

# Nitromethane and Methyl Nitrite Adsorption on Au(111) Surfaces

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Received December 20, 1996. In Final Form: March 20, 1998

The adsorption of nitromethane (CH<sub>3</sub>NO<sub>2</sub> and CD<sub>3</sub>NO<sub>2</sub>) and *d*<sub>3</sub>-methyl nitrite (CD<sub>3</sub>ONO) on Au(111) was studied by temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). These molecules are only weakly adsorbed on Au(111), and adsorption is completely reversible in both cases. Adsorbed CH<sub>3</sub>NO<sub>2</sub> and CD<sub>3</sub>ONO in the monolayer each give rise to one thermal desorption peak in TPD with desorption activation energies of 10.5 and 8 kcal/mol, respectively. These desorption energies are close to the values for the heats of adsorption of these molecules, since there is no appreciable activation energy for molecular adsorption. HREELS confirms weak, molecular adsorption in the monolayer for both molecules. Furthermore, nitromethane is bonded on Au(111) in an upright, strongly tilted geometry, suggesting a monodentate coordination to the surface. Methyl nitrite adsorbs on Au(111) with the O–N=O group in a flat-lying geometry, with evidence for both *cis* and *trans* forms. The Au(111) surface does not sufficiently activate nitromethane and methyl nitrite for dissociation or isomerization (CH<sub>3</sub>NO<sub>2</sub> ↔ CH<sub>3</sub>ONO) to occur under UHV conditions. Thus the activation energies for dissociation and isomerization of nitromethane on Au(111) exceed 10.5 kcal/mol.

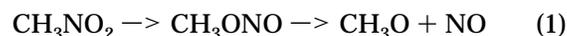
## 1. Introduction

Previously we have studied the chemisorption of NO<sub>2</sub> on Au(111) and on polycrystalline gold surfaces.<sup>1,2</sup> Even though gold has little activity for chemisorption compared to the other late transition metals, we found that NO<sub>2</sub> is chemisorbed on Au(111) with an adsorption energy of about 14 kcal/mol. NO<sub>2</sub> bonds to the surface in an O,O'-chelating adsorption geometry in the chemisorbed monolayer and is reversibly adsorbed. In part due to the possibilities of using gold as a highly selective partial oxidation catalyst, we are interested in pursuing further fundamental studies of organic molecules containing the NO<sub>2</sub> functional group in order to create coadsorbed layers of surface-bound hydrocarbons and reactive oxygen species on Au surfaces. For example, very selective hydrocarbon oxidation reactions have been reported in the presence of a gold catalyst using NO<sub>2</sub> as the oxidant.<sup>3</sup>

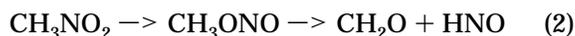
The surface and condensed-phase chemistry of nitromethane (CH<sub>3</sub>NO<sub>2</sub>) is particularly interesting also because it is the archetype of an important class of high explosives.<sup>4</sup> Its structural simplicity and ease of handling are well suited to fundamental study. Technical applications of CH<sub>3</sub>NO<sub>2</sub> itself as an explosive are somewhat specialized because it is a liquid, but its high power and low sensitivity are sometimes advantageous.<sup>5</sup>

Homogeneous nitromethane reactions have been the subject of extensive studies.<sup>4–7</sup> Perche et al.<sup>8</sup> carried out

a kinetics study of the thermal decomposition mechanism of CH<sub>3</sub>NO<sub>2</sub> and found that the reaction proceeds via homolysis of the C–N bond as the rate-limiting step, producing CH<sub>4</sub>, NO, CO, and H<sub>2</sub>O as the major products. Wodtke et al.<sup>9</sup> studied the dissociation of nitromethane in a molecular beam by multiple absorption of IR photons and found CH<sub>3</sub>O among the products, which they ascribed to the reaction



They estimated the branching ratio (homolysis/isomerization) to be 0.6 ± 0.2. The potential energy surface for rearrangement of nitromethane has been calculated by Dewar et al.,<sup>10</sup> and they find that the preferred pathway for decomposition of nitromethane involves rearrangement to methyl nitrite followed by elimination of nitroxyl:



Dewar et al. also calculated that the activation energy for rearrangement is 47 kcal/mol, lower than that for homolysis of the C–N bond.

There are no previous studies of either nitromethane or methyl nitrite adsorbed on Au surfaces, but several related investigations have been carried out. Hwang et al.<sup>11</sup> previously examined CH<sub>3</sub>NO<sub>2</sub> decomposition on a Pt(111) surface, and we have recently reinvestigated this chemistry<sup>12</sup> and find some important differences from their work. We find weak CH<sub>3</sub>NO<sub>2</sub> adsorption on Pt(111), with an adsorption energy of about 11 kcal/mol. High-resolution electron energy loss spectroscopy (HREELS) showed that nitromethane adsorbs in an upright, pseudobidentate

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adsorption geometry using the  $\text{NO}_2$  group, such that the Pt–O bonds are not equivalent. About 25% of the chemisorbed monolayer decomposes during temperature-programmed desorption (TPD), with evolution of  $\text{H}_2\text{O}$ , HCN, NO, and CO (and no methane) into the gas phase. On the Pt(111) surface, extensive cleavage of the C–N bond does not occur even though it is the weakest bond in gas-phase nitromethane. Hwang et al.<sup>11</sup> also reported on  $\text{CH}_3\text{NO}_2$  decomposition on Rh(111), and they found complete decomposition in the monolayer to form CO,  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{CO}_2$  as major gas-phase products from complete dissociation of the C–N and N–O bonds. Benziger<sup>13</sup> studied adsorption of  $\text{CH}_3\text{NO}_2$  on clean and oxygen-pre dosed Ni(111) by TPD and Fourier transform-reflection–absorption infrared spectroscopy (FT-RAIRS). He reported that  $\text{CH}_3\text{NO}_2$  decomposed on Ni(111) to produce the major products HCN,  $\text{H}_2$ , and adsorbed oxygen, while the oxygen-pre dosed Ni(111) was largely inert to  $\text{CH}_3\text{NO}_2$  reaction. He proposed that  $\text{CH}_3\text{NO}_2$  adsorbs on the Ni surface via the oxygen in the nitro group, reducing the N–O bond order from 1.5 to 1. Adsorption thus weakens the N–O bond so that it is broken more easily than the C–N bond.

Recently, Pressley et al.<sup>14</sup> found no thermal dissociation of methyl nitrite on Ag(111) but used electron and photon activation to cause reaction. They observed NO, methane, and formaldehyde products after irradiation. Heating to 500 K left a clean Ag(111) surface. We have also investigated methyl nitrite ( $\text{CH}_3\text{ONO}$  and  $\text{CD}_3\text{ONO}$ ) adsorption on Pt(111).<sup>15</sup> Molecular adsorption occurs at 100 K, but methyl nitrite completely decomposes upon heating to 190 K, evolving mostly NO,  $\text{H}_2$ , and CO, but with some  $\text{CH}_3\text{OH}$  desorbed at high coverages. No other studies of methyl nitrite chemistry on metals have been done.

