Surface Science Letters

Coordination and bonding geometry of nitromethane (CH₃NO₂) on Au(1 1 1) surfaces

Jiang Wang, Harald Busse, Denis Syomin, Bruce E. Koel *

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482, USA

Abstract

The adsorption and bonding geometry of nitromethane (CH_3NO_2) on a Au(1 1 1) single crystal surface was studied by temperature programmed desorption and infrared reflection–absorption spectroscopy (IRAS). Nitromethane weakly adsorbs on Au(1 1 1) with an adsorption energy of only 10.5 kcal/mol. Adsorption is completely reversible; no thermal decomposition occurs under UHV conditions. Consistent with weak binding, IRAS does not reveal any significant chemical shifts for the vibrational modes of CH_3NO_2 at monolayer and submonolayer coverages compared to solid multilayer films. Based on the intensities in IRAS and the surface selection rule, we propose that CH_3NO_2 adsorbs on the Au(1 1 1) surface with C_s symmetry in a monodentate geometry using one oxygen atom to bind to the surface with a large tilt of the C–N bond away from the surface normal. This bonding interaction is 25% less than that of adsorbed NO_2 on Au(1 1 1) which chemisorbs in an O,O′-chelating geometry with C_{2v} symmetry. While isomerization of nitromethane to from methyl nitrite ($CH_3NO_2 \leftrightarrow CH_3ONO$) occurs during thermal decomposition in the gas phase, the Au(1 1 1) surface does not sufficiently activate CH_3NO_2 for dissociation or isomerization to occur under UHV conditions, and so the activation energies for these processes exceed 10.5 kcal/mol on Au(1 1 1). © 2001 Published by Elsevier Science B.V.

1. Introduction

Interactions of NO_2-containing organic molecules with metal surfaces are of interest for a wide range of applications, from metal-organic contacts in non-linear optical materials, to producing self-assembled monolayers on metals, to basic studies of surface-bound hydrocarbons and reactive oxygen species on metal surfaces related to heterogenous catalysis. For example, nitromethane (CH_3NO_2) and other nitroparaffins are potentially useful as probe molecules and as oxygen providers for redox catalytic reactions because their C–N bond dissociation energy is quite weak (57 ± 2 kcal/mol) compared to the other bonds in these molecules [1].

On Au surfaces, adsorption of NO_2 and CH_3NO_2 has been investigated. NO_2 chemisorbs rather strongly on Au(1 1 1) with an adsorption energy of 14 kcal/mol [2,3]. It is reversibly adsorbed in an O,O′-chelating geometry with C_{2v} symmetry and

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* Corresponding author. Tel.: +1-2137407036; fax: +1-2137402701.
E-mail address: koel@chem1.usc.edu (B.E. Koel).

bonds to the surface through both oxygen atoms [2,3]. CH_3NO_2 was also found to be reversibly and molecularly adsorbed on Au(1 1 1) with an adsorption energy of 10.5 kcal/mol [4]. However, the orientation of adsorbed nitromethane was proposed to be a monodentate geometry with C_s symmetry, i.e., with a bonding interaction on the Au(1 1 1) surface in which CH_3NO_2 uses only one oxygen atom. Because this assignment was based on analysis of the vibrational spectra obtained by using HREELS [4] and this technique can suffer from problems of poor resolution (70 cm^{-1} in Refs. [2,4]) and breakdown of the dipole selection rule due to impact scattering mechanisms for electrons, we decided to reinvestigate the bonding geometry of nitromethane on Au(1 1 1) using infrared reflection–absorption spectroscopy (IRAS).

Our IRAS studies reported here confirm and extend the previous assignments of the bonding geometries of CH_3NO_2, along with both NO_2 and N_2O_3, establishing that adsorbed CH_3NO_2 on the Au(1 1 1) surface has a preferential orientation with C_s symmetry and a large tilt of the C–N bond away from the surface normal, consistent with a monodentate coordination using one oxygen atom to bind to the surface.

2. Experimental methods

Studies were carried out in a UHV chamber (2×10^{-10} Torr base pressure) equipped for AES, LEED, TPD and Fourier-transform IRAS [5].

IRAS studies were carried out at a grazing angle of ∼86° with a Mattson Galaxy 6020 FTIR spectrometer using a narrow-band, liquid-nitrogen cooled mercury cadmium telluride (MCT) detector. All of the spectra were taken with 1000 scans and the sample temperature held at 110 K, with a resolution of 4 or 8 cm^{-1} for monolayer or multilayer coverages, respectively. All spectra were ratioed against a clean surface background.

