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# Reactions of molybdenum and tungsten atoms with nitrous oxide in excess argon: A combined matrix infrared spectroscopic and theoretical study

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Reactions of laser-ablated Mo and W atoms with the N<sub>2</sub>O molecules in excess argon have been investigated using matrix-isolation infrared spectroscopy. In the reaction of the N<sub>2</sub>O molecule with the Mo atom, the absorptions at 1960.3 and 934.4 cm<sup>-1</sup> are assigned to the N–N and Mo–O stretching vibrations of the OMoNN complex, respectively. An analogous OWNN complex has also been observed in the W+N<sub>2</sub>O reaction. Infrared spectroscopy also provides evidence for the formation of the OW(NN)<sub>2</sub> complexes. Density functional theory calculations have been performed on the products. Overall agreement between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts supports the identification of these species from the matrix infrared spectra. Furthermore, a plausible reaction mechanism for the formation of these products has been proposed. © 2010 American Institute of Physics.

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## I. INTRODUCTION

The reaction of metal atoms with nitrous oxide (N<sub>2</sub>O) molecule is of considerable interest due to the fact that N<sub>2</sub>O exhibits a global warming potential about 310 times that of CO<sub>2</sub> on a per molecule basis<sup>1</sup> and is responsible for the destruction of the ozone layer in the stratosphere.<sup>2</sup> N<sub>2</sub>O also acts as a potentially clean and highly selective oxygen donor for catalytic oxidation processes.<sup>2</sup> Extensive efforts have been made on the catalytic removal of N<sub>2</sub>O from industrial exhaust gases. Supported transition metals (i.e., Rh, Co, Ru, Fe, Ni, Pd, and Pt) on oxides and/or zeolites have been widely used in such processes.<sup>3–9</sup> It has been found that Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibits high performance of the removal of N<sub>2</sub>O.<sup>5,9</sup>

Gas-phase reactions of various metal atoms with N<sub>2</sub>O have been extensively investigated both experimentally and theoretically.<sup>10–18</sup> It has been found that the reaction of transition-metal atoms with N<sub>2</sub>O leads to N–O bond activation to form the metal oxide and N<sub>2</sub>. Previous experimental study reveals that Mo<sub>2</sub> is reactive toward N<sub>2</sub>O, whereas the Mo is nonreactive toward N<sub>2</sub>O at room temperature.<sup>19</sup> Theoretical investigation indicate that the detachments of N<sub>2</sub> are kinetically effective processes for the reactions of N<sub>2</sub>O with Mo and Mo<sub>2</sub> and the Mo+N<sub>2</sub>O reaction should be a slow process due to the presence of spin-forbidden transitions.<sup>20</sup>

Reactions under nontraditional experimental conditions can often yield new and exciting species not accessible from normal chemical reaction conditions.<sup>21</sup> Recent studies have shown that, with an aid of isotopic substitution technique, matrix isolation infrared (IR) spectroscopy combined with quantum chemical calculation is very powerful in investigat-

ing the spectrum, structure, and bonding of novel species.<sup>22,23</sup> Argon matrix investigations of the reactions of laser-ablated Ti, Cr, groups 3, 10, and 13, and lanthanoid metal atoms with N<sub>2</sub>O have characterized a series of neutral metal monoxide-dinitrogen and metal nitrous oxide complexes and cationic metal monoxide-dinitrogen complexes.<sup>24–30</sup> Copper and silver chloridenitrous oxide complexes ClCuNNO and ClAgNNO have also been obtained in the reactions of metal chlorides with nitrous oxide.<sup>31</sup> Some recent investigations presented the evidence for selective nitrous oxide N–N bond cleavage of by molybdenum complexes,<sup>32,33</sup> whereas there are no reports of the activation of N–O bond by the simple molybdenum and tungsten atoms to our knowledge. Herein, we report a combined matrix IR spectroscopic and theoretical study of the reactions of molybdenum and tungsten atoms with nitrous oxide molecules in excess argon. IR spectroscopy coupled with density functional theory (DFT) calculation provides evidence for the formation of the OMNN (*M*=Mo, W) and OW(NN)<sub>2</sub> complexes.