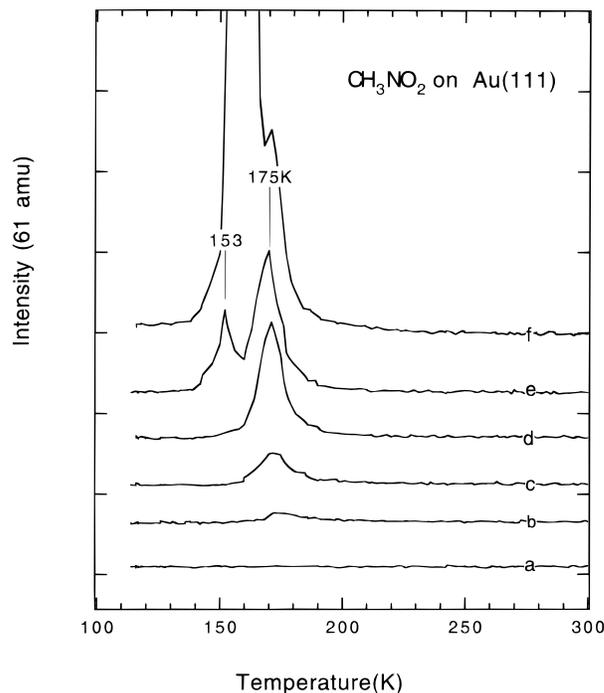
In this paper, we report on the adsorption of nitromethane and methyl nitrite on Au(111) studied by means of AES, TPD, and HREELS. We find that both of these molecules are only weakly, molecularly adsorbed on this surface, and we determine some aspects of the adsorption geometry. Au does not activate either molecule for dissociation or isomerization under UHV conditions.

## 2. Experimental Section

The experiments were performed in a UHV chamber which has been described previously.<sup>2</sup> This system has a base pressure of  $6 \times 10^{-11}$  Torr and was equipped with the instrumentation necessary to perform AES, TPD, HREELS, and low-energy electron diffraction (LEED). The Au(111) crystal could be heated resistively to 1200 K and cooled to 100 K by direct contact of the crystal mounting block with a liquid nitrogen reservoir. The temperature of the Au(111) crystal was monitored directly by means of a Chromel–Alumel thermocouple. The Au(111) was cleaned by  $\text{Ar}^+$  sputtering at 880 K, under an Ar pressure of  $5 \times 10^{-5}$  Torr and then annealed at 1000 K for 5–10 min. The sample treated in this way showed a good ( $1 \times 1$ ) LEED pattern, and no carbon could be detected by AES.

TPD experiments were performed with the sample in line-of-sight of the mass spectrometer ionizer. A heating rate of  $\sim 5$  K/s was used in the TPD experiments. Signals at 2, 16, 18, 27, 28, 30, 32, 46, 61, and 64 amu corresponding to  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , HCN, CO, NO,  $\text{NO}_2$ , and  $\text{CH}_3\text{NO}_2$  products were examined in preliminary TPD experiments.

All HREELS spectra were taken with the sample at 110–115 K, typically with a resolution of about  $75 \text{ cm}^{-1}$ , a count rate of 5–35 kcps, and an incident beam energy of 3 eV.



**Figure 1.**  $\text{CH}_3\text{NO}_2$  TPD spectra after  $\text{CH}_3\text{NO}_2$  exposures on Au(111) at 115 K: (a) 0.07 L; (b) 0.14 L; (c) 0.21 L; (d) 0.9 L; (e) 1.35 L; (f) 6 L.

Nitromethane (99+%, Aldrich) and methyl nitrite were degassed by several freeze–pump–thaw cycles before dosing. *d*<sub>3</sub>-Methyl nitrite was synthesized according to a standard method<sup>16</sup> and checked for purity. Nitromethane and methyl nitrite were dosed onto the Au(111) surface at 115–120 K through a leak valve connected to a microchannel plate array to form a directed beam gas doser. In this paper, we assume a doser enhancement factor of 50, and no correction is made for ion gauge sensitivity.

## 3. Results

**3.1. Temperature-Programmed Desorption. 3.1.1. Nitromethane.** Thermal desorption spectra of  $\text{CH}_3\text{NO}_2$  following exposures of  $\text{CH}_3\text{NO}_2$  on Au(111) at 115 K are shown in Figure 1. At low exposures, only one  $\text{CH}_3\text{NO}_2$  peak is observed at 175 K. This state grows in intensity at constant peak temperature with increasing exposures until about 0.9 L, where it saturates in size. The desorption activation energy  $E_d$  for this state, which we assign to the monolayer, is estimated to be 10.5 kcal/mol from Redhead analysis by assuming first-order desorption kinetics and a preexponential factor of  $10^{13} \text{ s}^{-1}$ . Following larger exposures of  $\text{CH}_3\text{NO}_2$ , another desorption peak developed initially at 153 K and then shifted to higher temperatures with increasing exposures. This behavior and the identical leading edge rates of these curves indicate zero-order desorption kinetics for this state, and we assign it to the physisorbed multilayer of  $\text{CH}_3\text{NO}_2$ . The activation energy for desorbing the multilayer is about 9 kcal/mol.

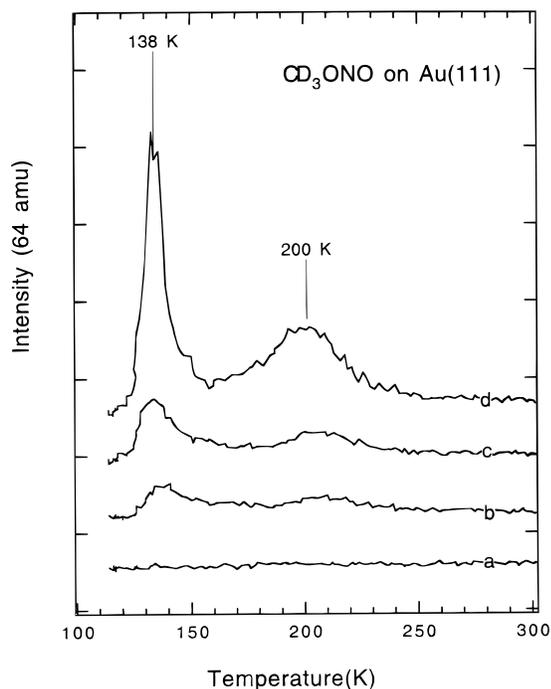
During these TPD studies, no other peaks associated with  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , HCN, CO, NO, and  $\text{NO}_2$  (except those expected from  $\text{CH}_3\text{NO}_2$  cracking in the mass spectrometer ionizer) were observed. Also, AES analysis following the TPD experiments could not detect any decomposition products and showed only clean Au signals. This indicates that  $\text{CH}_3\text{NO}_2$  adsorption is completely reversible and decomposition does not occur on Au(111) under UHV conditions.

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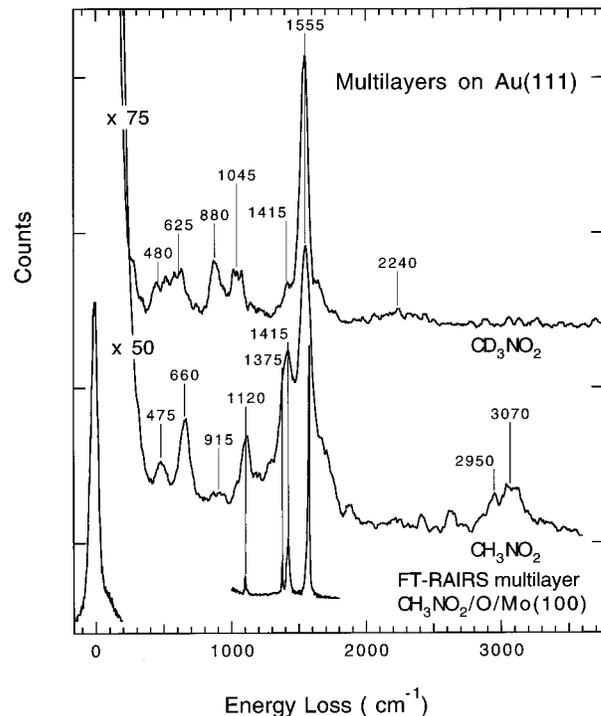
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**Figure 2.**  $\text{CD}_3\text{ONO}$  TPD spectra after  $\text{CD}_3\text{ONO}$  exposures on Au(111) at 120 K; (a) 0.09 L; (b) 0.225 L; (c) 0.45 L; (d) 0.9 L.

