [a.u.]
0.22	$E_{3/2}$	0.526
1.67	$E_{5/2}$	0.006
2.26	$E_{5/2}$	0.015
2.31	$E_{3/2}$	0.017
2.34	$E_{1/2}$	0.006
2.43	$E_{3/2}$	0.002
2.50	$E_{5/2}$	0.076
2.61	$E_{1/2}$	0.005

spectrum is presented in Fig. 1. There, we introduce the quantity $I = E|\mu|^2$ proportional to intensity, where E denotes the transition energy. For the second excited state

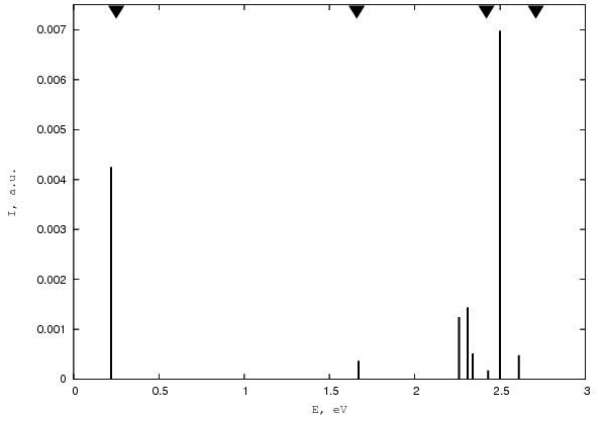

Figure 1. Au_3 model spectrum. Experimental energies are marked with black triangles.

(1.67 eV above the ground state) the transition moment value yields a state lifetime of 34.7 μs, which is in good agreement with the experimental value of 28.3 μs for the state lying 1.66 eV above the ground state.

We have also studied the open isomer. The transitions with non-negligible intensities in the open (C_{2v}) isomer occur at 0.77 (the lowest-energy transition), 0.93, 1.01, 1.46, 1.61, 2.07, 2.46, and 2.74 eV. As the lowest excitation energy for the C_{2v} isomer is shifted by about 0.5 eV with respect to that of the D_{3h} isomer, the experimental 0.25 eV transition is more likely to pertain to the D_{3h} isomer. Transitions with energies close to 1.0 eV have not been detected in experiments, thus hinting at the highly symmetric isomer.

The situation with the 2.42 and 2.71 eV transitions is rather obscure. As reported in Ref. [3], the absorption-intensity ratio of the 2.42 and 2.71 eV transitions is close to 1:6. The calculated transition energies 2.43 and 2.61 eV for the D_{3h} isomer match the experimental values within a reasonable error corridor of 0.1 eV with the intensity ratio being 0.37. For the open C_{2v} isomer there is also good agreement between the calculated transition energies (2.46 and 2.74 eV) and the observed spectral band positions, but the 2.46 eV transition appears to be much stronger than the 2.74 eV one. Therefore, the experimental 2.42 and 2.71 eV transitions most probably originate from the highly symmetric isomer.

4. Conclusions

The excited states of Au_3 have been studied with the relativistic MPPT method within the small-core relativistic pseudopotential model. Transition energies and dipole transition moments have been estimated for the two stable isomers. The assignment of the electronic transitions has been carried out. The calculated transition energies of the D_{3h} isomer match (within the 0.1 eV error corridor) the experimental values, and the dipole transition moment magnitudes are in reasonable agreement with the experimentally measured relative intensities advocating the highly symmetric isomer to be observed.

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