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Reactions of Gold Atoms with Nitrous Oxide in Excess Argon: A Matrix Infrared Spectroscopic and Theoretical Study

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Reactions of laser-ablated Au atoms with N_2O molecules in excess argon have been investigated using matrix-isolation infrared spectroscopy and density functional theory calculation. On the basis of isotopic shifts, mixed isotopic splitting patterns, CCl_4-doping experiments, and the comparison with theoretical calculations, the absorption at 2047.5 cm^{-1} is assigned to the $OAuNN^-$ anion, and the absorption at 1512.3 cm^{-1} is assigned to the $AuNO^-$ anion, respectively. No evidence is found for the formation of new neutral and cationic products in the present experiments. It is predicted that the $OAuNN^-$ anion is a linear singlet molecule and the $AuNO^-$ anion is a bent doublet molecule. The agreement between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts supports the identifications of these species from the matrix infrared spectra. Plausible reaction pathways have also been discussed for the formation of these products.

Introduction

Reactions under nontraditional experimental conditions can often yield new and exciting species not accessible from normal chemical reaction conditions.[1] Recent studies have shown that, with an aid of isotopic substitution technique, matrix isolation infrared spectroscopy combined with quantum chemical calculation is very powerful in investigating the spectrum, structure, and bonding of novel species.[2,3] Nitrous oxide (N_2O) is isoelectronic with carbon dioxide (CO_2) but exhibits a global warming potential about 310 times that of CO_2 on a per molecule basis.[4] N_2O also acts as a potentially clean and highly selective oxygen donor for catalytic oxidation processes.[4] Gas-phase reactions of various metal atoms with N_2O have been extensively investigated both experimentally and theoretically.[5−13] It is now well-known that gold becomes catalytically active when deposited on select metal oxides as hemispherical nanoparticles with diameters smaller than 5 nm.[14] The supported Au nanoparticles exhibit remarkable catalytic activities and/or excellent selectivities in a number of reactions such as the low-temperature CO oxidation, epoxidation of propylene, and the reduction of nitrogen oxides.[14]

These findings of remarkable catalytic properties of nanosized gold particles have aroused great current interests in the reactivity of species containing gold.[15] It is also very interesting to note that gold clusters composed of less than 100 atoms are very active as catalyst for the oxidation of CO and hydrocarbons.[16−18] Furthermore, reactions of group 11 metal atoms with the CO/O_2 mixtures revealed that carbonylmetal oxides might act as the precursors for the oxidation of CO to CO_2.[19−21] Recent infrared spectroscopic study reveals that CO molecules react with gold atoms and small clusters in a rare gas matrix to generate gold complexes, $Au(CO)_n$ ($n = 1, 2$) and $Au_n(CO)$ ($n = 1-5$).[22,23] Interestingly, a combined photoelectron spectroscopic and theoretical investigation of $Au_6(CO)_n^-$ ($n = 0-3$) has indicated that an electron shuttling from the outer triangle to the inner triangle takes place upon CO chemisorption in the negatively charged systems and the neutral $Au_6(CO)_n$ complexes should be reactive toward O_2 due to the destabilization of the HOMO of Au_6 upon CO chemisorption.[24] Very recently, infrared photodissociation spectroscopy and theoretical calculation provide evidence for the formation of nonclassical gold carbonyls, $Au^+(CO)_n$ ($n = 1-12$).[25] Such information would be valuable in the mechanistic understanding for the catalytic CO oxidation by gold nanoparticles.

Argon matrix investigations of the reactions of laser-ablated Ti, Cr, and groups 3, 10, and 13 metal atoms with N_2O have characterized a series of neutral metal monoxide−dinitrogen and metal nitrous oxide complexes and cationic metal monoxide−dinitrogen complexes.[26−31] Copper and silver chloride−nitrous oxide complexes ClCuNNO and ClAgNNO have also been obtained in the reactions of metal chlorides with nitrous oxide.[32] To the best of our knowledge, there has been no report so far on the anionic product from the reactions of metal atoms with nitrous oxide molecules. Here, we report a study of the reaction of laser-ablated gold atoms with nitrous oxide molecules in excess argon. Infrared spectroscopy coupled with density functional theory (DFT) calculation provides evidence for the formation of the $OAuNN^-$ and $AuNO^-$ anions, with the absence of new neutral and cationic products.