## II. EXPERIMENTAL AND THEORETICAL METHODS

The experiments for laser ablation and matrix-isolation IR spectroscopy are similar to those previously reported.<sup>34</sup> In short, the Nd: yttrium aluminum garnet laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating Mo and W targets. The laser-ablated Mo and W atoms were codeposited with N<sub>2</sub>O in excess argon onto a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator. Typically, 1–25 mJ/pulse laser power was used. N<sub>2</sub>O (99.5%, Taiyo Nippon Sanso Co.), <sup>15</sup>N<sub>2</sub>O (98%, Cambridge Isotopic Laboratories), and <sup>14</sup>N<sub>2</sub>O+<sup>15</sup>N<sub>2</sub>O mixtures were used in different experiments. In general, matrix samples were deposited for 30–60 min

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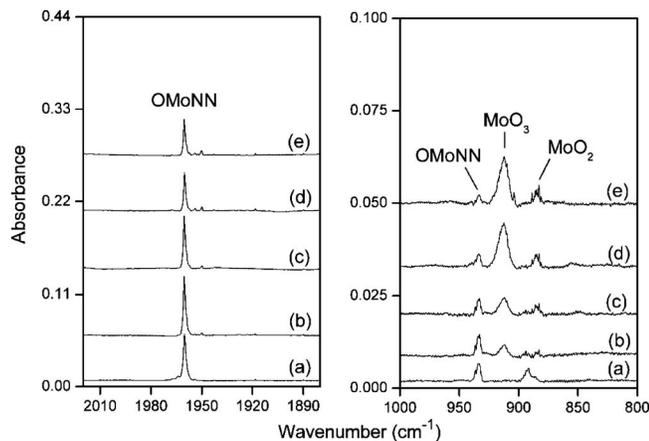


FIG. 1. IR spectra in the 2010–1890 and 1000–800  $\text{cm}^{-1}$  regions from codeposition of laser-ablated Mo atoms with 0.2%  $\text{N}_2\text{O}$  in Ar at 4 K. (a) Spectrum obtained from initial deposited sample for 1 h, (b) spectrum after annealing to 30 K, (c) spectrum after annealing to 35 K, (d) spectrum after 10 min of broad-band irradiation, and (e) spectrum after annealing to 38 K.

with a typical rate of 2–4 mmol/h. After sample deposition, IR spectra were recorded on a BIO-RAD FTS-6000e spectrometer at 0.5  $\text{cm}^{-1}$  resolution using a liquid nitrogen cooled HgCdTe (MCT) detector for the spectral range of 5000–400  $\text{cm}^{-1}$ . Samples were annealed at different temperatures and subjected to broad-band 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.<sup>35</sup> All the present computations employed the Becke three parameter hybrid functional with the Lee–Yang–Parr correlation corrections (B3LYP).<sup>36</sup> The 6–311+ $G(d)$  basis set was used for the N and O atoms,<sup>37</sup> and the Los Alamos effective core potential plus double zeta (LANL2DZ) was used for the Mo and W

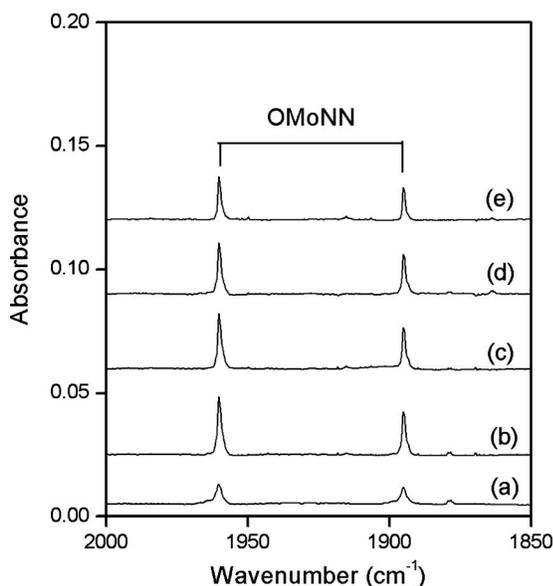


FIG. 2. IR spectra in the 2000–1850  $\text{cm}^{-1}$  region from codeposition of laser-ablated Mo atoms with 0.15%  $^{14}\text{N}_2\text{O}$ +0.15%  $^{15}\text{N}_2\text{O}$  in Ar at 4 K. For the meaning of (a)–(e) see Fig. 1.

