

Gold dimer in neon: An absorption and fluorescence study

S. Lecoultre, A. Rydlo, C. Félix, W. Harbich

Institut de Physique des Nanostructures, EPFL, CH-1015 Lausanne, Switzerland

Received: date / Revised version: date

Abstract. We report for the first time the absorption and fluorescence spectra of gold dimers in a neon matrix. The dimer absorption spectra show the $A \leftarrow X$ transition predicted from measurements in the gas phase and not observed so far in a matrix, as well as the so-called $B \leftarrow X$ and $C \leftarrow X$ transitions. Fluorescence measurements on the atom reveals new emission lines at 1.97, 3.59 and 4.09 eV that can be assigned to the ${}^2P_{1/2} \rightarrow {}^2D_{3/2}$, ${}^2P_{1/2} \rightarrow {}^2D_{5/2}$ and the ${}^2P_{3/2} \rightarrow {}^2D_{5/2}$ transitions. For the dimer, excitation of both A and B state results in distinct emission spectra with vibrational structure.

PACS. 36.40.Vz Optical properties of clusters

1 Introduction

One of the objectives of the field of cluster science is to understand the evolution of the properties of matter as a function of the number of atoms. In this respect the dimer has a special interest, since it is the first building block in which the nature of the bonding between atoms appears. Furthermore a detailed comparison between theory and experiment is possible due to the small number of atoms involved.

Optical spectroscopy is a powerful technique to investigate the electronic properties of small clusters. However, measurements on free mass selected species are limited by the low densities of particles. We have thus undertaken since several years [1] to condense mass selected clusters in rare gas matrices in order to study their optical properties. Recently new developments have allowed us to study not only Ag clusters, but also Au and Cu clusters in neon matrices with good signal to noise ratio. Neon matrices have the advantage to be the most inert matrices because of their low polarizability and their higher crystallinity compared to the other rare gas matrices. This helps to diminish undesirable effects, such as electronic level shifting, additional splitting or line broadening.

In particular the bonding in Au clusters, in which relativistic effects manifest strongly, is substantially different from that of silver clusters. Surprisingly, despite several previous studies, neither absorption nor fluorescence spectra of the gold dimer embedded inside a neon matrix have been reported. Furthermore in the visible range, where the main transitions are known to happen from gas-phase measurements [2,3], the existing spectra for Au_2 in argon [4–6] or krypton [7] do not report any transition below 3.2 eV. In this paper absorption and fluorescence measurements have been obtained in the UV-Visible range for the gold dimer embedded in neon. They are in excellent agreement with the gas-phase measurements.

2 Experimental Setup

Although the main principles of the measurement procedure are similar to those described in ref.[8], we have recently modified the setup in order to improve the control over the deposition of clusters and to reach lower temperatures that allow condensation of neon.

Briefly, the clusters are formed from a metal target sputtered by a 10 mA Xe^+ ion beam at 25 keV. The gold cations are then focused into a "Bessel Box" type (BB) energy filter which also acts as a beam stop for the intense flux of neutral. The cations of interest are mass-selected and directed towards the sample holder, which consists in a superpolished Aluminium mirror (obtained at Valley design corp.). The sample holder is fixed to a cold head cryostat (SRP-052A Cryocooler, Sumitomo Heavy Industries Ltd.) that allows refrigeration to about 6 K. During sample preparation, the size-selected clusters are accumulated together with the neon matrix for 1 to 1.5 h while a 50 μm thick matrix is grown.

Optical absorption measurements are performed by injecting light through the 2 mm length of matrix and collecting the residual light on the other side with an optical fiber of 400 μm core diameter. The collected light is then analyzed by an optical spectrometer coupled with a liquid-nitrogen-cooled charge coupled device (CCD). Comparing the intensity of the light passing through a matrix doped with clusters with a reference signal of light passing through a pure neon matrix yields the absorption spectrum.

For excitation, we use a frequency doubled optical parametric oscillator OPO pumped by a Nd:YAG laser onto the sample, translated vertically from its initial position in front of a CaF_2 window. The fluorescence is collected by the same lens that focuses the laser onto the mirror, in order to form a parallel beam. The collected beam is then focalized in the entrance slit of the spectrometer[9].