Experimental and Theoretical Methods

The experiments for laser ablation and matrix-isolation infrared spectroscopy are similar to those previously reported.[33] In short, the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating pure gold targets. The laser-ablated Au atoms were codeposited with N_2O in excess argon onto a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator.

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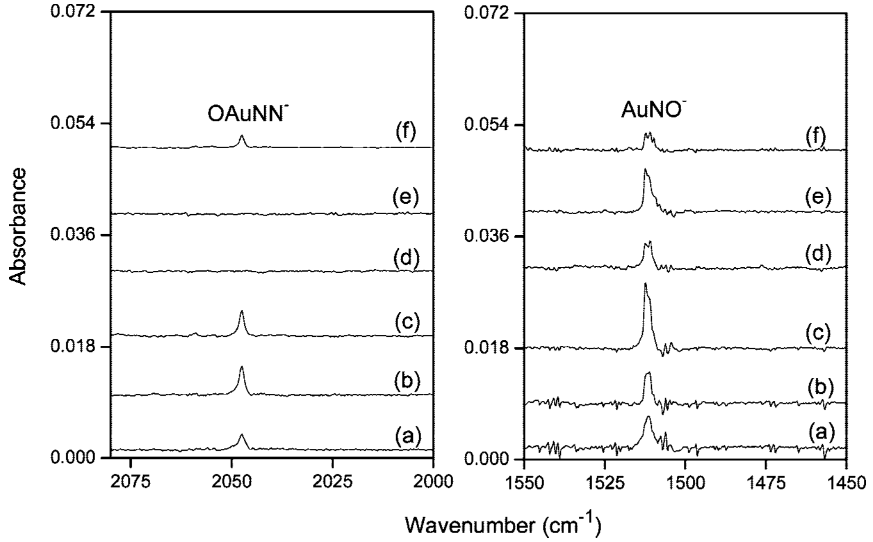

Figure 1. Infrared spectra in the 2075−2000 and 1550−1450 cm^{-1} regions from codeposition of laser-ablated Au atoms with 0.2% N_2O in Ar at 4 K. (a) Spectrum obtained from initial sample deposited for 1 h, (b) spectrum after annealing to 30 K, (c) spectrum after annealing to 34 K, (d) spectrum after 10 min of broadband irradiation, (e) spectrum after annealing to 38 K, and (f) spectrum obtained by depositing laser-ablated Au atoms with 0.2% N_2O + 0.03% CCl_4 in Ar at 4 K for 1 h and annealing to 34 K.