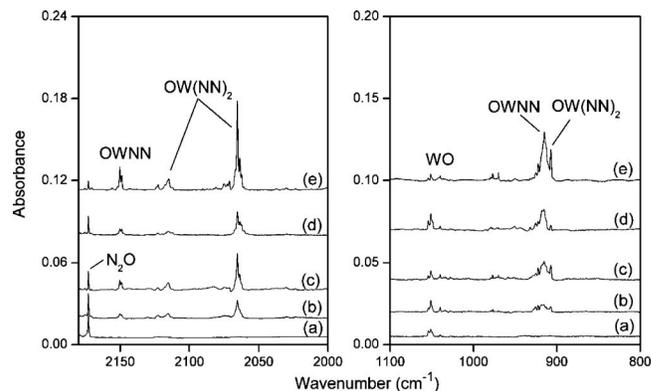


FIG. 3. IR spectra in the 2150–2000 and 1100–800  $\text{cm}^{-1}$  regions from codeposition of laser-ablated W atoms with 0.2%  $\text{N}_2\text{O}$  in Ar at 4 K. (a) Spectrum obtained from initial deposited sample for 1 h, (b) spectrum after annealing to 25 K, (c) spectrum after annealing to 30 K, (d) spectrum after 10 min of broad-band irradiation, and (e) spectrum after annealing to 35 K.

atoms.<sup>38</sup> Geometries were fully optimized and vibrational frequencies were calculated with analytical second derivatives. The transition states were located with the synchronous transit-guided quasi-Newton method and were verified by intrinsic-reaction-coordinate calculations. Zero-point vibrational energy contributions have been taken into account. Recent investigations have shown that such computational methods can provide reliable information for metal complexes, such as IR frequencies, relative absorption intensities, and isotopic shifts.<sup>24–31,39–42</sup>

### III. RESULTS AND DISCUSSION

Experiments have been done with nitrous oxide concentrations ranging from 0.02% to 1.0% in excess argon. Typical IR spectra for the reactions of laser-ablated Mo and W atoms with  $\text{N}_2\text{O}$  molecules in excess argon in the selected regions are illustrated in Figs. 1–4, and the absorption bands in different isotopic experiments are listed in Table I. The stepwise annealing and irradiation behavior of the product absorptions is also shown in the figures and will be discussed below.

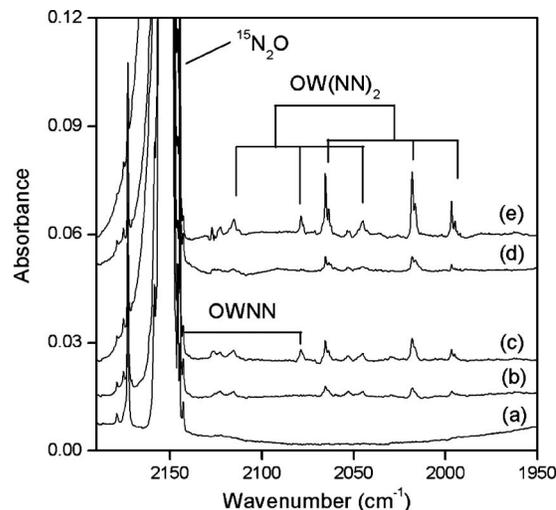


FIG. 4. IR spectra in the 2150–1950  $\text{cm}^{-1}$  region from codeposition of laser-ablated W atoms with 0.15%  $^{14}\text{N}_2\text{O}$ +0.15%  $^{15}\text{N}_2\text{O}$  in Ar at 4 K. For the meaning of (a)–(e) see Fig. 3.

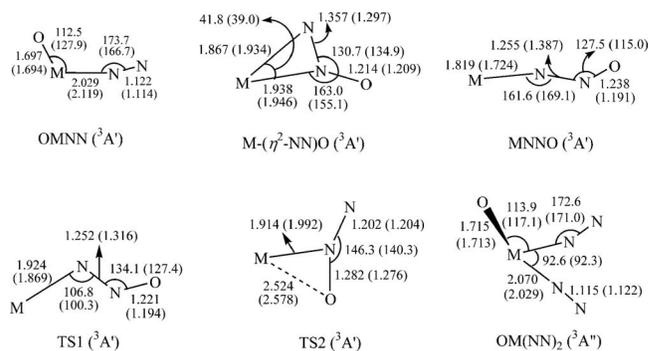
TABLE I. IR absorptions (in cm<sup>-1</sup>) observed from codeposition of laser-ablated Mo and W atoms with N<sub>2</sub>O in excess argon at 4 K.

