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レーザーアブレーションマトリックス単離赤外分光法による金クラスターとNOとの反応の研究

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Matrix-Isolation Infrared Spectroscopic Studies on Reactions of Laser-Ablated Gold Clusters with NO Molecules (National Institute of Advanced Industrial Science and Technology (AIST)^a and Kobe University^b) TENG, Yun-Lei;^{a,b} JIANG, Ling;^a XU, Qiang^{a,b}

Introduction Because nitric oxide is one of the most insidious pollutants, considerable efforts have been expended for catalytic conversion of NO. The adsorption behavior of nitric oxide on Au has been widely studied using both theoretical and experimental methods to understand the catalytic mechanism.¹ Recent studies have shown that, with the aid of isotopic substitution techniques, matrix isolation infrared spectroscopy combined with quantum chemical calculation is very powerful for investigating structure and bonding of novel species.² To further understand the formation of gold nitrosyls, the reactions of laser-ablated gold atoms with nitric oxide in a solid-argon matrix have been performed under the conditions of low NO concentrations and high laser energies. IR spectroscopy and theoretical calculations provide evidence for the formation of products, Au₂NO, Au₃NO, Au₄NO, and Au₅NO.

Experimental Method The experiment employed the laser ablation and matrix isolation infrared spectroscopy. Briefly, the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating gold target. The laser-ablated species were co-deposited with NO in excess argon onto a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator. Typically, a 3–30 mJ/pulse laser power was used. NO (Taiyo Nippon Sanso Co.), ¹⁵N¹⁶O (MSD isotopes, 99%), and ¹⁴N¹⁸O (Isotec, 99%) were used to prepare the NO/Ar mixtures. Samples were annealed at different temperatures.

Theoretical Method Quantum chemical calculations were performed to predict the structures and vibrational frequencies of the observed reaction products using the Gaussian 03 program. The B3LYP density functional methods were utilized. The 6-311++G(d,p) basis set was used for N and O atoms, and LANL2DZ for Au atoms. Geometries were fully optimized and vibrational frequencies were

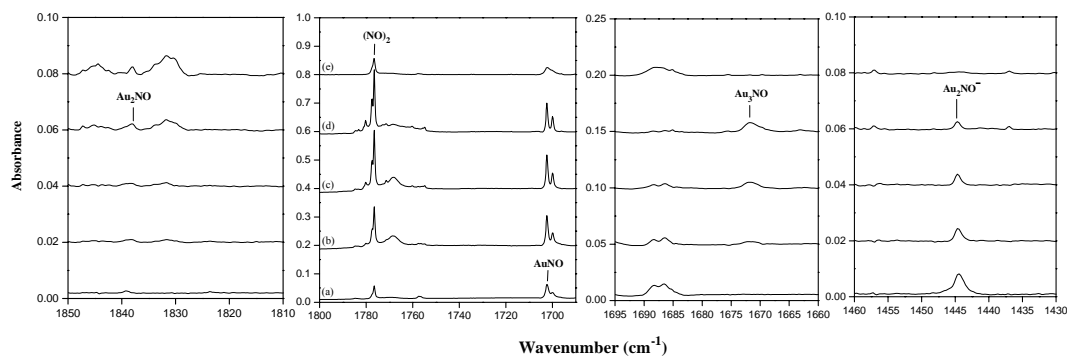


Figure 1. Infrared spectra in the 1850–1810, 1800–1690, 1680–1655, and 1460–1430 cm⁻¹ regions from codeposition of laser-ablated gold atoms with 0.2% NO using 20 mJ/pulse laser energy in argon: (a) 1 h sample deposition at 4 K; (b) after annealing to 25 K; (c) after annealing to 30 K; (d) after annealing to 35 K; (e) 0.2% NO + 0.05% CCl₄, after 1 h sample deposition at 4 K.

calculated with analytical second derivatives.