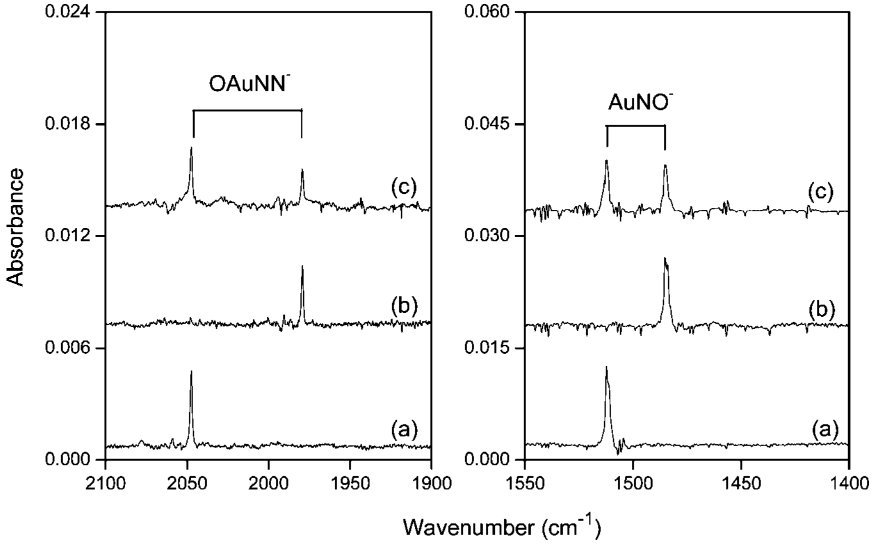

Figure 2. Infrared spectra in the 2100−1900 and 1550−1400 cm^{-1} regions from codeposition of laser-ablated Au atoms with isotopic N_2O in Ar after annealing to 34 K. (a) 0.2% $^{14}N_2O$, (b) 0.2% $^{15}N_2O$, and (c) 0.2% $^{14}N_2O$ + 0.2% $^{15}N_2O$.

Typically, 1−30 mJ/pulse laser power was used. N_2O (99.5%, Taiyo Nippon Sanso Co.), $^{15}N_2O$ (98%, Cambridge Isotopic Laboratories), and $^{14}N_2O$ + $^{15}N_2O$ mixtures were used in different experiments. In general, matrix samples were deposited for 30−60 min with a typical rate of 2−4 mmol per hour. After sample deposition, IR spectra were recorded on a BIO-RAD FTS-6000e spectrometer at 0.5 cm^{-1} resolution using a liquid nitrogen cooled HgCdTe (MCT) detector for the spectral range of 5000−400 cm^{-1}. Samples were annealed at different temperatures and subjected to broadband irradiation ($\lambda > 250$ nm) using a high-pressure mercury arc lamp (Ushio, 100 W).

DFT calculations were performed to predict the structures and vibrational frequencies of the observed reaction products using the Gaussian 03 program.[34] All of the present computations employed the BP86 density functional method, but comparisons were done with the B3LYP and mPW1PW91 density functional methods as well.[35] The 6-311+G(d) basis set was used for the N and O atoms,[36] and the Los Alamos ECP plus DZ (LANL2DZ) was used for the Au atoms.[37] Geometries were fully optimized, and vibrational frequencies were calculated with analytical second derivatives. Recent investigations have shown that such computational methods can provide reliable information for transition-metal complexes, such as infrared frequencies, relative absorption intensities, and isotopic shifts.[38−40]

Results and Discussion

Experiments have been done with nitrous oxide concentrations ranging from 0.02% to 1.0% in excess argon. Typical infrared spectra for the reactions of laser-ablated Au atoms with N_2O molecules in excess argon in the selected regions are illustrated in Figures 1 and 2, and the absorption bands in different isotopic experiments are listed in Table 1. The stepwise annealing and irradiation behavior of the product absorptions is also shown in the figures and will be discussed below. Experiments were also done with different concentrations of CCl_4 serving as an electron scavenger.[38]

Quantum chemical calculations have been carried out for the possible isomers and electronic states of new products. The comparison of the observed and calculated IR frequencies and

TABLE 1: IR Absorptions (in cm^{-1}) Observed from Codeposition of Laser-Ablated Au Atoms with N_2O in Excess Argon at 4 K

$^{14}N_2O$	$^{15}N_2O$	$^{14}N_2O/^{15}N_2O$	assignment
2218.5	2149.5	1.0321	N_2O
2047.5	1979.3	1.0345	$OAuNN^-$
1871.8	1838.8	1.0179	NO
1512.3	1485.1	1.0183	$AuNO^-$
1282.7	1263.1	1.0155	N_2O
1205.3	1181.5	1.0201	NNO_2^-

TABLE 2: Comparison of Observed and Calculated IR Frequencies (in cm^{-1}) and Isotopic Frequency Ratios for the Products

		observed		calculated		
species	mode	freq	$^{14}N_2O/^{15}N_2O$	method	freq	$^{14}N_2O/^{15}N_2O$
$OAuNN^-$	ν_{N-N}	2047.5	1.0345	BP86	2042.5	1.0350
				B3LYP	2184.1	1.0350
				mPW1PW91	2234.3	1.0350
$AuNO^-$	ν_{N-O}	1512.3	1.0183	BP86	1505.4	1.0178
				B3LYP	1605.9	1.0179
				mPW1PW91	1634.5	1.0179