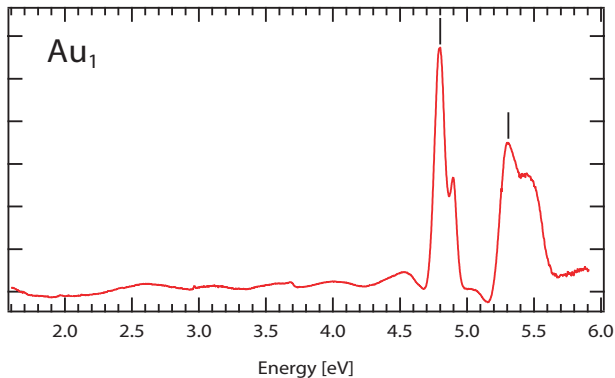


Fig. 1. Absorption spectrum of Au_1 in neon at 7K. The excitation energies for fluorescence (see Fig. 3) are marked by an arrow

3 Results and Discussion

The electronic properties of gold clusters can be best understood by first looking at the atomic properties of gold. We have therefore achieved preliminary measurements on the atom and compared them with already existing results in order to test our new experimental setup.

The experimental spectrum of gold atoms in neon is shown on Fig. 1. It contains a well defined transition at 4.8 eV with a shoulder at 4.9 eV as well as a larger structure with two maxima between 5.25 and 5.6 eV. Comparison with previous measurements in neon [10] and other matrices [6] confirm this spectrum except for the small secondary peak at 4.9 eV. This measurement of atomic gold inside a matrix is the first one to show such a sharp transition close to the 4.8 eV one. In other works by Gruen *et al.* [10], the neon matrices were systematically annealed at 10 K and it is possible that such heating of the matrix made the system possible to evolve towards a more stable configuration by suppressing metastable sites. Indeed, this secondary peak might be due to the existence of a less favorable second site isomer for the gold atoms inside the neon matrix. This is the case for silver atoms where two site isomers of 3 and 4 vacancies of neon are in competition [11,12]. This hypothesis is emphasized by the fact that silver and gold atoms have a very similar size due to relativistic effects that tend to confine the s electrons of gold. [13]

Figure 2 shows the absorption spectrum of Au_2 in neon. It consists of 3 narrow peaks at 2.58, 3.13 and 3.30 eV and a weak absorption at 3.96 eV. Although attention was paid to reduce fragmentation of the dimer by decreasing the deposition energy, it remains difficult to avoid the atom signal. This might be due to the large energy distri-

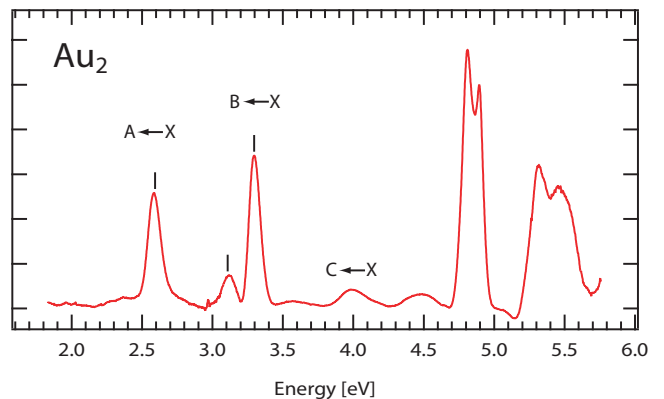


Fig. 2. Absorption spectrum of Au_2 in neon at 7K. The excitation energies for fluorescence (see Fig. 5) are marked by an arrow

bution of the dimers that are produced by the sputtering process.

Other measurements recently done in our group for bigger cluster sizes in neon unambiguously confirm these transitions, for instance by looking at the trimer spectrum that includes a large contribution due to the Au_2 spectrum via fragmentation.

As already mentioned, the gold dimer has been studied in the gas phase [2,14,15], in argon [4–6] and krypton matrices [7]. The gas-phase measurements have shown the presence of two absorption bands at low energies: $A \leftarrow X$ around 2.44 eV and $B \leftarrow X$ centered around 3.18 eV [16]. With good certainty we can attribute the peak measured at 2.58 eV to the $A \leftarrow X$ absorption measured in the gas phase, and the peak measured at 3.3 eV to the $B \leftarrow X$ transition.

Measurements in matrices have found transitions around 3.3–3.5 eV, 3.9–4.1 eV and 5.9–6 eV depending on the measurement and the type of matrix. To our knowledge however, no other measurement in matrix has ever confirmed the existence of the low energy $A \leftarrow X$ transition. The $B \leftarrow X$ dimer absorption has been reported by Klotzbücher *et al.* [6] at 3.40 eV and by Fedrigo *et al.* [5] at 3.47 eV in argon. The weak absorption at 3.96 eV, denoted $C \leftarrow X$ has also been observed in argon matrices around 4 eV [5], it is however not visible in the gas phase. This suggests that it is due to a symmetry forbidden transition, which is allowed by the interaction with the matrix. The secondary peak at 3.13 eV, next to the $B \leftarrow X$ transition, has neither been observed in the gas phase, nor in other matrices. Its origin is therefore hard to understand. Notice however in Fig. 5 that excitation at 3.13 and 3.30 eV result in the same emission spectra. The relaxation following excitation of the 3.13 eV peak is therefore similar to the $B \leftarrow X$ one, this indicates that it is not due to a second site isomer.

