V@Au$_{12}$⁻: An Improved Novel Catalyst for CO Oxidation?

Jesús Graciani,* Jaime Oviedo, and Javier F. Sanz

Departamento de Química Física, Facultad de Química, Universidad de Sevilla E−41012, Sevilla, Spain

Received: December 15, 2005

The catalytic properties toward CO combustion of an encapsulated cluster, V@Au$_{12}$⁻, have been explored by means of plane-wave pseudopotential density-functional theory calculations. Single adsorption of both O$_2$ and CO as well as coadsorption have been considered. The adsorption energy for the O$_2$ molecule is about 0.3−0.4 eV which limits its use to low temperatures. However, in contrast to what happens for pure gold clusters, this system shows a remarkable capacity to bind a high number of oxygen molecules. Moreover, its icosahedral cluster is able to bind 12 CO molecules, since all of the gold atoms are available.The bond between the metal cluster and the oxygen molecule mainly arises from a charge transfer from the metal toward the π_g antibonding O$_2$ orbitals, while in the case of CO molecule, the classical σ-donation π-back-donation mechanism is observed. Finally, no coadsorption effects are found when both molecules are adsorbed, the interaction properties between the cluster and the substrates remain basically unaltered.

Introduction

In recent years there has been an increasing interest in studying the capacity of free gold clusters to catalyze the CO oxidation.[1−11] This is a preliminary step to better understand the behavior of real catalysts, which are usually composed of metallic clusters supported on a surface. Several experimental[1,3] and theoretical[10,11] studies have shown that the key step in the oxidation process is the activation of molecular oxygen on the cluster. It has been suggested that the oxygen molecule gets some electron density from the cluster to form a superoxo state (O$_2$⁻) which reacts with a coadsorbed CO molecule. From these studies, several conclusions have been established. For example, only clusters with an odd number of electrons can bind oxygen, which seems to be linked to their ability to transfer one electron from an open shell to the molecule.[3] Even in this favorable case, since no more electrons are available, the clusters are saturated after binding a single oxygen molecule,[1,3] which might limit its utility as a catalyst. The size and the charge state of gold clusters also play an important role in the interaction between gold clusters and adsorbed molecules.[4,11] This also holds for supported clusters, where the presence of defects seems to favor oxidation.[12−14]

After a seminal work by Pyykkö et al. several encapsulated clusters such as M@Au$_{12}$ (M = W and Mo) or M@Au$_{12}$⁻ (M = V, Nb, and Ta) have been predicted and experimentally produced.[15−18] These clusters owe their stability to aurophilic attraction, relativity, and the 18-electron rule. They present unique electronic properties such a wide HOMO−LUMO gap, which might be responsible for an enhanced stability. They also possess a highly degenerated HOMO that, in principle, could be oxidized to a maximum loss of 10 electrons.[19]

In this work we theoretically explore the possibility of using the V@Au$_{12}$⁻ cluster as a catalyst for CO oxidation. We choose this potential candidate because it shows several advantages when compared to pure gold clusters. First, it adopts an icosahedral geometry, which implies a very stable and well-known structure.[18] This is not usually the case for gold clusters,

where a planar or an amorphous structure is predicted.[20−23] Second, its unique cluster electronic structure, where a highly degenerate HOMO holds 10 electrons, might facilitate a charge transfer from the cluster to adsorbed molecules. In addition, the cluster shows important technological properties; since it is charged, cluster sintering is hindered and at the same time, because its icosahedral geometry it would have a high gold vaporization energy (i.e., it is very difficult to remove gold atoms from the cluster).