Results and Discussion In addition to the AuNO, Au(NO)₂, and Au₂NO⁻ anion absorptions, the present experiments provide evidence for the formation of small gold cluster nitrosyls in excess argon matrixes. New bands at 1838.1 and 1671.9 cm⁻¹ are observed in the experiment with 0.2% NO using 20 mJ/pulse laser energy (Figure 1). New bands at 1784.8 and 1757.4 cm⁻¹ are observed in the experiment with 0.1% NO using 30 mJ/pulse laser energy (Figure 2). The observations imply that the 1784.8 and 1757.4 cm⁻¹ species involve more Au atoms than the 1838.1 and 1671.9 cm⁻¹ species. The experimental condition of lower NO concentration and higher laser power favors the formation of these species, suggesting that these species are gold cluster nitrosyls.

The 1838.1, 1671.9, 1784.8, and 1757.4 cm⁻¹ bands shift to 1805.8, 1642.2, 1753.5, and 1725.6 cm⁻¹ with ¹⁵N¹⁶O and to 1790.4, 1629.1, 1738.3, and 1711.0 cm⁻¹ with ¹⁴N¹⁸O, exhibiting isotopic frequency ratios (¹⁴N¹⁶O/¹⁵N¹⁶O, 1.0179, 1.0181, 1.0179, 1.0184; ¹⁴N¹⁶O/¹⁴N¹⁸O, 1.0266, 1.0263, 1.0268, 1.0271) characteristic of N–O stretching vibration. In the mixed ¹⁴N¹⁶O + ¹⁵N¹⁶O and ¹⁴N¹⁶O + ¹⁴N¹⁸O experiments only pure isotopic counterparts are observed, which indicates that only one NO subunit is involved in this mode. Doping with CCl₄ has no effect on these bands, suggesting that the products are neutral. On the basis of the growth/decay characteristics measured as a function of changes of experimental conditions, along with comparison between the experimental and calculated frequencies and isotopic frequency ratios, these four bands can be assigned to (Au)_nNO with n = 2-5.

On the basis of the behavior of sample annealing together with the observed species and calculated stable isomers, plausible reaction pathways can be proposed. With low NO concentrations and high laser energies the laser-ablated gold atoms react with NO molecules in the excess argon matrixes to produce the small gold cluster nitrosyls, Au_nNO (n = 2-5), in addition to AuNO and Au(NO)₂. The absorptions of gold cluster nitrosyls increase on annealing (Figures 1, 2), suggesting the reactions to form these cluster nitrosyls are spontaneous. All possible reactions of gold atoms and small clusters with NO to form Au_nNO (n = 2-5) are predicted to be exothermic (–33.5 to –340.2 kJ mol⁻¹), in agreement with the experimental observations.

References:

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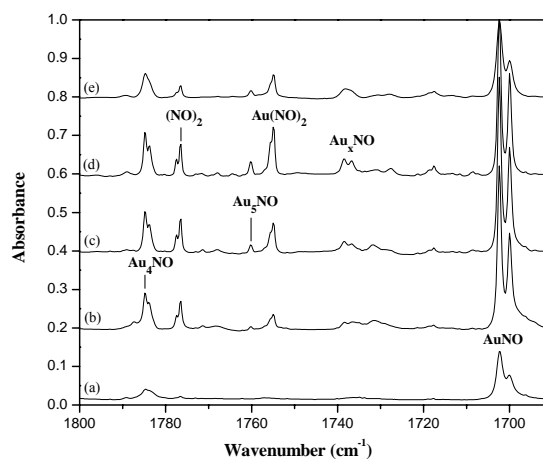


Figure 2. Infrared spectra in the 1800–1690 cm⁻¹ region from codeposition of laser-ablated gold atoms with 0.1% NO using 30 mJ/pulse laser energy in argon: (a) 1 h sample deposition at 4 K; (b) after annealing to 25 K; (c) after annealing to 30 K; (d) after annealing to 35 K; (e) 0.1% NO + 0.025% CCl₄, after annealing to 30 K.