The low desorption temperature and concomitant small value of  $E_d$  indicate that the chemisorption bonding interaction between adsorbed  $\text{CH}_3\text{NO}_2$  and the Au(111) surface is quite weak, about 10.5 kcal/mol. Since we can assume that this weak molecular adsorption is not appreciably activated, the value for  $E_d$  corresponds closely to the adsorption energy or chemisorption bond energy. The adsorption behavior of  $\text{CH}_3\text{NO}_2$  on Au(111) can be compared with that in our previous study of the adsorption of  $\text{NO}_2$  on the Au(111) surface.<sup>1</sup> For chemisorbed  $\text{NO}_2$ , a desorption peak at 235 K was observed which corresponds to an adsorption energy of about 14 kcal/mol. This was surprising to us, since we had expected a similar adsorption energy for  $\text{CH}_3\text{NO}_2$ . Evidently, the weaker adsorption of  $\text{CH}_3\text{NO}_2$  is due to the methyl group in  $\text{CH}_3\text{NO}_2$ , which weakens the bonding capability of the oxygen atoms with the surface compared to  $\text{NO}_2$ .

**3.1.2. Methyl nitrite.** Figure 2 shows the TPD spectra of perdeutero-methyl nitrite ( $\text{CD}_3\text{ONO}$ ) after increasing  $\text{CD}_3\text{ONO}$  exposures on Au(111) at 120 K. A low-temperature peak at 138 K developed immediately at the lowest exposures, and this peak can be saturated using higher exposures. Physisorbed multilayers of methyl nitrite were not observed because they desorb at about 115 K,<sup>14</sup> a temperature that is lower than the dose temperature we used. The peak at 138 K does not shift with increasing exposure, indicating lateral interactions do not change much with coverage, possibly due to 2D clustering at low coverages. This desorption peak temperature can be used to estimate an  $E_d$  of about 8 kcal/mol for methyl nitrite in the monolayer. Another weak desorption feature centered near 200 K is due to electron-induced dissociation (EID)<sup>17</sup> of methyl nitrite in the monolayer during TPD. EID is a particularly significant problem for these TPD spectra because of the large EID cross-section for weakly adsorbed species, in this case methyl nitrite. An increasing amount of  $\text{NO}_2$  was also detected for larger exposures, consistent with this effect. At low coverages, we did not



**Figure 3.** HREELS spectra of multilayer films of  $\text{CH}_3\text{NO}_2$  and  $\text{CD}_3\text{NO}_2$  on Au(111) at 115 K. The condensed multilayer of  $\text{CH}_3\text{NO}_2$  was from a dose of 10.5 L ( $\sim 11$  layers thick), and the film of  $\text{CD}_3\text{NO}_2$  was from a dose of 2.4 L ( $\sim 2.7$  layers thick). For comparison, we also show a FT-RAIRS spectrum of a thick film of  $\text{CH}_3\text{NO}_2$  condensed on an oxygen-precured Mo(100) surface.

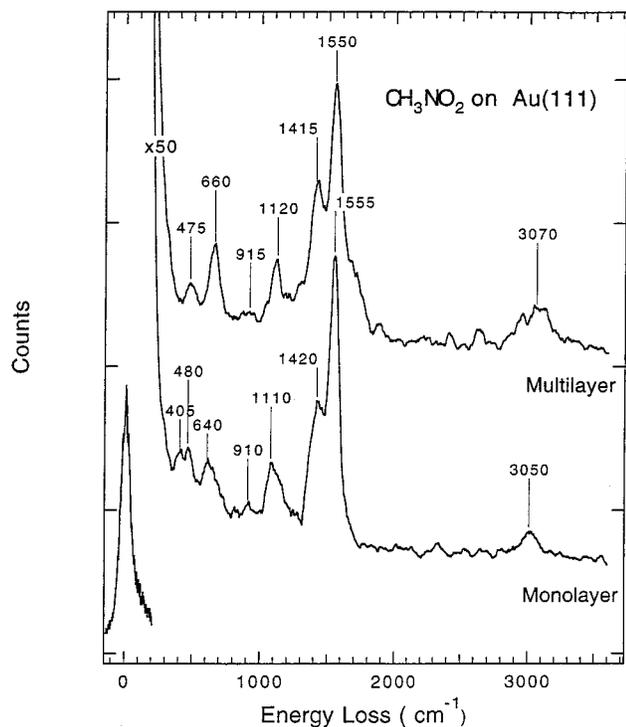
**Table 1.** Assignment of the HREELS Spectra for Adsorbed Nitromethane<sup>a</sup>

assignment <sup>b</sup>	$\text{CH}_3\text{NO}_2$ <sup>18</sup>		$\text{CH}_3\text{NO}_2$ on Au(111)	
	IR(liquid)	IR(solid)	multilayer	monolayer
$\nu_{\text{as}}(\text{C}-\text{H})$	3040 (2300)	3072, 3037	3070 (2240)	3050
$\nu_{\text{s}}(\text{C}-\text{H})$	2946 (2189)	2962, 2948	2950	(2125)
$\nu_{\text{as}}(\text{NO}_2)$	1558 (1544)	1561	1555 (1555)	1555 (1530)
$\delta_{\text{as}}(\text{CH}_3)$	1423 (1073)	1438, 1426	1415 (1045)	1420 (1055)
$\delta_{\text{s}}(\text{CH}_3)$	1402 (1039)	1409, 1405		
$\nu_{\text{s}}(\text{NO}_2)$	1378 (1391)	1374, 1373	(1415)	(1380)
r( $\text{CH}_3$ )	1098 (880)	1104, 1102	1120 (880)	1110 (890)
$\nu(\text{C}-\text{N})$	916 (895)	919, 913	915	910
$\delta_{\text{s}}(\text{NO}_2)$	654 (626)	662, 660	660 (625)	640 (620)
r( $\text{NO}_2$ )	479 (431)	482	475 (480)	480 (465)

<sup>a</sup> Values for  $\text{CD}_3\text{NO}_2$  shown in parentheses. <sup>b</sup>  $\nu$  = stretching;  $\delta$  = bending; r = rocking.

detect any decomposition products desorbed in TPD. Methyl nitrite does not thermally decompose on Au(111) under UHV conditions.

**3.2. High-Resolution Electron Energy Loss Spectroscopy.** **3.2.1. Nitromethane.** As a benchmark for the monolayer spectra, we show in Figure 3 a comparison of the vibrational spectra from HREELS of  $\text{CH}_3\text{NO}_2$  and  $\text{CD}_3\text{NO}_2$  multilayers on Au(111) and an FT-RAIRS spectrum of a  $\text{CH}_3\text{NO}_2$  multilayer on an oxygen-precured Mo(100) surface. Assignments of all of the molecular vibrations are given in Table 1, and these are made by comparison with the liquid and solid-phase IR spectra<sup>18</sup> and the H,D isotopic shifts. The HREELS data for adsorbed nitromethane films agree well with the IR data on condensed phases of nitromethane.<sup>18</sup> Upon deuteration, the  $\text{CH}_3$

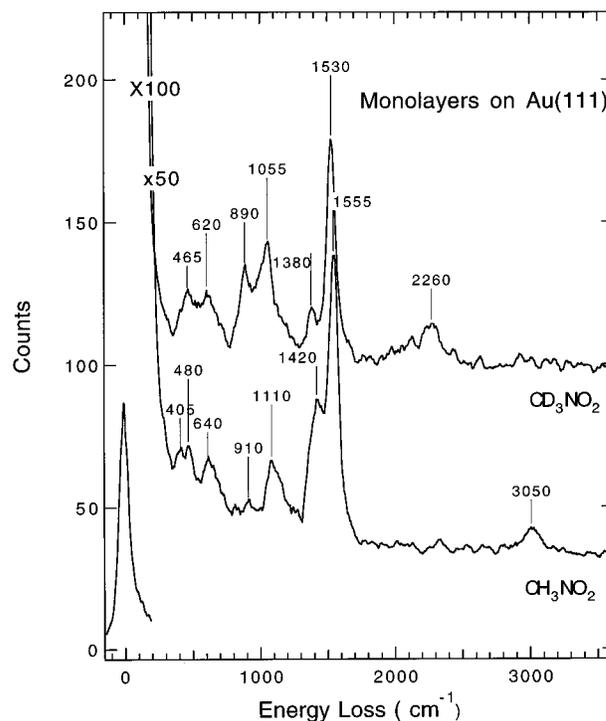


**Figure 4.** HREELS spectra of monolayer and multilayer nitromethane on Au(111). The multilayer was produced by a 10.5 L  $\text{CH}_3\text{NO}_2$  dose, and the monolayer was obtained by heating the substrate covered by a multilayer to 157 K.