<sup>14</sup> N <sub>2</sub> O	<sup>15</sup> N <sub>2</sub> O	<sup>14</sup> N <sub>2</sub> O + <sup>15</sup> N <sub>2</sub> O	<sup>14</sup> N <sub>2</sub> O / <sup>15</sup> N <sub>2</sub> O	Assignment
1960.3	1895.1	1960.3, 1895.1	1.0344	OMoNN
934.4	934.4		1.0000	OMoNN
2150.2	2078.6	2150.2, 2078.6	1.0344	OWNN
2114.9	2045.0	2114.9, 2078.6, 2045.0	1.0342	OW(NN) <sub>2</sub>
2065.4	1996.7	2065.4, 2018.3, 1996.7	1.0344	OW(NN) <sub>2</sub>
915.1	915.1		1.0000	OWNN
907.3	907.3		1.0000	OW(NN) <sub>2</sub>

Quantum chemical calculations have been carried out for the possible isomers and electronic states of the species involved in the reactions of N<sub>2</sub>O with Mo and W atoms. The comparison of the observed and calculated IR frequencies and isotopic frequency ratios for the N–N and M–O stretching modes of the products are summarized in Table II. The ground electronic states, point groups, vibrational frequencies, and intensities of the products are listed in Table III. Figure 5 shows the optimized structures of the species involved in the reactions of N<sub>2</sub>O with the Mo and W atoms. The potential energy surface of the reaction of N<sub>2</sub>O with the Mo and W atoms is depicted in Fig. 6. Molecular orbital depictions of the highest occupied molecular orbitals (HOMOs) and HOMO–1s of the OMoNN (M=Mo, W) and OW(NN)<sub>2</sub> complexes are illustrated in Fig. 7.

### A. OMoNN (M=Mo, W)

In the reaction of Mo atoms with N<sub>2</sub>O in excess argon, the absorptions at 1960.3 and 934.4 cm<sup>-1</sup> appear together during sample deposition, change little after sample annealing, but decrease upon broad-band irradiation and after further annealing to higher temperature (Table I and Fig. 1). The upper band at 1960.3 cm<sup>-1</sup> shifts to 1895.1 cm<sup>-1</sup> with <sup>15</sup>N<sub>2</sub>O, exhibiting an isotopic frequency ratio (<sup>14</sup>N<sub>2</sub>O/<sup>15</sup>N<sub>2</sub>O, 1.0344) characteristic of a N–N stretching vibration. The mixed <sup>14</sup>N<sub>2</sub>O/<sup>15</sup>N<sub>2</sub>O isotopic spectra (Fig. 2) only provide the sum of pure isotopic bands, which indicates only one N<sub>2</sub> unit is involved in the complex.<sup>43</sup> The 934.4 cm<sup>-1</sup> band, which is in the spectral range expected for the terminal Mo–O stretching mode,<sup>44</sup> shows no nitrogen isotopic shift. The features of the IR spectra in the present matrix experiments are reminiscent of those of the end-on-bonded struc-

FIG. 5. Optimized structures (bond lengths in angstrom, bond angles in degree) of the species involved in the reactions of N<sub>2</sub>O with molybdenum and tungsten (in parentheses) atoms.

ture of OS<sub>c</sub>NN, in which the corresponding N–N and Sc–O stretching vibrational frequencies appear at 1849.2 and 894.6 cm<sup>-1</sup> in the argon matrix experiments,<sup>26</sup> respectively. Accordingly, the 1960.3 and 934.4 cm<sup>-1</sup> bands are assigned to the N–N and Mo–O stretching vibrations of the OMoNN complex, respectively.