Technical Details

In the present work, we used the implementation of density functional theory (DFT) with plane waves[24] and the PAW (plane augmented waves) potentials.[25] We employed the generalized gradient approximation (GGA) due to Perdew et al.[26] for the exchange-correlation energy, which seems to describe better the formation and creation of bonds. The calculations were performed with the VASP (Vienna ab initio simulation package) code.[27,28]

The calculations were carried out at the Γ point of the Brillouin zone with an energy cutoff of 400 eV. Since the oxygen molecule ground state is a triplet, we carried out spin polarized calculations when O$_2$ was present. Spin−orbit (SO) coupling is not included in this work. However, it is considered an acceptable approximation as SO coupling is known not to affect the relative stability of isomers and to have small influence on the band gaps.[29] The periodic unit cell consisted of a cubic box 15 Å side. In this kind of calculations, we must decide which states are treated as core states and which as valence states. For oxygen and carbon the valence states consisted of s^{2}p^4 and s^{2}p^2 respectively whereas for gold the valence electrons were in the d^{10}s^1 configuration. Finally, for vanadium the five 4s^{2}3d^3 electrons were included as valence, the reference state for the potential generation being d^{4}s^1. We used the PAW potentials included in the VASP package.[30] For cases with a multiple adsorption we did not carry out a systematic search for the global minimum. We simply started from an initial guess and performed a geometry optimization. Even in the worse case, starting from several initial geometries is enough to give a

---

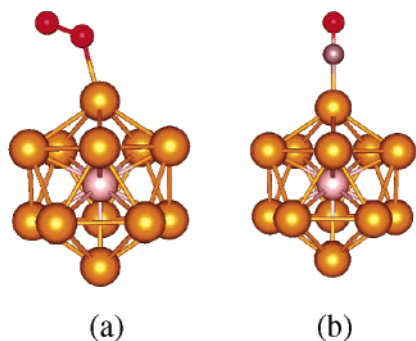* Corresponding author. E-mail: graciani@us.es. Fax: +34954557174.

Figure 1. Optimized adsorption geometries for (a) EC-O$_2$ and (b) EC-CO.

representative structure. We have checked that small changes in the geometry of the molecules do not essentially change the character of the bonding.

Results

As previously reported, the I_h icosahedral structure of V@Au$_{12}$$^-$ (Figure 1) is clearly preferred over other isomers.[18] The HOMO exhibits 5-fold degeneracy with 10 electrons, h_g,[10] and the ground state is $^1A_{1g}$. Distortion of this icosahedron leads to two highly symmetric structures commonly related to this cage cluster having O_h and D_{5h} symmetry. Our calculations show them to be less favored by 17.5 and 36.9 kJ/mol, respectively. These values are in good agreement with those reported by Zhai et al. computed through scalar-relativistic (SR) calculations and uncontracted all-electron Slater basis set (20.5 and 39.3 kJ/mol). We found a V−Au bond distance of 2.716 Å in the I_h structure, somewhat shorter than that reported from S−R calculations. This bond distance increases by 0.05−0.07 Å in the lower symmetry structures (O_h, 2.776 Å; D_{5h}, 2.767 and 2.792 Å). The external Au−Au is found to be 2.856 Å (I_h), 2.776 Å (O_h) and 2.809 (×10), 2.836 (×10), and 2.708 (×5) Å in the D_{5h} structure. These distances compare reasonably well with previous values for this and related compounds estimated from S−R computations,[15,18] although they all are found to be 0.03−0.04 Å shorter.

When an O$_2$ molecule is adsorbed we find that the most stable geometry is for the molecule in its triplet state, on top of a gold atom. The calculated adsorption energy is 0.36 eV. This is a small value and indicates that the adsorption would only be possible at low temperatures. This has to be compared with 0.51 eV for the Au$_{13}$−O$_2$ system[2] although the reported value for small anionic gold clusters can be larger than 1 eV.[7,8,10] We performed additional calculations that showed that other possible adsorption sites, like adopting a bridge position between two gold atoms were not stable.

In the most stable geometrical configuration the oxygen molecule binds the cluster in a tilted way forming a bent-triatomic structure with an Au−O−O angle bond of 125°. The optimized O−O bond distance elongates from 1.24 Å in a vacuum to 1.28 Å after adsorption and the oxygen−oxygen vibrational frequency shifts from 1553 cm^{-1} for the free molecule to 1270 cm^{-1} after adsorption. Such a bond weakening reveals that upon adsorption some charge transfer from the cluster toward the oxygen π_g antibonding molecular orbitals takes place.[10]