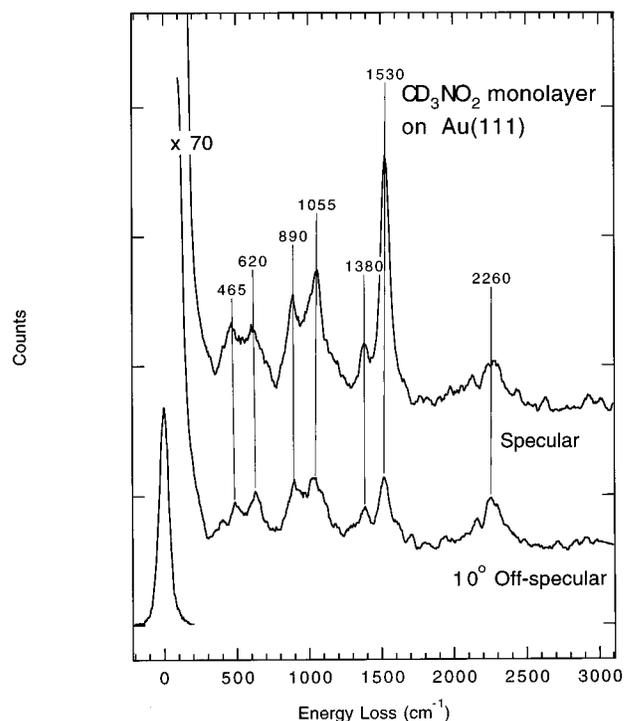
bending modes ( $\delta_{\text{as}}(\text{CH}_3)$  and  $\delta_{\text{s}}(\text{CH}_3)$ ) near  $1415\text{ cm}^{-1}$  are shifted to a peak at  $1045\text{ cm}^{-1}$ , and the rocking mode of the  $\text{CH}_3$  group ( $\nu_{\text{r}}(\text{CH}_3)$ ) at  $1120\text{ cm}^{-1}$  is shifted to  $880\text{ cm}^{-1}$ . The  $\text{CH}_3\text{NO}_2$  peak at  $1415\text{ cm}^{-1}$  includes symmetric and asymmetric bending modes of  $\text{CH}_3$  along with the symmetric stretching mode of  $\text{NO}_2$ . These peaks are not resolved in the HREELS spectra, but they can be resolved at higher resolution using FTIR, as shown at the bottom of Figure 3. In the FT-RAIRS spectrum, the  $\nu_{\text{s}}(\text{NO}_2)$  peak is at  $1375\text{ cm}^{-1}$ , and the  $\delta_{\text{s}}(\text{CH}_3)$  and  $\delta_{\text{as}}(\text{CH}_3)$  peaks are at  $1414$  and  $1420\text{ cm}^{-1}$ , respectively. The IR spectrum demonstrates that the HREELS peak at  $1415\text{ cm}^{-1}$  for  $\text{CH}_3\text{NO}_2$  should be attributed principally to the  $\text{CH}_3$  bending modes. This explains the large decrease in intensity of this peak in the  $\text{CD}_3\text{NO}_2$  spectra.

Figure 4 compares the HREELS spectra of a monolayer and a physisorbed multilayer of  $\text{CH}_3\text{NO}_2$ . The two spectra have very similar vibrational frequencies, and thus the assignment of the vibrations in the monolayer can be easily done, as shown in Table 1. Figure 5 shows the HREELS spectra for  $\text{CH}_3\text{NO}_2$  and  $\text{CD}_3\text{NO}_2$  monolayers on Au(111). The same isotope effects were found as for the multilayer spectra. Clearly  $\text{CH}_3\text{NO}_2$  is adsorbed molecularly on the Au(111) surface and the surface bonding interaction must be weak, hardly perturbing vibrations within the molecule.

Information on the adsorption geometry of adsorbed nitromethane, and hence the nature of the surface chemical bond, was obtained by performing off-specular scattering studies in HREELS and utilizing the surface dipole selection rule. To avoid the complicating overlap of the  $\text{CH}_3$  bending modes and the  $\nu_{\text{s}}(\text{NO}_2)$  mode and obtain reliable intensities for the  $\nu_{\text{as}}(\text{NO}_2)$  and  $\nu_{\text{s}}(\text{NO}_2)$  peaks,  $\text{CD}_3\text{NO}_2$  was utilized. Specular and off-specular HREELS spectra of the  $\text{CD}_3\text{NO}_2$  monolayer are shown in Figure 6. As can be seen in Table 1, only three peaks— $\nu_{\text{as}}(\text{NO}_2)$ ,  $\nu_{\text{s}}(\text{NO}_2)$ , and  $\delta_{\text{s}}(\text{NO}_2)$ —have no overlapping bands in these spectra so that changes in their intensities can be meaningfully interpreted. Figure 6 shows that the largest

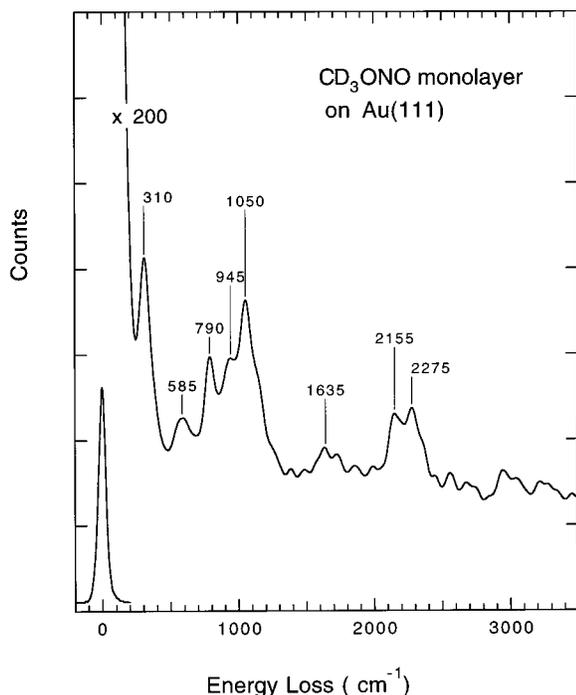


**Figure 5.** HREELS spectra of monolayer  $\text{CH}_3\text{NO}_2$  and  $\text{CD}_3\text{NO}_2$  on Au(111). The monolayers were obtained by heating the substrate covered by the respective multilayers to 157 K.



**Figure 6.** Specular and off-specular ( $\Delta\theta = 10^\circ$ ) HREELS spectra of a monolayer of  $\text{CD}_3\text{NO}_2$  on Au(111). The monolayer was obtained by heating a multilayer to 157 K.

change in the off-specular spectrum is for the  $\nu_{\text{as}}(\text{NO}_2)$  peak at  $1415\text{ cm}^{-1}$ , which is decreased by about a factor of 4, indicating that it has a significant component due to dipole scattering in the specular spectrum. The elastic peak intensity in this spectrum decreased by a factor of 16. The symmetric  $\text{NO}_2$  stretching peak,  $\nu_{\text{s}}(\text{NO}_2)$  at  $1380\text{ cm}^{-1}$ , is reduced only slightly by a factor of  $<1.5$  in the off-specular scan. As a result the  $\nu_{\text{as}}(\text{NO}_2)/\nu_{\text{s}}(\text{NO}_2)$  intensity ratio decreases from  $\sim 5$  in the specular scan to  $\sim 2$



**Figure 7.** HREELS spectrum of adsorbed CD<sub>3</sub>ONO on Au(111) at 120 K. The CD<sub>3</sub>ONO dose used was 15 L, which produces a maximum coverage of one monolayer at 120 K.