DFT calculations predict the OMoNN complex to have a <sup>3</sup>A' ground state with C<sub>s</sub> symmetry (Table III and Fig. 5), which is consistent with the previous calculation.<sup>20</sup> The Mo–O and Mo–N distances are calculated to be 1.697 and 2.029 Å (Fig. 5), respectively. The N–N distance in the OMoNN complex (1.122 Å) is about 0.026 Å longer than that in an isolated N<sub>2</sub> (1.096 Å). The N–N and Mo–O stretching vibrational frequencies are calculated to be 2148.2 and 956.0 cm<sup>-1</sup> (Tables II and III). As listed in Table II, the calculated <sup>14</sup>N<sub>2</sub>O/<sup>15</sup>N<sub>2</sub>O isotopic frequency ratios for the N–N and Mo–O stretching vibrations (1.0350 and 1.0000) are consistent with the experimental values (1.0344 and 1.0000), respectively. These agreements between the experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts confirm the identification of the OMoNN complex from the matrix IR spectra.

In the W+N<sub>2</sub>O experiments, the N–N and W–O stretching vibrations for the analogous OWNN complex have been observed at 2150.2 and 915.1 cm<sup>-1</sup> (Table I and Figs. 3 and 4), respectively. The OWNN complex is predicted to have a <sup>3</sup>A' ground state with C<sub>s</sub> symmetry (Table III and Fig. 5). The N–N distance in the OWNN complex is calculated to be 1.114 Å, which is about 0.008 Å shorter than that in the OMoNN complex and 0.018 Å longer than that in an isolated

TABLE II. Comparison of observed and calculated IR frequencies (in cm<sup>-1</sup>) and isotopic frequency ratios for the products.

Species	Vibrational mode	Observed		Calculated	
		Freq.	<sup>14</sup> N <sub>2</sub> O / <sup>15</sup> N <sub>2</sub> O	Freq.	<sup>14</sup> N <sub>2</sub> O / <sup>15</sup> N <sub>2</sub> O
OMoNN	$\nu_{N-N}$	1960.3	1.0344	2148.2	1.0350
	$\nu_{Mo-O}$	934.4	1.0000	956.0	1.0000
OWNN	$\nu_{N-N}$	2150.2	1.0344	2169.2	1.0350
	$\nu_{W-O}$	915.1	1.0000	1004.4	1.0001
OW(NN) <sub>2</sub>	$\nu_{N-N, sym}$	2114.9	1.0342	2169.8	1.0350
	$\nu_{N-N, asym}$	2065.4	1.0344	2115.7	1.0350
	$\nu_{W-O}$	907.3	1.0000	966.5	1.0000

TABLE III. Ground electronic states, point groups, vibrational frequencies (in  $\text{cm}^{-1}$ ), and intensities (km/mol) of the products.

Species	Elec. state	Point group	Frequency (intensity, mode)
OMoNN	$^3A'$	$C_s$	2148.2 (811, $A'$ ), 956.0 (191, $A'$ ), 407.1 (11, $A'$ ), 327.1 (1, $A''$ ), 323.5 (16, $A'$ ), 133.5 (17, $A'$ )
			2169.2 (698, $A'$ ), 1004.4 (117, $A'$ ), 346.7 (5, $A'$ ), 289.4 (3, $A''$ ), 249.2 (7, $A'$ ), 98.5 (17, $A'$ )
OWNN	$^3A'$	$C_s$	2169.8 (415, $A'$ ), 2115.7 (1214, $A''$ ), 966.5 (150, $A'$ ), 486.1 (1, $A'$ ), 396.3 (25, $A''$ ), 393.3 (7, $A'$ ), 374.6 (3, $A''$ ), 359.0 (4, $A'$ ), 327.5 (4, $A''$ ), 127.7 (18, $A''$ ), 117.7 (11, $A'$ ), 79.9 (0.01, $A'$ )
OW(NN) <sub>2</sub>	$^3A''$	$C_s$	

$\text{N}_2$ , respectively. The N–N and W–O stretching vibrations of the OWNN complex are calculated to be 2169.2 and 1004.4  $\text{cm}^{-1}$  (Table III), respectively. The calculated  $^{14}\text{N}_2\text{O}/^{15}\text{N}_2\text{O}$  isotopic frequency ratios for the N–N and W–O stretching vibrations of 1.0350 and 1.0001 are consistent with the corresponding experimental values of 1.0344 and 1.0000 (Table II), respectively.