Several calculations have studied the electronic transitions of Au_2 . In particular recent studies have been done in the framework of the TDDFT scheme [16–18], in which the relativistic corrections are taken in an average sense, i.e. without introducing explicitly the spin-orbit coupling. These calculations show clearly the two major effects of

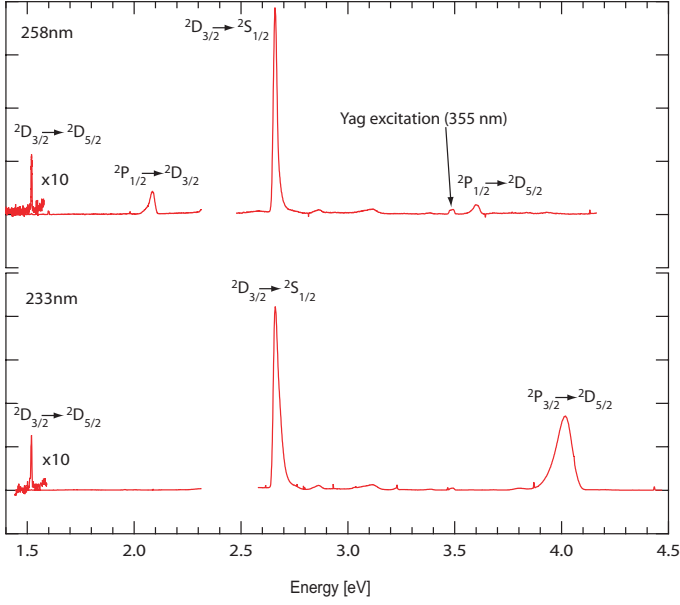


Fig. 3. Fluorescence spectra of Au_1 excited at 233 nm (5.32 eV) and 258 nm (4.80 eV)

the d electrons on the optical properties of gold clusters, namely the quenching of the oscillatory strength and the strong s - d hybridization in the low energy transitions. Due to the absence of the spin-orbit term, the agreement with the experiment is only partial. These calculations suggest however that an orbital forbidden transition at 2.7 eV [17], could be responsible for the $\text{C} \leftarrow \text{X}$ absorption observed in matrices. More elaborate calculations, that explicitly take into account the spin-orbit coupling [19–21], are in excellent agreement with the $\text{A} \leftarrow \text{X}$ and $\text{B} \leftarrow \text{X}$ transitions observed in the gas phase.

Turning to fluorescence, Fig. 3 shows the fluorescence spectra of gold atoms under excitations at 233 nm (5.32 eV) and 258 nm (4.80 eV).

Two narrow peaks at 1.52 and 2.66 eV are visible under both excitation wavelengths whereas wider emissions at 4.09 eV, 3.59 eV and 2.08 eV are only seen for one excitation wavelength. The tiny structures at 2.86 and 3.10 eV are artifacts due to the residual light in the laboratory, while the small structure at 3.49 eV is due to the YAG laser excitation. Existing measurements[22] on the same system assign the peak at 2.66 eV to the ${}^2\text{D}_{3/2} \rightarrow {}^2\text{S}_{1/2}$ transition and the one at 1.52 to the ${}^2\text{D}_{3/2} \rightarrow {}^2\text{D}_{5/2}$ transition while the ${}^2\text{D}_{5/2} \rightarrow {}^2\text{S}_{1/2}$ emission line reported at 1.21 eV lies beyond our measurement range. The narrowness of the $\text{D} \rightarrow \text{D}$ transition is due to the localized character of the electronic levels that are involved [23]. The wider peaks have not been reported so far. We assign the 4.09 eV emission line to the ${}^2\text{P}_{3/2} \rightarrow {}^2\text{D}_{5/2}$ deexcitation channel, this in agreement with the observation that it is only present by excitation of the ${}^2\text{P}_{3/2}$ level at 5.3 eV. The emission lines at 2.08 eV and 3.59 eV are only observed by excitation of the ${}^2\text{P}_{1/2}$ state, they are respectively assigned to the ${}^2\text{P}_{1/2} \rightarrow {}^2\text{D}_{3/2}$ and ${}^2\text{P}_{1/2} \rightarrow {}^2\text{D}_{5/2}$ transitions.