**Chart 1**



in the off-specular scan. The symmetric NO<sub>2</sub> bending peak,  $\delta_s(\text{NO}_2)$  at 620 cm<sup>-1</sup>, is not changed in the off-specular spectrum, indicating that it has no significant component due to dipole scattering in the specular spectrum.

In this study, the monolayer was obtained by warming up a multilayer coverage to 157 K. Our ongoing FT-RAIRS studies of this system show that this warm-up procedure does not influence the orientation of nitromethane in the monolayer.

**3.2.2. Methyl Nitrite.** Methyl nitrite is an isomer of nitromethane, as shown in Chart 1. It has an exceptionally weak CH<sub>3</sub>O–NO bond (42 kcal/mol in the gas phase) which dominates its chemistry both in solution and in the gas phase. It is less stable and more reactive than nitromethane. Methyl nitrite has two conformers, *cis*-methyl nitrite and *trans*-methyl nitrite. These conformers exist together at room temperature, although *cis*-methyl nitrite is reported to be more stable.<sup>19–21</sup>

Figure 7 is a HREELS spectrum of a monolayer of CD<sub>3</sub>ONO. The assignments are given in Table 2 to be consistent with those of the IR spectra of solid-state CD<sub>3</sub>ONO.<sup>19–21</sup> The good agreement of the vibrational frequencies observed for a monolayer of CD<sub>3</sub>ONO with those of CD<sub>3</sub>ONO in the solid state supports the TPD results that adsorption of methyl nitrite on Au(111) at 120 K is molecular rather than dissociative and that the

**Table 2.** Assignment of the HREELS Spectra for Adsorbed d<sub>3</sub>-Methyl Nitrite<sup>a</sup>

assignment <sup>b</sup>	CD <sub>3</sub> ONO IR(solid) <sup>19–21</sup>		CD <sub>3</sub> ONO monolayer on Au(111)	
	cis	trans	cis	trans
$\nu_{\text{as}}(\text{C}-\text{D})$	2275 (3031)	2180 <sup>c</sup> (2913)	2275	2155
$\nu_{\text{s}}(\text{C}-\text{D})$	2219 <sup>c</sup> (2952)	2038 <sup>c</sup> (2823)		
$\nu(\text{N}=\text{O})$	1610 (1613)	1664 <sup>c</sup> (1665)		1635
$\nu_{\text{as}}(\text{CD}_3)$	1091 <sup>c</sup> (1452)	1055 <sup>c</sup> (1444)		1050
$\nu_{\text{s}}(\text{CD}_3)$	1045 (1406)	1039 <sup>c</sup> (1422)		
$\nu(\text{C}-\text{O})$	897 <sup>c</sup> (985)	950 <sup>c</sup> (1043)		945
$\nu(\text{N}-\text{O})$	798 (838)	775 (806)		790
$\delta(\text{ONO})$	595 (625)	551 (565)		585
$\delta(\text{CON})$	307 <sup>c</sup> (351)	335 <sup>c</sup> (370)		310

<sup>a</sup> Values for CH<sub>3</sub>ONO shown in parentheses. <sup>b</sup>  $\nu$  = stretching;  $\delta$  = bending; r = rocking. <sup>c</sup> Calculated values.<sup>19–21</sup>

bonding to the surface is weak. The assignments in Table 2 could not be made as precisely as those of nitromethane, since two methyl nitrite conformers may coexist and these would have many combination bands and overlapping peaks in HREELS (and even in the IR spectra). At our resolution using HREELS, the only peaks in the spectrum that can be resolved as due to either *cis* or *trans* structures are the stretching modes of the methyl group. We tentatively assign the peak at 2275 cm<sup>-1</sup> to  $\nu_{\text{as}}(\text{CD})$  in *cis*-CD<sub>3</sub>ONO and the 2155 cm<sup>-1</sup> peak to the same mode in *trans*-CD<sub>3</sub>ONO, concluding that both *cis* and *trans*-methyl nitrite are coadsorbed on the Au(111) surface at 120 K. An assignment of the HREELS spectrum in Figure 7 to only the *cis* conformer could be made. This would also be consistent with the greater stability of the *cis* conformer. However, we slightly favor the other interpretation, since the large width (285 cm<sup>-1</sup> fwhm) of this unresolved peak indicates that more than two peaks are present in the spectrum.

Quenching experiments show that the equilibrium *cis*/*trans* ratio of 1.75<sup>22</sup> in the gas phase at 300 K is not strongly altered (1.4 ± 0.25) at low temperatures in an Ar matrix.<sup>20</sup> One can roughly estimate from our HREELS spectrum that there are similar amounts of *cis* and *trans* conformers on the basis of the observed relative intensities of the  $\nu_{\text{as}}(\text{C}-\text{H})$  modes of the conformers, assuming similar impact scattering cross-sections and that this mechanism dominates the observed  $\nu(\text{CD})$  intensities. We also found both conformers of methyl nitrite in multilayer adsorption on Pt(111) at 110 K.<sup>15</sup>

The spectra in Figures 5 and 7 demonstrate the dramatic differences in the HREELS spectra for the two isomeric compounds CD<sub>3</sub>NO<sub>2</sub> and CD<sub>3</sub>ONO. Principally, nitromethane has a strong peak at 1550 cm<sup>-1</sup> arising from the asymmetric NO<sub>2</sub> stretching mode that methyl nitrite does not have. This means that vibrational spectroscopy is a powerful technique to study the isomerization of nitromethane to methyl nitrite and that the studies can be carried out conveniently using HREELS.

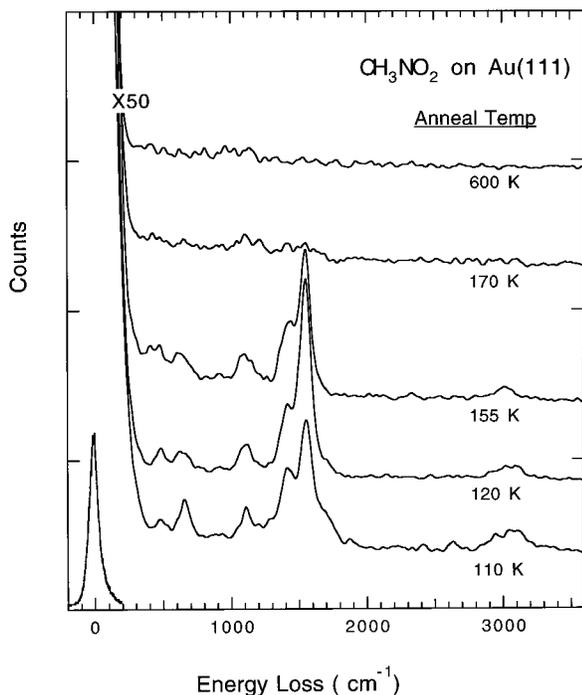
**3.3. Warm-Up Studies of Nitromethane.** HREELS warm-up spectra for adsorbed nitromethane are shown in Figure 8. It is evident that the spectra at different temperatures can be assigned completely to nitromethane vibrations and that no methyl nitrite produced via isomerization or coadsorbates due to decomposition were found by HREELS. As the multilayer is annealed, the relative intensity of the  $\nu_{\text{as}}(\text{NO}_2)$  peak changes, indicating that some structural rearrangement within the multilayer occurs during the annealing process that results in a

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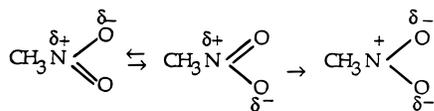
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**Figure 8.** HREELS warm-up spectra beginning with a  $\text{CH}_3\text{NO}_2$  multilayer (2.4 L) on Au(111) at 110 K. The sample was heated successively to the temperatures indicated.