TABLE 3: Ground Electronic States, Point Groups, Vibrational Frequencies (in cm^{-1}), and Intensities (km/mol) of the Products Using the BP86 Functional

species	elec. state	point group	frequency (intensity, mode)
$OAuNN^-$	$^1\Sigma^+$	$C_{\infty v}$	2042.5 (1009, σ), 702.3(135, σ), 457.3 (2 × 2, π), 399.4 (2, σ),131.3 (13 × 2, π)
$AuNO^-$	$^2A''$	C_s	1505.4 (749, A′), 383.4(9, A′), 171.0 (0.2, A′)

TABLE 4: Energetics for Possible Reactions of Gold Atoms with the N_2O, NO, N_2O^-, and NNO_2^- Molecules Calculated at the BP86 Level of Theory

no.	reaction	reaction energy[a] (kJ mol^{-1})
1	$Au + e \rightarrow Au^-$	−237.3
2	$Au + N_2O \rightarrow AuNNO$	−8.8
3	$Au + N_2O \rightarrow OAuNN$	−62.8
4	$Au + N_2O^- \rightarrow OAuNN^-$	−326.1
5	$Au^- + N_2O \rightarrow OAuNN^-$	−94.2
6	$Au + NNO_2^- \rightarrow AuNO^- + NO$	−104.7
7	$Au^- + NO \rightarrow AuNO^-$	−80.8

[a] A negative value of energy denotes that the reaction is exothermic.

isotopic frequency ratios for the N−N and N−O stretching modes of the products is summarized in Table 2. It has been found that the BP86 functional gives calculated vibrational frequencies much closer to the experimental values than do the B3LYP and mPW1PW91 density functionals, as was found in many cases such as metal complexes.[38−41] Hereafter, mainly BP86 results are presented for discussion. The ground electronic states, point groups, vibrational frequencies, and intensities of the products are listed in Table 3. Energetics for possible reactions of Au atoms with the N_2O, NO, N_2O^-, and NNO_2^- molecules is given in Table 4. Figure 3 shows the optimized structures of new products. Molecular orbital pictures for the $OAuNN^-$ and $AuNO^-$ anions are illustrated in Figure 4.

A. $OAuNN^-$. The absorption at 2047.5 cm^{-1} that appears during sample deposition increases visibly after sample annealing, but disappears upon broadband irradiation, and does not reappear after further annealing to higher temperature (Table 1 and Figure 1). This band shifts to 1979.3 cm^{-1} with $^{15}N_2O$, exhibiting an isotopic frequency ratio ($^{14}N_2O/^{15}N_2O$, 1.0345) characteristic of a N−N stretching vibration.[26−32] The mixed $^{14}N_2O + {}^{15}N_2O$ isotopic spectra (Figure 2, trace c) only provide the sum of pure isotopic bands, which indicates only one N_2 unit is involved in the complex.[42] Furthermore, doping with CCl_4 sharply decreases this band (Figure 1, trace f), suggesting that the product is anionic.[38] Thus, the anions such as $AuNN^-$, $OAuNN^-$, and O_2AuNN^- are suggested for consideration.

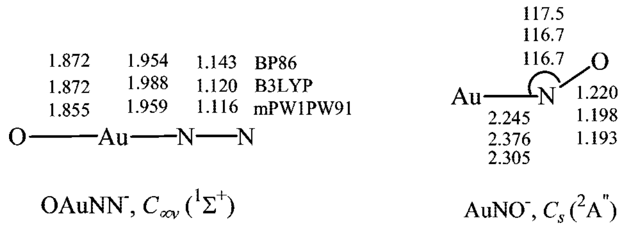

Figure 3. Optimized structures (bond lengths in angstroms, bond angles in degrees) of the $OAuNN^-$ and $AuNO^-$ molecules at the BP86, B3LYP, and mPW1PW91 levels of theory.