To illustrate this point, we have carried out an analysis of the electronic structure for the adsorbed system, and the electron density difference, $\Delta\rho$, computed as the difference between the electron density of the adsorbed system and that of the separated entities appears to be especially meaningful. The 3D isosurfaces
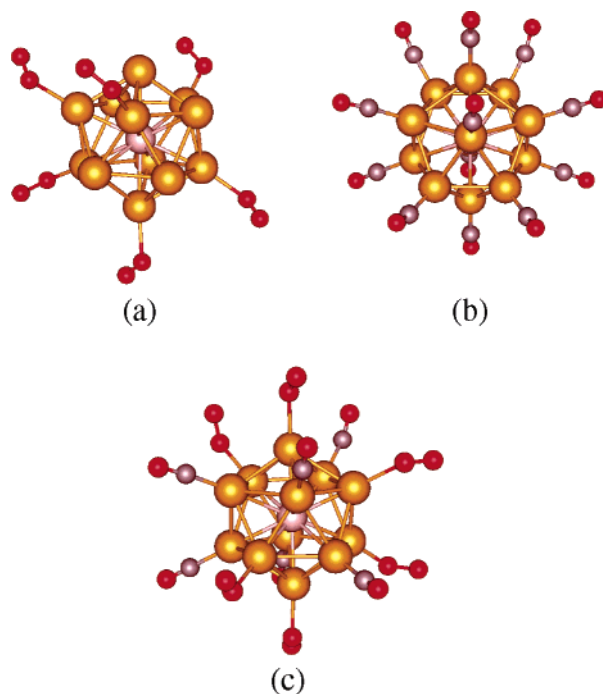

Figure 2. Optimized geometries for multiple adsorption: (a) EC-6O$_2$; (b) EC-12CO (top view); and (c) EC-6CO-6O$_2$.
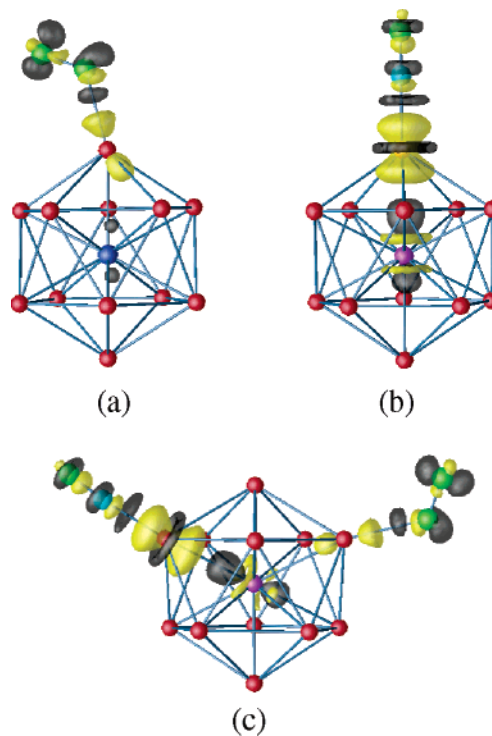

Figure 3. Electron density difference maps. They are computed as the difference between the electron density of the adsorbed system and the separated entities. a) EC−O$_2$, b) EC−CO and (c) EC−CO−O$_2$. Negative and positive values are represented in gray and dark gray, respectively.

reported in Figure 3a show the variations of electron density involved upon adsorption of O$_2$ molecule. The cluster provides some charge for the formation of the molecule-cluster bond although the affected area is almost restricted to the gold atom directly bound to the molecule. The Au−V bond distance is elongated upon the adsorption by around 0.05 Å whereas the rest of Au−V distances shorten a little. There is also a clear charge transfer toward the antibonding π_g orbitals of the O$_2$

TABLE 1: Average and Incremental Adsorption Energies and Average Geometrical Parameters for Multiple O_2 Adsorption onto the Cluster[a]

	V−Au	Au−O	O−O	Au−O−O	E_{ads}(av)	E_{ads}(inc)
EC-O_2	2.72	2.23	1.28	124.8	0.37	0.37
EC-2O_2	2.72	2.23	1.28	123.4	0.30	0.23
EC-6O_2	2.73	2.25	1.27	119.6	0.30	
EC-9O_2	2.73	2.29	1.27	121.7	0.29	
EC-10O_2	2.74	2.29	1.27	120.1	0.28	0.20
EC-11O_2	2.74	2.29	1.27	121.4	0.27	0.14