**Scheme 1**



greater tilt of the C–N bond away from the surface normal, and more nearly parallel with the surface, or that significant changes occur in the intermolecular interactions that change the dynamic dipole moment. Upon annealing to 155 K, the multilayer desorbs and only the monolayer of  $\text{CH}_3\text{NO}_2$  remains. The primary difference in the spectra is that the peak in the C–H stretching region is much narrower for the monolayer compared to the multilayer. We interpret this as evidence for hydrogen bonding in condensed nitromethane multilayers. Hydrogen bonding among nitromethane molecules has been considered as a bonding force in dimers of liquid nitromethane.<sup>23</sup> HREELS spectra show that the surface is clean when the annealing temperature is above 170 K, in agreement with the TPD results. Hence, the Au(111) surface does not sufficiently activate nitromethane or methyl nitrite for dissociation or isomerization to occur under UHV conditions.

#### 4. Discussion

**4.1. Adsorption Geometry of Nitromethane on Au(111).** The nitromethane molecule effectively exhibits  $C_{2v}$  symmetry in its free (gaseous) state, where the methyl group can be treated as a point mass. It has a strong electron-withdrawing group ( $\text{NO}_2$ ) and an electron-donating group ( $\text{CH}_3$ ). Several resonance structures contribute to a description of nitromethane, as shown in Scheme 1. Electron donation from the  $\text{CH}_3$  group may be used to rationalize the smaller  $\text{ONO}$  angle ( $125^\circ$ ) and the longer  $\text{NO}$  bond (1.224 Å) compared to those of  $\text{NO}_2$  ( $134.1^\circ$  and

1.193 Å).<sup>24</sup> Because of the presence of two oxygen atoms, nitromethane can be either a monodentate or a bidentate ligand in inorganic complexes. Both bonding modes ( $\eta^1(\text{O})$  and  $\eta^2(\text{O},\text{O})$ ) are known for nitromethane coordination complexes,<sup>25–27</sup> and so we can propose several surface structures (linkage isomers) for adsorbed nitromethane, as shown in Figure 9. In Figure 9a–c, nitromethane is bound to the surface with two oxygens ( $\eta^2(\text{O},\text{O})$ ) in a chelating geometry. Nitromethane in Figure 9a retains two symmetry planes perpendicular to the surface, and thus it possesses  $C_{2v}$  symmetry. The structures in Figures 9b and c show a tilted geometry compared to that in part a with only one symmetry plane perpendicular to the surface, either in the molecular plane for part b or bisecting the molecular plane of nitromethane for part c. Figure 9d shows a special limiting case for part c in which nitromethane is flat-lying on the surface with the molecular plane parallel to the surface (still with only one symmetry plane), bonding through interactions with the oxygens and/or the  $\pi$  orbital. The geometries shown in Figure 9b–d have  $C_s$  symmetry. Three other adsorption geometries are associated with nitromethane using one oxygen ( $\eta^1(\text{O})$ ) to bond to the surface. The structures in Figure 9e and f have a symmetry plane (the molecular plane) perpendicular to the surface, but in part e the C–N bond is significantly tilted away from the surface normal and in part f the C–N bond is parallel to the surface. Figure 9g illustrates the geometry if the nitromethane in part e has the molecular plane tilted away from the surface normal. This geometry can be characterized by  $C_1$  symmetry. A special limiting case for part g would have nitromethane flat-lying on the surface as in part d. We will now use our HREELS data to gain some important insights into the bonding geometry and orientation of adsorbed nitromethane in the monolayer on Au(111).

The surface selection rule for HREELS can be stated as “only those vibrations which belong to the totally symmetric representations  $A_1$ ,  $A'$ , and  $A$  are observed as fundamentals in dipole scattering”.<sup>28</sup> This selection rule applies to specular (dipole) scattering of electrons from molecules adsorbed on metallic surfaces which effectively screen dynamic dipole moments parallel to the surface and strongly reduce excitation of these modes. Table 3 is a correlation table showing how several normal modes of gas-phase nitromethane transform for different symmetries of the adsorbed complex. Here we focus on just three modes,  $\nu_{\text{as}}(\text{NO}_2)$ ,  $\nu_{\text{s}}(\text{NO}_2)$ , and  $\delta_{\text{s}}(\text{NO}_2)$ , which do not overlap with any other modes in  $\text{CD}_3\text{NO}_2$ . We chose not to utilize the  $r(\text{NO}_2)$  modes in our analysis because we do not have a clear assignment of these peaks. Formate species have an analogous structure to nitromethane, and Haq et al.<sup>29</sup> have used a similar analysis of IR data on the corresponding three modes to determine the adsorption geometry of formate on Ni(110) surfaces.

Our assignment of the adsorption geometry of nitromethane on Au(111) is based mainly on the observation that the asymmetric  $\text{NO}_2$  stretching mode,  $\nu_{\text{as}}(\text{NO}_2)$ , is dipole active and the dynamic dipole of this mode is not parallel (or nearly parallel) to the surface. The peak due to  $\nu_{\text{as}}(\text{NO}_2)$  is the largest peak in the specular spectrum

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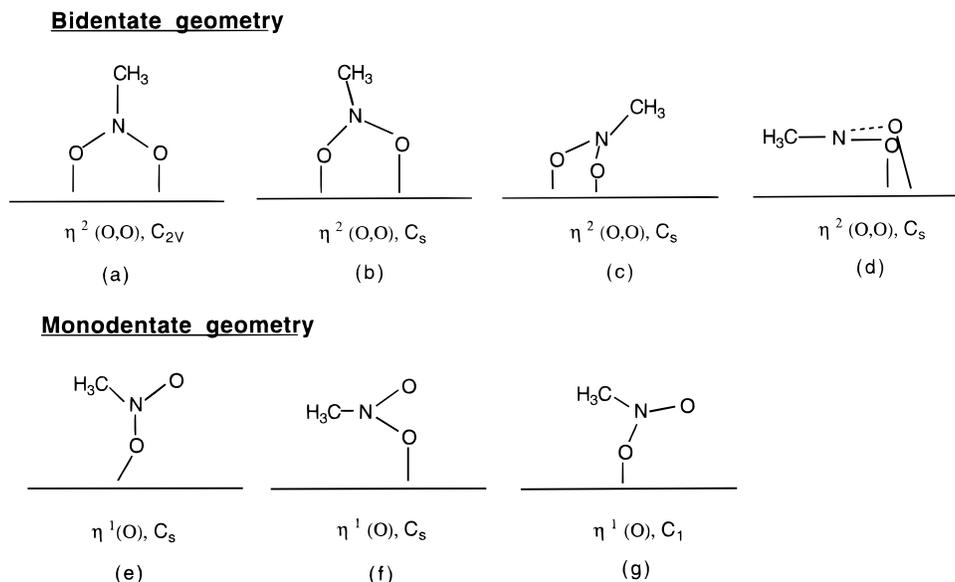
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**Figure 9.** Possible adsorption geometries of nitromethane on Au(111) surfaces. Bidentate, chelating geometries include (a)  $C_{2v}$  symmetry, (b)  $C_s$  symmetry with the molecular plane perpendicular to the surface but with  $\text{CH}_3\text{NO}_2$  tilted away from the surface normal with two inequivalent Au–O bonds, (c)  $C_s$  symmetry with two equivalent Au–O bonds but with the molecular plane tilted away from the surface normal, and (d) flat-lying with  $C_s$  symmetry. Monodentate geometries bonding through one oxygen atom include (e)  $C_s$  symmetry with the C–N bond strongly tilted away from the surface normal, (f)  $C_s$  symmetry with the C–N bond parallel to the surface, and (g)  $C_1$  symmetry in which the molecular plane is tilted away from the surface normal.