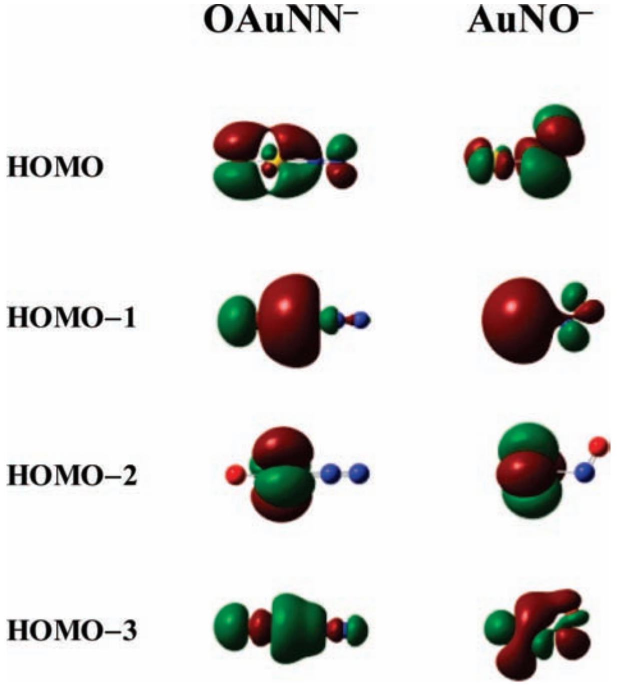

Figure 4. Molecular orbital pictures for the $OAuNN^-$ and $AuNO^-$ anions, showing the highest occupied molecular orbitals down to the third valence molecular orbital from the HOMO. Each HOMO and HOMO−2 of $OAuNN^-$ and HOMO−2 and HOMO−3 of $AuNO^-$ consists of one degenerate pair, and only one of them is plotted.

At the BP86 level of theory, the N−N stretching vibrational frequencies of the $AuNN^-$, $OAuNN^-$, and O_2AuNN^- anions are calculated to be 2241.4, 2042.5, and 1791.5 cm^{-1}, respectively. The Au−O stretching vibration of the $OAuNN^-$ anion is predicted to be 702.3 cm^{-1} (Table 3). With its small intensity (135 km/mol) relative to the N−N stretching vibration (1009 km/mol) (Table 3), it is not readily observed. Accordingly, the observed band at 2047.5 cm^{-1} is assigned to the N−N stretching vibration of the $OAuNN^-$ anion on the basis of the results of isotopic shifts, mixed isotopic splitting patterns, CCl_4-doping experiments, and the comparison with density functional theory calculations. The $OAuNN^-$ anion is predicted to have a $^1\Sigma^+$ ground-state with $C_{\infty v}$ symmetry (Table 3 and Figure 3). As listed in Table 2, the calculated $^{14}N_2O/^{15}N_2O$ isotopic frequency ratio of 1.0350 is consistent with the experimental value of 1.0345, which supports the above assignment of the $OAuNN^-$ anion.

B. $AuNO^-$. The absorption at 1512.3 cm^{-1} appears during sample deposition, increases visibly after sample annealing, decreases sharply upon broadband irradiation, and recovers slightly after further annealing to higher temperature (Table 1 and Figure 1). This band shifts to 1485.1 cm^{-1} with $^{15}N_2O$. The isotopic frequency ratio ($^{14}N_2O/^{15}N_2O$, 1.0183) implies that the band at 1512.3 cm^{-1} is mainly due to a N−O stretching mode.[39] Only the pure isotopic counterparts have been observed in the mixed $^{14}N_2O + ^{15}N_2O$ isotopic spectra (Figure 2, trace c), suggesting only one NO subunit is involved in this mode.[42] Doping with CCl_4 decreases sharply this band (Figure 1, trace f), suggesting that the product is anionic.[38] The 1512.3 cm^{-1} band is therefore assigned to the N−O stretching vibration of the $AuNO^-$ anion. The corresponding N−O stretching vibration of neutral AuNO molecule in solid argon has been observed at 1701.9 cm^{-1},[43] which is 189.6 cm^{-1} red-shifted from the anionic counterpart (1512.3 cm^{-1}).