[a] EC is a shortname for the encapsulated cluster. The adsorption energy for a molecule is defined as the energy required to remove it from the cluster and is computed as the energy difference between the whole system and the isolated fragments. For multiple adsorption we have distinguished between the incremental adsorption energy that is the energy to remove the nth molecule to give a $(n − 1)$th adsorbed system and the average adsorption energy that is the energy to remove n molecules from the cluster to give n free molecules, divided by n. Geometrical parameters for multiple adsorption are averaged.

molecule,[7,10] which explains the lengthening of the O−O bond distance. We cannot properly quantify the amount of charge transferred since a population analysis is ambiguous. However, the analysis of the DOS plots does not show clear evidence of the transfer of a full electron as it was suggested for pure gold clusters.[1] Analysis of Figure 3a also shows the local character of the interaction, which concerns only the central V and the Au atom involved in the adsorption.

Further addition of O_2 molecules to the cluster was also considered. When we optimize the position of two adsorbed molecules we find essentially the same geometry we obtained before but the adsorption energy slightly lowered (Table 1). To get a deeper insight into the adsorption energy diminution we continue adding more adsorbed O_2 to the system and performed calculations with 1, 2, 6, 9, 10, and 11 molecules. Incremental adsorption energies were found to slowly decrease as we add more molecules and become 0.14 eV for the 11th one.

The properties of the adsorbed molecules remain the same even when a high number of O_2 are present (Table 1). After analyzing charge densities (not shown) we conclude that the charge-transfer mechanism described for a single molecule still holds in this case. We do not see an abrupt change when passing from 10 to 11 adsorbed molecules which suggests that, since there are 10 electrons available, the transfer mechanism do not consist on donating a full electron. We speculate that the cluster is a source of electronic charge so the O_2 takes some charge from the gold atom which is bound to. As more molecules are added, either the electronic repulsion grows or the cluster is not able to transfer enough charge to fully bind the molecule so the adsorption energy diminishes. The latter possibility is less suitable since all the molecules are adsorbed with similar geometries and with the same bond characteristics. Nevertheless, it is worth to stress that the V@Au$_{12}^-$ molecule has potential for adsorbing a remarkably high number of oxygen molecules, which opens the possibility of acting as an active catalyst in CO oxidation.

After studying the oxygen, we carried out calculations for adsorption of a single CO molecule. We find that the most stable configuration is in a linear Au−C−O geometry, with the C atom bound to the cluster on top of a gold atom site whereas adsorption on the O end of the molecule is not stable. The optimized geometry is shown in Figure 1b and some adsorption parameters are given in Table 2. The CO adsorption energy, 1.05 eV, is comparable to that reported for adsorption on pure gold clusters.[10] We find that the CO distance is slightly elongated compared to that of the isolated molecule (1.16 vs 1.14 Å) and

TABLE 2: Average Adsorption Energies and Geometrical Parameters for Multiple CO Adsorption onto the Cluster, Where Data are Evaluated as in Table 1

	V−Au	Au−C	C−O	E_{ads}(av)
EC-CO	2.72	1.97	1.16	1.05
EC-6CO	2.73	1.98	1.16	0.97
EC-12CO	2.75	1.98	1.16	0.98

the vibrational CO frequency is shifted from 2138 (gas phase) to 2005 cm^{-1} when the molecule is adsorbed. These variations are again evidence of a charge transfer from the cluster to the CO molecule. In Figure 3b, we present electron density difference isosurfaces which show that there is a donation from the molecule to the cluster leading to a reinforcement of the Au−V bond. In addition, there is also a back-donation from the gold atom to the antibonding π orbitals of the CO molecule. This σ-donation/π-back-donation scheme is analogous to the Blyholder mechanism already known for many transition metal surfaces.[31]

In previous theoretical work on pure icosahedral gold clusters, it has been shown that upon CO adsorption there is some charge transfer from the central atom to the external cage atoms.[2] To compare the atomic electron densities (and the donation capabilities) of these clusters with the present case we might use CO as a probe molecule[32] assuming that there is a linear relationship between the charge on the metal and the charge transferred back to the antibonding π orbitals of the CO molecule (and, hence, the red-shift induced on the CO vibrational frequency). We found out that for a CO molecule adsorbed on an icosahedral Au$_{13}^-$ cluster the frequency was 2025 cm^{-1}, i.e., a red shift of 113 cm^{-1}. The larger red shift estimated for the V encapsulated cluster reflects the fact that there is an increase of the electron density on the gold atoms when vanadium is present. This might constitute an advantage for adsorbing molecules.