**Table 3. Correlation Table of Gas-Phase and Adsorbed Nitromethane**

gas-phase	adsorbed nitromethane geometry						
	$C_{2v}$ (a)	$C_s$ (b)	$C_s$ (c)	$C_s$ (d)	$C_s$ (e)	$C_s$ (f)	$C_1$ (g)
$\nu_{\text{as}}(\text{NO}_2)$	$B_2$	$A'$	$A''$	$A''$	$A'$	$A'$	$A'$
$\nu_{\text{s}}(\text{NO}_2)$	$A_1$	$A'$	$A'$	$A'$	$A'$	$A'$	$A'$
$\delta_{\text{s}}(\text{NO}_2)$	$A_1$	$A'$	$A'$	$A'$	$A'$	$A'$	$A'$

and undergoes the largest decrease in intensity in the off-specular scan. In structures a, c, and d in Figure 9, the dynamic dipole of  $\nu_{\text{as}}(\text{NO}_2)$  is polarized perpendicular to the mirror plane and parallel to the surface. Also, the correlation diagram in Table 3 shows that the  $\nu_{\text{as}}(\text{NO}_2)$  vibration is not dipole active for the adsorption geometries a, c, and d since its symmetry representation is  $B_2$  or  $A''$ . Thus, we can eliminate the chelating adsorption geometries of structures a, c, and d in Figure 9. Structure b can also be eliminated since the O–O distance (2.198 Å) forces the oxygens bonding to the surface to be in nearly symmetric sites, causing only a small tilt to the molecular axis, and this is inconsistent with a relatively large dynamic dipole perpendicular to the surface for  $\nu_{\text{as}}(\text{NO}_2)$  in the adsorbed species and weak  $\nu_{\text{s}}(\text{NO}_2)$  and  $\delta_{\text{s}}(\text{NO}_2)$  peaks. Further support for this conclusion comes from a comparison to the HREELS spectra of nitromethane adsorbed on Pt(111),<sup>12</sup> where we observed relatively strong  $\delta_{\text{s}}(\text{NO}_2)$  and  $\nu_{\text{s}}(\text{NO}_2)$  peaks and assigned the geometry as in part b. This indicates that in adsorbed nitromethane on Au(111) the C–N bond is significantly tilted away from the surface normal in a monodentate configuration.

For each of the monodentate geometries shown, the correlation table shows that all three vibrational modes are dipole-allowed, since they belong to the  $A'$  or  $A$  representation. A consideration of the relative intensities of these allowed modes, however, provides an effective tool for distinguishing between the different adsorption geometries. Geometries that cause the vibrations to generate the greatest dipole moment change perpendicular to the surface will cause the most intense peaks. For the geometry in Figure 9e, the dynamic dipoles of  $\nu_{\text{s}}(\text{NO}_2)$  and  $\delta_{\text{s}}(\text{NO}_2)$  are almost parallel to the surface, and conse-

quently they are effectively screened. This structure is the most consistent with the data shown in Figure 6, in which no change was observed for the  $\delta_{\text{s}}(\text{NO}_2)$  peak in moving from a specular to off-specular scan. The small decrease in the  $\nu_{\text{s}}(\text{NO}_2)$  peak could have been due to overlap with the more intense  $\nu_{\text{as}}(\text{NO}_2)$  peak. Given the relatively weak specular scattering measured for this crystal and the limited off-specular data, the bonding geometry is not definitively determined by our study. However, we conclude that nitromethane is bonded to the surface through one oxygen atom in a monodentate configuration, most likely as in structure f with the C–N bond axis nearly parallel to the surface.

One might imagine that if nitromethane was adsorbed on the surface in a monodentate fashion, then the  $\nu_{\text{as}}(\text{NO}_2)$  frequency would shift to higher values and the  $\nu_{\text{s}}(\text{NO}_2)$  frequency would shift to lower values, increasing the  $\nu_{\text{as}}(\text{NO}_2) - \nu_{\text{s}}(\text{NO}_2)$  splitting. The increase in the corresponding  $\nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$  splitting is well-known for adsorbed acetate and other carboxylates.<sup>30</sup> Thus one might expect that monodentate adsorption of nitromethane would give rise to a larger splitting between the  $\nu_{\text{as}}(\text{NO}_2)$  and  $\nu_{\text{s}}(\text{NO}_2)$  modes compared to that for bidentate adsorption. However, there is no such simple correlation for nitromethane complexes in the inorganic literature. The IR frequencies for two nitromethane complexes are listed in Table 4. In  $[\text{TiCl}_4(\text{CH}_3\text{NO}_2)]_2$ <sup>25</sup> and  $\text{TiCl}_4(\text{CH}_3\text{NO}_2)$ ,<sup>26</sup> nitromethane bonds to the Ti metal center as a monodentate and bidentate ligand, respectively. In comparing the IR data of these two complexes, there are no remarkable differences, and therefore the  $\nu_{\text{as}}(\text{NO}_2) - \nu_{\text{s}}(\text{NO}_2)$  splitting is not a valid indicator to distinguish the coordination of nitromethane. Another example is the copper(II) nitrate-nitromethane complex,  $\text{Cu}(\text{NO}_3)_2(\text{CH}_3\text{NO}_2)$ .<sup>27</sup> X-ray diffraction reveals that nitromethane is a monodentate ligand and that the Cu(II)–O bond is quite long at 2.31 Å. Due to this weak coordination, the nitromethane ligand does not change its structure com-

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**Table 4. Comparison of Vibrational Data for Nitromethane Complexes with Adsorbed Nitromethane on Au(111)**

mode	[TiCl <sub>4</sub> CH <sub>3</sub> NO <sub>2</sub> ] <sub>2</sub> monodentate IR <sup>25</sup> (cm <sup>-1</sup> )	TiCl <sub>4</sub> CH <sub>3</sub> NO <sub>2</sub> bidentate IR <sup>26</sup> (cm <sup>-1</sup> )	CH <sub>3</sub> NO <sub>2</sub> /Au(111) monolayer HREELS (cm <sup>-1</sup> ) (this work)
$\nu_{as}(\text{NO}_2)$	1553, 1520	1570, 1562	1555
$\delta_{as}(\text{CH}_3)$	1412		1420
$\delta_s(\text{CH}_3)$	1370	1410	1420
$\nu_s(\text{NO}_2)$	1405, 1350	1378	1380
$r(\text{CH}_3)$	1100	1100	1110
$\nu(\text{C-N})$	880	900	910
$\delta_s(\text{NO}_2)$	650	655	640

pared with that of free nitromethane and the two N–O bond lengths are identical. These examples demonstrate that weak coordination of nitromethane to the metal center does not strongly perturb the structure of nitromethane. Nitrobenzene is another nitro compound that is known to be a weak ligand in coordination complexes and can be bonded both as a monodentate or bidentate ligand. Similar to nitromethane, monodentate and bidentate nitrobenzene in the complexes Zn(PhNO<sub>2</sub>)<sub>n</sub>(OTeF<sub>5</sub>)<sub>2</sub> with  $n = 2$  or 3<sup>31</sup> displayed identical FTIR spectra.