The $AuNO^-$ anion is predicted to have a $^2A''$ ground state with C_s symmetry (Table 3 and Figure 3), which is consistent with the previous theoretical calculations.[44] At the BP86 level of theory, the calculated N−O stretching frequency of the $AuNO^-$ anion, 1505.4 cm^{-1} (Table 2), agrees within 7 cm^{-1} with the observed value (1512.3 cm^{-1}). The calculated $^{14}N_2O/^{15}N_2O$ isotopic frequency ratio (1.0178) is consistent with the experimental observation (1.0183) (Table 2). The Au−N stretching frequency of the $AuNO^-$ anion is calculated to be 383.4 cm^{-1} (Table 3), which is beyond the present spectral range of 5000−400 cm^{-1}. These agreements between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts confirm the identification of the $AuNO^-$ anion from the matrix IR spectra.

C. Reaction Pathways and Bonding Consideration. On the basis of the behavior of sample annealing and irradiation, together with the observed species and calculated stable isomers, plausible reaction pathways can be proposed as follows. In the present experiments, strong N_2O fundamentals and weak overtone and combination absorptions appear during sample deposition.[45] Weak absorptions of NO (1871.8 cm^{-1}) and NNO_2^- (1205.3 cm^{-1})[46−48] are also presented in the current matrix experiments. Meanwhile, the temporarily existing N_2O^- anion may be generated by photoionization of the N_2O molecule via radiation in the ablation plume,[47] which has been confirmed by the previous mass spectrometric studies of ionization processes of N_2O.[49] Furthermore, recent investigations have shown that laser ablation of metal targets produces not only neutral metal atoms, but also metal cations and electrons. Ionic metal complexes can also be formed in the reactions with small molecules.[38]

The energetic analysis for possible reactions of Au atoms with the N_2O, NO, N_2O^-, and NNO_2^- molecules has been performed at the BP86 level of theory (Table 4). The formation of the $OAuNN^-$ anion (reactions 4 and 5) is predicted to be more energetically favorable than that of the neutral OAuNN complex (reactions 2 and 3), which is consistent with the observation of the $OAuNN^-$ anionic complex and the absence of the AuNNO and OAuNN neutral complexes. For the formation of the $OAuNN^-$ anion, the contribution from the reaction of Au atom with the N_2O^- anion (reaction 4, −326.1 kJ mol^{-1}) is larger than that from the reaction of the Au anion with the N_2O molecule (reaction 5, −94.2 kJ mol^{-1}). For the formation of the $AuNO^-$ anion, the reaction energy of reaction 6 is predicted to be −104.7 kJ mol^{-1}, which is also more energetically favorable than those of reactions 2 and 3. Furthermore, the reaction of the Au anion with the NO molecule may be also responsible for the formation of the $AuNO^-$ anion (reaction 7, −80.8 kJ mol^{-1}).

As illustrated in Figure 4, the highest occupied molecular orbitals (HOMOs) of the $OAuNN^-$ anion are π-type bonds, which comprise the synergic donations of filled orbitals of N_2 into the empty acceptor orbitals of the AuO^- anion and the back-donation of the AuO^- electrons into the empty orbitals of N_2. The HOMO−1 is largely Au 6s in character. The HOMO−2s are δ-type nonbonding orbitals, which are largely Au 5d in character. The HOMO−3 is a σ-type bond. For the $AuNO^-$ anion, the HOMO comprises the $d\sigma$ + sp hybridized orbital of Au and the $p\pi^*$ orbital of NO, which is a nonbonding molecular orbital. The HOMO−1 and HOMO−2s are largely Au 6s and 5d in character, respectively, similar to those of the $OAuNN^-$ anion. The HOMO−3s are π-type bonds, which illustrates the overlap between the Au atom and the NO molecule.

Conclusions

Reactions of laser-ablated gold atoms with nitrous oxide molecules in excess argon have been investigated using matrix-isolation infrared spectroscopy and density functional theory calculation. The $OAuNN^-$ and $AuNO^-$ anions have been formed during sample deposition and identified on the basis of isotopic shifts, mixed isotopic splitting patterns, CCl_4-doping experiments, and the comparison with theoretical predictions. The agreement between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts supports the identifications of these species from the matrix infrared spectra. The energetic analysis for possible reactions of gold atoms with the N_2O, NO, N_2O^-, and NNO_2^- molecules has been performed, and plausible reaction pathways for the formation of these products have been proposed.