Pure gold clusters can adsorb more than one CO molecule and their saturation number depends on cluster size. For example, it has been reported that Au$_{13}^-$ clusters can bind up to six molecules.[3] We have carried out calculations to study multiple CO adsorption. We find that when more than one molecule is adsorbed, the adsorption energy does not significantly decrease and it is still large for 12 molecules, which indicates low repulsion between adsorbed molecules. The main difference with pure gold clusters is that the saturation number is exceptionally high, which reflects that for the icosahedral geometry all the gold atoms are practically equivalent and available for adsorption. This is a distinct advantage compared to pure clusters where amorphous isomers are usually the most stable.[21]

One of the most striking conclusions obtained from previous studies on pure gold clusters is that the adsorption could be cooperative: i.e., it is easier to adsorb an O_2 molecule when some CO is already present.[3,4] Therefore, one of the aims of this work was to study the coadsorption of CO and O_2 molecules on the cluster. We have tried several combinations of adsorption sites and the optimized geometrical parameters and adsorption energies are presented in Table 3. Bond distances, angles, and charge distributions are quite similar to what is found when the molecules are adsorbed alone. This indicates that the presence of dissimilar molecules does not alter the bond character. The adsorption energies are still positive, i.e., the adsorption is favorable, although they are slightly reduced so the process is not cooperative. However, the reduction is small and possibly owed to repulsion between molecules. Therefore, we conclude that the adsorption is neither cooperative nor

TABLE 3: Average Adsorption Energies and Geometrical Parameters for the CO and O$_2$ Coadsorption, Where Data are Evaluated as in Table 1

	Au−C	C−O	Au−O	O−O	E_{ads} (CO)	E_{ads}(O$_2$)
EC−CO−O$_2$	1.97	1.16	2.26	1.28	1.03	0.35
EC-6CO−O$_2$	1.98	1.16	2.31	1.27	0.98	0.28
EC-6CO-6O$_2$	1.98	1.16	2.31	1.27	0.96	0.29

competitive; adsorption of molecules of different kind is quite independent. This is further confirmed by electron density difference maps (Figure 3c) in which the adsorption mechanism of one molecule is basically unaltered when the other molecule is present. This is a general statement even when the number of adsorbed molecules is high. It is remarkable that the cluster can bind a high number of molecules of both species so potentially could be a good catalyst for CO oxidation at low temperatures.

Conclusions

The isolated V@Au$_{12}$$^-$ cluster shows an enhanced electron density on gold atoms. Adsorption of oxygen molecules onto the cluster is possible, although the adsorption energy is low, about 0.3−0.4 eV which limits the adsorption to low temperatures. The bond mechanism essentially consists of a charge transfer from the cluster to the antibonding π_g orbitals of the oxygen molecule, which causes the molecule to adopt a triatomic bent geometry. A remarkable property for the cluster is that it can bind a high number of oxygen molecules which is a distinct advantage over pure gold clusters.

The adsorption energy of carbon monoxide is larger, about 1 eV, and the saturation number is 12, as high as the number of available gold sites. The adsorption mechanism consists of a charge donation from the molecule to the cluster and a back-donation from the cluster to antibonding π CO orbitals. Finally, in the coadsorption the interaction properties are basically unaltered which allows the presence of several adsorbed molecules. As a consequence the cluster has potential to act as a catalyst since it might enhance the CO combustion under favorable conditions. We plan to extend our work to include dynamical effects and possibly to extend it other encapsulated clusters such as W@Au$_{12}$.

References and Notes

(1) Salisbury, B. E.; Wallace, W. T.; Whetten, R. L. *Chem. Phys.* **2000**, *262*, 131.