TPD measurements were made with the sample surface in line-of-sight to the QMS ionizer and using a linear heating rate of 3.5 K/s. Signals at 2, 16, 18, 27, 28, 30, 32, 46 and 61, corresponding to H_2, CH_4, H_2O, HCN, CO, NO, NO_2 and CH_3NO_2, were examined.

The Au(1 1 1) crystal could be resistively heated to 1000 K and cooled to 85 K. The surface was cleaned by cycles of Ar$^+$ ion sputtering (0.5 keV, 6×10^{-5} Torr) at 300 K for 10 min, and annealing at 1000 K for 10 min in UHV. This procedure resulted in a clean Au(1 1 1) surface which showed the ($\sqrt{3} \times 22$) reconstruction [6] in LEED.

CH_3NO_2 (99+%, Aldrich) was degassed by several freeze–pump cycles before dosing onto Au(1 1 1) at 108–110 K via a leak valve connected to a directed beam gas doser.

CH_3NO_2 coverages are referenced to $\Theta = 1$ for the saturation monolayer (ML) of chemisorbed CH_3NO_2 on Au(1 1 1). The CH_3NO_2 does required to obtain this coverage was determined by TPD.

3. Results

Thermal desorption spectra of CH_3NO_2 following exposures of CH_3NO_2 on Au(1 1 1) at 110 K are shown in Fig. 1. These spectra are fully
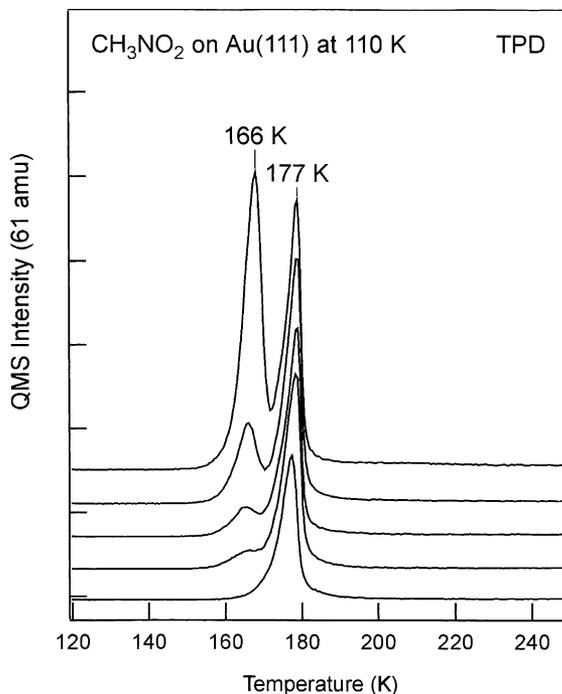

Fig. 1. CH_3NO_2 TPD spectra after CH_3NO_2 exposures on Au(1 1 1) at 110 K.

consistent with those reported previously [4]. Nitromethane reversibly adsorbs on the Au(1 1 1) surface at 110 K, and desorbs without any decomposition in two TPD peaks at 177 and 166 K from the chemisorbed monolayer and physisorbed multilayer states, respectively. Desorption activation energies E_d for these monolayer and multilayer states are estimated to be 10.5 and 9.5 kcal/mol, respectively, using Redhead analysis and assuming a prefactor of 10^{13} s^{-1} and first order kinetics for the monolayer and zero order kinetics for the multilayer.

Fig. 2 shows IRAS spectra of CH_3NO_2 on Au(1 1 1) at 110 K for different coverages. Assignments for all of the molecular vibrations are given in Table 1. These are made by comparing with the liquid and solid-phase IR spectra [7] and the IR spectra of two organometallic complexes involving nitromethane ligands [8,9]. We also show in Table 1 our previous HREELS data for CH_3NO_2 adsorbed on Au(1 1 1) [4]. Overall, there is good agreement between the previous HREELS
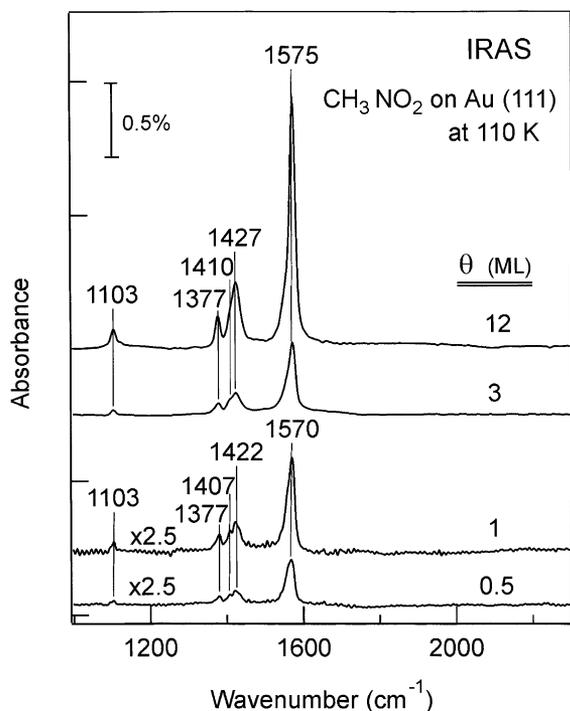