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References and Notes

(1) See, for example: Bandy, R. E.; Lakshminarayan, C.; Frost, R. K.; Zwier, T. S. *J. Chem. Phys.* **1993**, *98*, 5362. Wang, L. S.; Cheng, H. S.; Fan, J. *J. Chem. Phys.* **1995**, *102*, 9840. Duncan, M. A. *Int. Rev. Phys. Chem.* **2003**, *22*, 407.

(2) See, for example: Xu, C.; Manceron, L.; Perchard, J. P. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1291. Bondybey, V. E.; Smith, A. M.; Agreiter, J. *Chem. Rev.* **1996**, *96*, 2113. Fedrigo, S.; Haslett, T. L.; Moskovits, M. *J. Am. Chem. Soc.* **1996**, *118*, 5083. Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Rasanen, M. *Nature* **2000**, *406*, 874. Himmel, H. J.; Manceron, L.; Downs, A. J.; Pullumbi, P. *J. Am. Chem. Soc.* **2002**, *124*, 4448. Li, J.; Bursten, B. E.; Liang, B.; Andrews, L. *Science* **2002**, *295*, 2242. Andrews, L.; Wang, X. *Science* **2003**, *299*, 2049.

(3) Zhou, M. F.; Tsumori, N.; Li, Z.; Fan, K.; Andrews, L.; Xu, Q. *J. Am. Chem. Soc.* **2002**, *124*, 12936. Zhou, M. F.; Xu, Q.; Wang, Z.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **2002**, *124*, 14854. Jiang, L.; Xu, Q. *J. Am. Chem. Soc.* **2005**, *127*, 42. Xu, Q.; Jiang, L.; Tsumori, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 4338. Jiang, L.; Xu, Q. *J. Am. Chem. Soc.* **2005**, *127*, 8906. Jiang, L.; Xu, Q. *J. Am. Chem. Soc.* **2006**, *128*, 1394; Addition and Correction.

(4) Trogler, W. C. *Coord. Chem. Rev.* **1999**, *187*, 303. Kapteijn, F.; Rodriguez-Mirasol, J.; Moulijn, J. A. *Appl. Catal., B* **1996**, *9*, 25. Dandekar, A.; Vannice, M. A. *Appl. Catal., B* **1999**, *22*, 179. Burch, R.; Daniells, S. T.; Breen, J. P.; Hu, P. *J. Catal.* **2004**, *224*, 252.

(5) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2449.

(6) Ritter, D.; Weisshaar, J. C. *J. Phys. Chem.* **1989**, *93*, 1576.

(7) Ritter, D.; Weisshaar, J. C. *J. Phys. Chem.* **1990**, *94*, 4907.

(8) Futerko, P. M.; Fontijn, A. *J. Chem. Phys.* **1991**, *95*, 8065, and references therein.

(9) Futerko, P. M.; Fontijn, A. *J. Chem. Phys.* **1992**, *97*, 3861.

(10) Futerko, P. M.; Fontijn, A. *J. Chem. Phys.* **1993**, *98*, 7004.

(11) Campbell, M. L. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1687, and references therein.

(12) Stirling, A. *J. Phys. Chem. A* **1998**, *102*, 6565. Stirling, A. *J. Am. Chem. Soc.* **2002**, *124*, 4058.

(13) Campbell, M. L.; Kolsch, E. J.; Hooper, K. L. *J. Phys. Chem. A* **2000**, *104*, 11147.

(14) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301. Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175.

(15) For recent reviews, see: Haruta, M. *Catal. Today* **1997**, *36*, 153. Bond, G. C.; Thompson, D. T. *Catal. Rev.-Sci. Eng.* **1999**, *41*, 319. Haruta, M. *Stud. Surf. Sci. Catal.* **2001**, *145*, 31. Haruta, M. *Chem. Rec.* **2003**, *3*, 75.

(16) Cunningham, D. A. H.; Vogel, W.; Kageyama, H.; Tsubota, S.; Haruta, M. *J. Catal.* **1998**, *177*, 1.