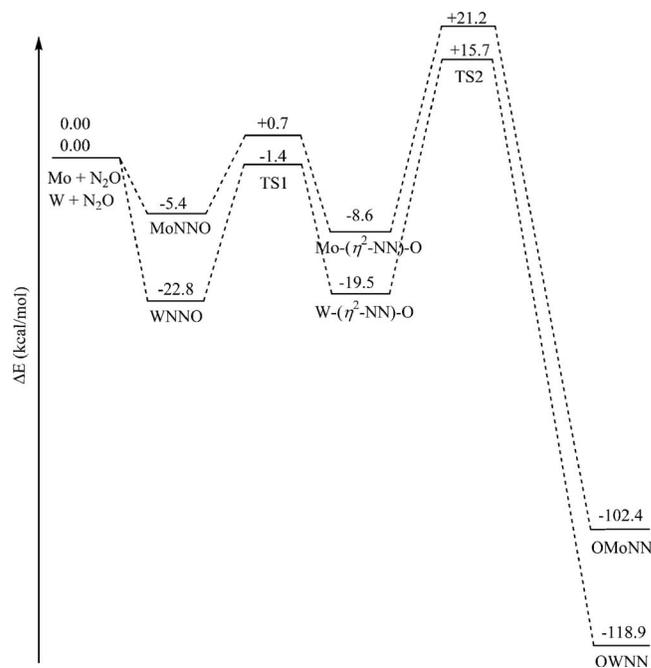
## B. OW(NN)<sub>2</sub>

In the  $\text{W}+\text{N}_2\text{O}$  experiments, the absorptions at 2114.9, 2065.4, and 907.3  $\text{cm}^{-1}$  appear together after sample annealing, decrease slightly upon broad-band irradiation, and increase sharply after further annealing to higher temperature (Table I and Fig. 3). The 2114.9 and 2065.4  $\text{cm}^{-1}$  bands shift to 2045.0 and 1996.7  $\text{cm}^{-1}$  with  $^{15}\text{N}_2\text{O}$ , respectively, exhibiting isotopic frequency ratios ( $^{14}\text{N}_2\text{O}/^{15}\text{N}_2\text{O}$ , 1.0342 and 1.0344) characteristic of N–N stretching vibrations. As can be seen in Fig. 4, two sets of triplet bands have been observed at 2114.9/2078.6/2045.0 and 2065.4/2018.3/1996.7  $\text{cm}^{-1}$  in the mixed  $^{14}\text{N}^{16}\text{O}+^{15}\text{N}^{16}\text{O}$  isotopic spectra (Table I), respectively, suggesting that two equivalent  $\text{N}_2$  subunits are involved in each mode.<sup>43</sup> The 907.3  $\text{cm}^{-1}$  band, which is in the spectral range expected for the terminal W–O stretching mode,<sup>44</sup> shows no nitrogen isotopic shift. Accordingly, the 2114.9, 2065.4, and 907.3  $\text{cm}^{-1}$  bands are assigned to the symmetric and asymmetric N–N and W–O stretching vibrations of the OW(NN)<sub>2</sub> complex, respectively.

DFT calculations predict the OW(NN)<sub>2</sub> complex to have a  $^3A''$  ground state with  $C_s$  symmetry (Table III and Fig. 5). The W–O and W–N distances in the OW(NN)<sub>2</sub> complex are calculated to be 1.713 and 2.029 Å, respectively. The N–N distance in the OW(NN)<sub>2</sub> complex is calculated to be 1.122 Å, which is about 0.008 Å longer than that in the OWNN complex and 0.026 Å longer than that in an isolated  $\text{N}_2$ , respectively. The symmetric and asymmetric N–N and W–O stretching vibrational frequencies are calculated to be 2169.8, 2115.7, and 966.5  $\text{cm}^{-1}$  (Tables II and III), respectively. The calculated  $^{14}\text{N}_2\text{O}/^{15}\text{N}_2\text{O}$  isotopic frequency ratios for the symmetric and asymmetric N–N and W–O stretching vibrations are consistent with the experimental values (Table II), respectively.