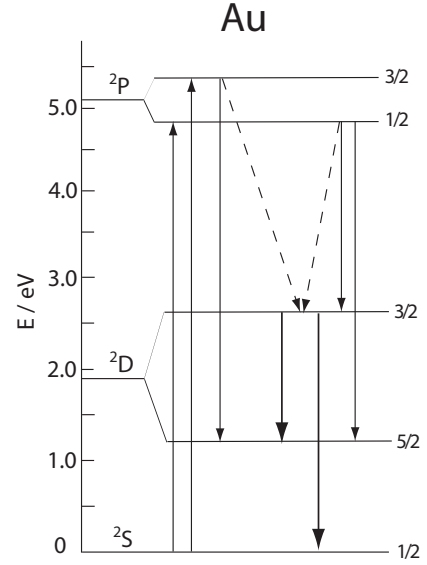


Fig. 4. Energy level diagram of Au_1 . Five emission lines correspond to the fluorescences observed on the spectra. ${}^2\text{D}_{3/2} \rightarrow {}^2\text{D}_{5/2}$ at 1.52 eV, ${}^2\text{P}_{1/2} \rightarrow {}^2\text{D}_{3/2}$ at 2.14 eV, ${}^2\text{D}_{3/2} \rightarrow {}^2\text{S}_{1/2}$ at 2.66 eV, ${}^2\text{P}_{1/2} \rightarrow {}^2\text{D}_{5/2}$ at 3.59 eV and ${}^2\text{P}_{3/2} \rightarrow {}^2\text{D}_{5/2}$ at 4.09 eV

Notice that the low intensity ${}^2\text{P}_{1/2} \rightarrow {}^2\text{D}_{5/2}$ is not allowed in the gas phase.

Fluorescence measurements of Au_2 in neon are given in Fig. 5 under excitations at 376 (3.30), 396 (3.13) and 480nm (2.58 eV). Three different emission bands with vibrational resolution have been obtained between 1.65 and 2.0 eV, 2.3 and 2.5 eV and 2.5 to 2.65 eV. The spectra for excitation at 376 nm (3.30 eV) and 396 nm (3.13) are quasi-identical and correspond to the same deexcitation channels. The spectrum resulting from excitation at 480 nm (2.58 eV) is different with one single vibrational band that is already present on the other spectra with smaller amplitude. It is probable that this fluorescence is resonant with the excitation of the dimer to the A state as the Stoke shift is only 0.13 eV. It is interesting to notice that the radiative deexcitation channel at 1.8 eV is only visible by excitation of the $\text{B} \leftarrow \text{X}$ transition. This suggest that the A state is not coupled by radiative or matrix assisted relaxation to the state responsible for the 1.8 eV radiative channel.

To our knowledge, these results show for the first time fluorescence spectra of the gold dimer in a neon matrix. Fluorescence of Au_2 in argon has been measured by Fedrigo *et al.* [1] and a large band without any structure has been reported between 1.41 and 1.91 eV, which should correspond to the lowest energy structure presented on Fig. 5.

The vibrational energy of the ground state deduced from the emission structures goes from 22.9 meV for the lowest energy structure to 22.8 meV and 23.5 meV for the next ones, which is in good agreement with the gas-phase measurement of 23.7 meV (190.9 cm^{-1}) given by Morse *et al.* [15]