(17) Turner, M.; Golovko, V. B.; Vaughan, O. P. H.; Abdulkin, P.; Berenguer-Murcia, A.; Tikhov, M. S.; Johnson, B. F. G.; Lambert, R. M. *Nature* **2008**, *454*, 981.

(18) Herzing, A. A.; Kiely, C. J.; Carley, A. F.; Landon, P.; Hutchings, G. J. *Science* **2008**, *321*, 1331.

(19) Huber, H.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 64.

(20) Huber, H.; McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 975.

(21) Xu, Q.; Jiang, L. *J. Phys. Chem. A* **2006**, *110*, 2655.

(22) Liang, B.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 9156.

(23) Jiang, L.; Xu, Q. *J. Phys. Chem. A* **2005**, *109*, 1026.

(24) Zhai, H. J.; Wang, L. S. *J. Chem. Phys.* **2005**, *122*, 051101. Zhai, H. J.; Kiran, B.; Dai, B.; Li, J.; Wang, L. S. *J. Am. Chem. Soc.* **2005**, *127*, 12098.

(25) Velasquez, J., III; Njegic, B.; Gordon, M. S.; Duncan, M. A. *J. Phys. Chem. A* **2008**, *112*, 1907.

(26) Chertihin, G. V.; Andrews, L. *J. Phys. Chem.* **1994**, *98*, 5891.

(27) Zhou, M. F.; Zhang, L. N.; Qin, Q. Z. *J. Phys. Chem. A* **2001**, *105*, 6407.

(28) Zhou, M. F.; Wang, G. J.; Zhao, Y. Y.; Chen, M. H.; Ding, C. F. *J. Phys. Chem. A* **2005**, *109*, 5079.

(29) Jin, X.; Wang, G. J.; Zhou, M. F. *J. Phys. Chem. A* **2006**, *110*, 8017.

(30) Wang, G. J.; Zhou, M. F. *Chem. Phys.* **2007**, *342*, 90.

(31) Jiang, L.; Xu, Q. *J. Phys. Chem. A* **2008**, *112*, 6289.

(32) Wang, G. J.; Jin, X.; Chen, M. H.; Zhou, M. F. *Chem. Phys. Lett.* **2006**, *420*, 130.

(33) Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991**, *95*, 8697. Zhou, M. F.; Tsumori, N.; Andrews, L.; Xu, Q. *J. Phys. Chem. A* **2003**, *107*, 2458. Jiang, L.; Xu, Q. *J. Chem. Phys.* **2005**, *122*, 034505. Jiang, L.; Teng, Y. L.; Xu, Q. *J. Phys. Chem. A* **2006**, *110*, 7092.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(35) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. Lee, C.; Yang, E.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.

(36) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(37) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(38) Zhou, M. F.; Andrews, L.; Bauschlicher, C. W., Jr. *Chem. Rev.* **2001**, *101*, 1931.

(39) Andrews, L.; Citra, A. *Chem. Rev.* **2002**, *102*, 885.

(40) Himmel, H. J.; Downs, A. J.; Greene, T. M. *Chem. Rev.* **2002**, *102*, 4191.

(41) Jiang, L.; Xu, Q. *J. Chem. Phys.* **2008**, *128*, 124317.

(42) Darling, J. H.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2496.

(43) Citra, A.; Wang, X. F.; Andrews, L. *J. Phys. Chem. A* **2002**, *106*, 3287.

(44) Ding, X.; Li, Z.; Yang, J.; Hou, J. G.; Zhu, Q. *J. Chem. Phys.* **2004**, *121*, 2558.

(45) Herzberg, G. *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1945.

(46) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1971**, *55*, 3404.

(47) Hacaloglu, J.; Suzer, S.; Andrews, L. *J. Phys. Chem.* **1990**, *94*, 1759.

(48) Jacox, M. E. *J. Chem. Phys.* **1990**, *93*, 7622.

(49) Schulz, G. J. *J. Chem. Phys.* **1961**, *34*, 1778. Chantry, P. J. *J. Chem. Phys.* **1969**, *51*, 3380.

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