## C. Reaction mechanism and bonding consideration

On the basis of the behavior of sample annealing and irradiation, together with the observed species and calculated stable isomers, a plausible reaction mechanism can be proposed as follows. Under the present experimental conditions, the OMNN ( $M=\text{Mo}, \text{W}$ ) complexes are the primary products during sample deposition or after sample annealing (Figs. 1 and 3), suggesting that the spontaneous insertion of laser-ablated Mo and W atoms into  $\text{N}_2\text{O}$  to form these metal monoxide-dinitrogen complexes is the dominant process (reactions 1–3). Taking the Mo reaction as an example, the reaction starts by binding the outer nitrogen atom of  $\text{N}_2\text{O}$  with the Mo atom to form a planar intermediate MoNNO (reaction 1) (Figs. 5 and 6). This step is predicted to be exothermic by 5.4 kcal/mol. Then, the isomerization proceeds by binding another nitrogen atom to form a side-bonded intermediate Mo-( $\eta^2$ -NN)O via transition state TS1. The barrier height for this process is predicted to be 6.1 kcal/mol. The oxygen atom is further transferred to form the OMoNN products via transition state TS2 at a barrier height of 29.9 kcal/mol. For W reaction, the barriers of such two

FIG. 6. Potential energy surfaces of the  $M+\text{N}_2\text{O}\rightarrow\text{OMNN}$  ( $M=\text{Mo}, \text{W}$ ) reactions.

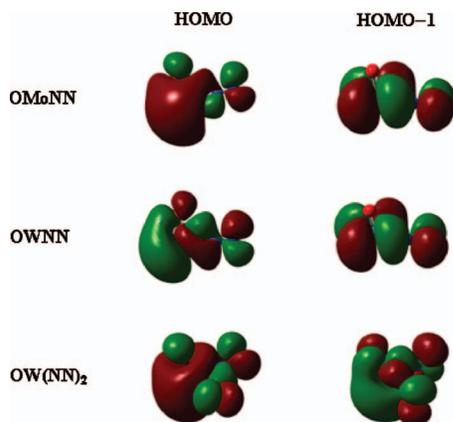
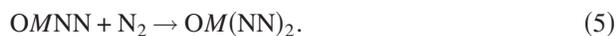


FIG. 7. Molecular orbital depictions of the HOMOs and HOMO-1s of the OMNN ( $M=Mo, W$ ) and OW(NN)<sub>2</sub> complexes. The orientation of the molecule is the same as that shown in Fig. 5.

isomerizations are 21.4 and 35.2 kcal/mol, respectively. The barriers for these isomerizations (6.1–35.2 kcal/mol) can be obtained by radiation in the ablation plume, which has been demonstrated by the previous experiment.<sup>29</sup> The formation of OWNN is more energetically favorable than that for OMoNN; furthermore, the formation of the OW(NN)<sub>2</sub> complex (reaction 5, -19.4 kcal/mol) is predicted to be more energetically favorable than that for the OMo(NN)<sub>2</sub> complex (-15.5 kcal/mol), which is consistent with the absence of the OMo(NN)<sub>2</sub> complex from the present matrix experiments.



As illustrated in Fig. 7, the HOMOs and HOMO-1s of OMNN ( $M=Mo, W$ ) and OW(NN)<sub>2</sub> are  $\sigma$ -type and  $\pi$ -type bonds, respectively, which are singly occupied molecular orbitals. They comprise the synergic donations of the filled orbitals of N<sub>2</sub> into the empty acceptor orbitals of MO and the back donation of the MO electrons into the empty orbitals of N<sub>2</sub>. The primary donor orbitals in the end-on-bonded OMNN and OW(NN)<sub>2</sub> complexes are the filled  $3\sigma_g$  orbitals of N<sub>2</sub>. The single occupied  $\delta$  orbitals are the back-donation orbitals.

#### IV. CONCLUSIONS

Reactions of laser-ablated molybdenum and tungsten atoms with nitrous oxide molecules in excess argon have been investigated using matrix-isolation IR spectroscopy and DFT computation. In the Mo+N<sub>2</sub>O experiments, the absorptions at 1960.3 and 934.4 cm<sup>-1</sup> are assigned to the N–N and Mo–O stretching vibrations of the OMoNN complex, respectively. An analogous OWNN complex has also been observed in the W+N<sub>2</sub>O reaction. IR spectroscopy also provides evidence for the formation of the OW(NN)<sub>2</sub> complexes. Furthermore, a plausible reaction pathway for the

formation of the products has been proposed. This work reveals that the reactivity of the W atom toward N<sub>2</sub>O is prior to the Mo atom.

#### ACKNOWLEDGMENTS

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