**4.2. Bonding of Nitromethane and Related Molecules on Au(111).** The bonding between nitromethane and the Au(111) surface is weak, only 10.5 kcal/mol. The primary bonding interaction is dative bonding through one of the oxygen atoms in the NO<sub>2</sub> group, causing a large tilt of the molecule such that the C–N bond is nearly parallel to the surface. This bonding interaction does not rehybridize the N atom in nitromethane, since no large shifts in the vibrational spectra were observed. Comparison of the adsorption of nitromethane with that of NO<sub>2</sub> and N<sub>2</sub>O<sub>3</sub> on the same Au(111) surface is instructive for interpreting this weak bonding, because all of these molecules have used oxygen in the NO<sub>2</sub> group to bond to the surface. NO<sub>2</sub> adsorption and bonding geometry has been studied on Au(111).<sup>1</sup> The heat of adsorption of NO<sub>2</sub> on Au(111) is 14 kcal/mol, and the adsorption geometry is a bidentate O,O-chelating geometry with C<sub>2v</sub> symmetry. Apparently, the methyl group in nitromethane causes a smaller adsorption energy and different adsorption geometry of nitromethane than those for NO<sub>2</sub>. The CH<sub>3</sub> group is an electron-donating substituent, and this reduces the interaction with the surface sufficiently to allow one of the oxygen atoms to move away from the surface.

N<sub>2</sub>O<sub>3</sub>, ON–NO<sub>2</sub>, can be formed on the Au(111) surface by the reaction of gas-phase NO with adsorbed chelating NO<sub>2</sub>.<sup>1</sup> The adsorption energy cannot be measured, since N–N bond scission occurs at 170 K to leave NO<sub>2</sub> on the surface, but this establishes a lower limit of about 10 kcal/mol for the N<sub>2</sub>O<sub>3</sub> adsorption energy. Previously the adsorbed N<sub>2</sub>O<sub>3</sub> structure was assigned as an O,O-chelating geometry with an overall symmetry of C<sub>s</sub> for the adsorbed complex.<sup>1</sup> In that work, it was implied that the NO<sub>2</sub> group in N<sub>2</sub>O<sub>3</sub> possessed C<sub>2v</sub> symmetry, with dative bonding through both oxygens to the surface. The reduction in symmetry to C<sub>s</sub> for the complex makes the  $\nu_{as}(\text{NO}_2)$  mode at 1270 cm<sup>-1</sup> in adsorbed N<sub>2</sub>O<sub>3</sub> dipole allowed, but especially in light of our results on nitromethane, it is possible that the strong intensity of this peak indicates a substantial tilt of the adsorbed complex due to a similar weakening of the surface interaction with one of the oxygens.

**4.3. Adsorption Geometry of Methyl Nitrite on Au(111).** The main purposes of this work was to examine

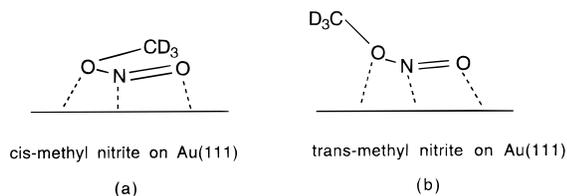
whether CD<sub>3</sub>ONO was adsorbed molecularly or dissociatively and whether isomerization between CH<sub>3</sub>ONO and CH<sub>3</sub>NO<sub>2</sub> could occur on Au(111) under our conditions. These questions have been answered. Some preliminary information can also be gleaned about the bonding geometry of CH<sub>3</sub>ONO on Au(111), and we discuss that here. Details of the bonding geometry of CD<sub>3</sub>ONO have not been probed adequately, and we are planning additional FT-RAIRS studies at this time.

Rock and Jacox<sup>32</sup> have reported gas-phase FTIR spectra of CD<sub>3</sub>ONO between 400 and 4000 cm<sup>-1</sup>. The intensities of the vibrational modes, including both *cis* and *trans* forms, are as follows:  $\nu(\text{N=O})$  at 790 cm<sup>-1</sup> >  $\nu(\text{N=O})$  at 1600–1700 cm<sup>-1</sup> >  $\nu(\text{C-O})$  and  $\delta(\text{CD}_3)$  at 1000 cm<sup>-1</sup>  $\approx$   $\delta(\text{ONO})$  at 590 cm<sup>-1</sup>  $\gg$   $\nu(\text{C-D})$  at 2030–2300 cm<sup>-1</sup>. This intensity distribution is quite different from the HREELS spectrum of monolayer CD<sub>3</sub>ONO. Because TPD clearly shows there is no methyl nitrite decomposition on Au(111), these intensity changes are mainly attributed to the effect of a preferred orientation of adsorbed methyl nitrite on the surface. The intensity differences arise due to screening of the dynamic dipoles parallel to the Au surface and the enhancement of those perpendicular to the surface. In the HREELS spectrum in Figure 7, the intensities of all of the peaks are comparable to that of the  $\nu(\text{C-D})$  peak, which is usually weak in HREELS and principally arises from impact scattering regardless of the adsorption geometry. This indicates that the dynamic dipoles for many of the molecular vibrations are oriented nearly parallel to the surface plane and that the intensities are weak because of strong screening by the surface of dipole scattering excitation of any of these modes. For example, the strong peak due to  $\nu(\text{N=O})$  at 1600–1700 cm<sup>-1</sup> in the gas-phase FTIR spectra is very weak in the HREELS spectrum for the adsorbed monolayer. This difference indicates that the N=O bond in adsorbed methyl nitrite is parallel to the surface. In addition to this, the strongest peak in the gas-phase FTIR spectrum due to  $\nu(\text{N=O})$  at 790 cm<sup>-1</sup> is also very weak for the adsorbate. This shows that the N–O bond is also parallel to the surface. Therefore methyl nitrite adsorbs in a geometry with the O–N=O plane lying flat, nearly parallel to the surface.

Our proposed adsorption geometries for *cis*- and *trans*-methyl nitrite on Au(111) are shown in parts a and b of Figure 10, respectively. We expect that these structures maximize the van der Waals type physisorption interactions between methyl nitrite molecules and the surface just like those for a large variety of hydrocarbons that also adopt flat-lying geometries on surfaces. Dative bonding interactions that delocalize electrons from lone-pair orbitals on the oxygens into Au orbitals also contribute to the adsorption energy. For the *cis* conformer, the entire molecular plane can be parallel to the surface. However, for the *trans* conformer, the methyl group does not lie in the plane of the N=O bond and the O–CH<sub>3</sub> bond is inclined from the O–N=O and surface plane. The energy loss peaks at 310 and 1050 cm<sup>-1</sup> are relatively strong compared to the other peaks in the monolayer spectrum, and this is much different from the gas-phase spectrum where the respective C–O–N bending and  $\nu(\text{C-O})$  modes of *trans*-methyl nitrite are weak. Figure 10b illustrates that these vibrations would generate dynamic dipole components perpendicular to the surface and thus could account for these stronger energy loss peaks.

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**Figure 10.** Proposed adsorption geometries of methyl nitrite on Au(111) surfaces. (a) *cis*-methyl nitrite lying flat on the Au(111) surface with all intramolecular bonds parallel to the surface; (b) *trans*-methyl nitrite “flat-lying” on Au(111) in which the O–N=O bonds are parallel to the surface but with the  $\text{CH}_3$ –O bond inclined to the surface lifting the methyl group out of the O–N=O plane.

### 5. Conclusions

Nitromethane and methyl nitrite adsorb on Au(111) weakly and molecularly, with adsorption energies of about 10.5 and 8 kcal/mol, respectively. The Au(111) surface does not sufficiently activate nitromethane or methyl

nitrite for dissociation or isomerization under UHV conditions, and thus the activation energy for either dissociation or isomerization of nitromethane on the Au(111) surface exceeds 10.5 kcal/mol. We propose that  $\text{CH}_3\text{-NO}_2$  is bonded on the Au(111) surface in a monodentate geometry in the monolayer, with the C–N bond nearly parallel to the surface and that *cis*- and *trans*-methyl nitrite are adsorbed on the Au(111) surface with the O–N=O plane parallel with the surface in relatively flat-lying configurations, consistent with the experimental HREELS findings.

**Acknowledgment.** We acknowledge support of this work by the Army Research Office. We thank Najat Saliba for many helpful discussions and Prof. J. M. White for providing us with a preprint of work from his group on methyl nitrite on Ag(111).

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