(2) Okumura, M.; Kitagawa, Y.; Haruta, M.; Yamaguchi, K. *Chem. Phys. Lett.* **2001**, *346*, 163.

(3) Wallace, W. T.; Whetten, R. L. *J. Am. Chem. Soc.* **2002**, *124*, 7499.

(4) Hagen, J.; Socaciu, L. D.; Elijazyfer, M.; Heiz, U.; Bernhardt, T. M.; Wöste, L. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1707.

(5) Wu, X.; Senapati, L.; Nayak, S. K.; Selloni, A.; Hajaligol, M. *J. Chem. Phys.* **2002**, *117*, 4010.

(6) Wells, D. H., Jr.; Delgass, W. N.; Thomson, K. T. *J. Chem. Phys.* **2002**, *117*, 10597.

(7) Mills, G.; Gordon, M. S.; Metiu, H. *Chem. Phys. Lett.* **2002**, *359*, 493.

(8) Varganov, S. A.; Olson, R. M.; Gordon, M. S.; Metiu, H. *J. Chem. Phys.* **2003**, *119*, 2531.

(9) Kimble, M. L.; Castleman, A. W., Jr.; Mitriæ, R.; Bürgel, C.; Bonaèiæ-Kouteck×c6, V. *J. Am. Chem. Soc.* **2004**, *126*, 2526.

(10) Yuan, D. W.; Zeng, Z. *J. Chem. Phys.* **2004**, *120*, 6574.

(11) Ding, X.; Li, Z.; Yang, J.; Hou, J. G.; Zhu, Q. *J. Chem. Phys.* **2004**, *120*, 9594.

(12) Sánchez, A.; Abbet, S.; Heiz, U.; Schneider, W. D.; Häkkinen, H.; Barnet, R. N.; Landman, U. *J. Phys.* Chem. A **1999**, *103*, 9573.

(13) Yan, Z.; Chinta, S.; Mohamed, A. A.; Fackler, J. P., Jr.; Goodman, D. W. *J. Am. Chem. Soc.* **2005**, *127*, 1604.

(14) Molina, L. M.; Hammer, B. *J. Chem. Phys.* **2005**, *123*, 161104.

(15) Pyykkö, P.; Runeberg, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 2174.

(16) Li, X.; Kiran, B.; Li, J.; Zhai, H.-J.; Wang, L.-S. *Angew. Chem., Int. Ed.* **2002**, *41*, 4786.

(17) Autschbach, J.; Hess, B. A.; Johansson, M. P.; Neugebauer, J.; Patzschke, M.; Pyykkö, P.; Reiher, M.; Sundholm, D. *Phys. Chem. Chem. Phys.* **2004**, *6*, 11.

(18) Zhai, H.-J.; Li, J.; Wang, L.-S. *J. Chem. Phys.* **2004**, *121*, 8369.

(19) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412.

(20) Garzón, I. L.; Michaelian, K.; Beltrán, M. R.; Posada-Amarillas, A.; Ordejón, P.; Artacho, E.; Sánchez-Portal, D.; Soler, J. M. *Phys. Rev. Lett.* **1998**, *81*, 1600.

(21) Oviedo, J.; Palmer, R. E. *J. Chem. Phys.* **2002**, *117*, 9548.

(22) Häkkinen, H.; Moseler, M.; Landman, U. *Phys. Rev. Lett.* **2002**, *89*, 033401.

(23) Häkkinen, H.; Yoon, B.; Landman, U.; Li, X.; Zhai, H.-J.; Wang, L.-S. *J. Phys. Chem. A* **2003**, *107*, 6168.

(24) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64*, 1045.

(25) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.

(26) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(27) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558.

(28) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.

(29) Xiao, L.; Wang, L. *Chem. Phys. Lett.* **2004**, *452*, 392.

(30) Kresse, G.; Joubert, J. *Phys. Rev. B* **1999**, *59*, 1758.

(31) Blyholder, G. *J. Phys. Chem.* **1964**, *68*, 2772.

(32) Frank, M.; Bäumer, M.; Kühnemuth, R.; Freund, H. J. *J. Phys. Chem. B* **2001**, *105*, 8569.