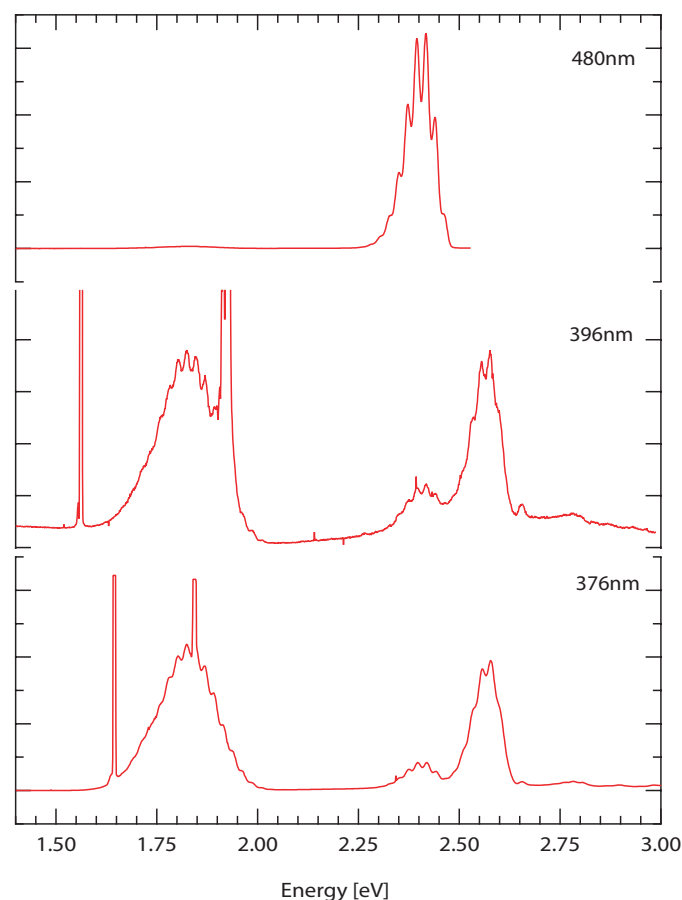


Fig. 5. Fluorescence spectra of Au_2 excited at 376 (3.30), 396 (3.13), 480nm (2.58 eV). Both narrow peaks at low energies are due to laser excitation

In this paper, we have reported the absorption spectra of Au_2 inside a neon matrix showing the two most intense $A \leftarrow X$ and $B \leftarrow X$ transitions at 2.58 and 3.30 eV. We have also reported new emission lines in the atom fluorescence that correspond well with the already known energy levels in the gold atom. Finally, the fluorescence spectra of the gold dimer resulting from the excitation of the A and B states has been shown. Vibrational energies of the ground state deduced from the emission bands are in good agreement with gas-phase measurements.

4 acknowledgments

The present authors express their sincere thanks to Prof. Jean Buttet who has discussed the present work with deep interest.

References

1. S. Fedrigo, W. Harbich, and J. Buttet, Phys. Rev. B **47**, 10706 (1993).
2. J. Ruamps, R. Hebd. Séances Acad. Sci. **238**, 1489 (1954).
3. R. C. Amme and P. O. Haugsjaa, Physical Review **177**, 230 (1969).
4. S. Fedrigo, W. Harbich, and J. Buttet, Int. J. Mod. Phys. B **6**, 3767 (1992).
5. S. Fedrigo, W. Harbich, and J. Buttet, J. Chem. Phys. **99**, 5712 (1993).
6. W. E. Klotzbücher and G. A. Ozin, Inorg. Chem. **19**, 3767 (1980).
7. W. Harbich, S. Fedrigo, and J. Buttet, J. Chem. Phys. **96**, 8104 (1992).
8. F. Conus, J. T. Lau, V. Rodrigues, and C. Félix, Rev. Sci. Instrum. **77**, 113103 (2006).
9. C. Sieber, Ph.D. thesis, EPFL, 2002.
10. D. M. Gruen and J. K. Bates, Inorg. Chem. **16**, 2450 (1977).
11. S. Ossicini and F. Forstmann, Inorg. Chem. **21**, 1755 (1982).
12. J. T. Zoueu, M. Vala, and J. C. Rivoal, Chem. Phys. **312**, 89 (2005).
13. D. M. Gruen, M. Moskovits, and G. A. Ozin, in *Cryochemistry*, edited by Wiley-Interscience (New-York, ADDRESS, 1976).
14. L. L. Ames and R. F. Barrow, Trans. Faraday Soc. **63**, 39 (1967).
15. M. D. Morse, Chem. Rev. **86**, 1049 (1986).
16. J. C. Idrobo, W. Walkosz, S. F. Yip, S. Ogut, J. Wang, and J. Jellinek, Physical Review B (Condensed Matter and Materials Physics) **76**, 205422 (2007).
17. X. Wang, X. Wan, H. Zhou, S. Takami, M. Kubo, and A. Miyamoto, J. Mol. Struct. **579**, 221 (2002).
18. S. Gilb, private communications (2008).
19. W. C. Ermler, Y. S. Lee, and K. S. Pitzer, J. Chem. Phys. **70**, 293 (1978).
20. I. Itkin and A. Zaitsevskii, Chem. Phys. Lett. **374**, 143 (2003).
21. F. Wang, T. Ziegler, and E. J. Baerends, J. Chem. Phys. **122**, 204103 (2005).
22. W. Schrittenlacher and D. M. Kolb, Ber. Bunsenges. Phys. Chem. **88**, 492 (1984).
23. W. Schrittenlacher, H. H. Rotermund, W. Schroeder, and D. M. Kolb, Surf. Sci. **156**, 777 (1985).