Fig. 2. IRAS spectra of CH_3NO_2 adlayers on Au(1 1 1) at 110 K.

Table 1
Vibrational frequencies (cm^{-1}) for CH_3NO_2 [a]

Mode assignment	CH₃NO₂ IR liquid [7]	IR solid [7]	[TiCl₄CH₃NO₂]₂ monodentate coordination IR [22]	TiCl₄CH₃NO₂ bidentate coordination IR [23]	CH₃NO₂/Au(1 1 1) Multilayer HREELS [4]	Multilayer IR (this work)	Monolayer HREELS [4]	Monolayer IR (this work)
ν_{as}(C–H)	3040	3072,3037	–	–	3070	–	3050	–
ν_s(C–H)	2946	2962,2948	–	–	2950	–	2915	–
ν_{as}(NO₂)	1558	1561	1553,1520	1570,1562	1555	1575	1555	1570
δ_{as}(CH₃)	1423	1438,1426	1412	–	1415	1427	1420	1422
δ_s(CH₃)	1402	1409,1405	1370	1410	–	1410	–	1407
ν_s(NO₂)	1378	1374,1373	1405,1350	1378	–	1377	–	1377
r(CH₃)	1096	1104,1102	1100	1100	1120	1103	1110	1103
ν(C–N)	916	919,913	880	900	915	–	910	–
δ_s(NO₂)	654	662,660	650	655	660	–	640	–
r(NO₂)	479	482	–	–	475	–	480	–

[a] ν: stretching; δ: bending; r: rocking.

data and our new IR data for adsorbed CH_3NO_2. In the multilayer IRAS spectra, all of the peaks at 1575, 1427, 1410, 1377, and 1103 cm^{-1} can be assigned to nitromethane vibrational modes as follows: $v_{as}(NO_2)$, $\delta_{as}(CH_3)$, $\delta_s(CH_3)$, $v_s(NO_2)$ and $\gamma(CH_3)$, respectively. The peaks in the monolayer ($\Theta = 1$) and submonolayer ($\Theta = 0.5$) spectra at 1570, 1422, 1407, 1377, and 1103 cm^{-1} are assigned to the same CH_3NO_2 modes, respectively. No peak shifts more than 5 cm^{-1} compared to the multilayer spectra, indicating that CH_3NO_2 is only weakly perturbed by coordination to the Au(1 1 1) surface.

Also, the relative intensities of the IRAS peaks were not changed substantially as the coverage increased from submonolayer to multilayers. For example, the $v_{as}(NO_2)/v_s(NO_2)$ intensity ratio for the four spectra in Fig. 2 was 6.5, 5.1, 5.5, and 7.2, respectively, for increasing coverage. This implies that the orientation of the molecular plane of nitromethane in the physisorbed multilayer film is similar to that in the monolayer. Either the adsorbed nitromethane monolayer forms a template for growth of an oriented multilayer film or similar forces (e.g., dipole–dipole [10]) that organize the multilayer play an important role in the structure of the monolayer.

IRAS warm-up spectra for a physisorbed multilayer film of CH_3NO_2 were obtained, but are not shown. These spectra show no evidence for the formation of the adsorbed isomer methyl nitrite or any adsorbed decomposition products. No significant changes in the peak positions or the $v_{as}(NO_2)/v_s(NO_2)$ intensity ratios occurred. Hence, the Au(1 1 1) surface does not sufficiently activate adsorbed or condensed CH_3NO_2 films for dissociation or isomerization (to methyl nitrite) to occur under UHV conditions. The activation energies for these two reaction pathways are higher than 10.5 kcal/mol.

Fig. 3 compares the IRAS spectra for a monolayer of each of three NO_2-containing species adsorbed on Au(1 1 1): N_2O_3, NO_2 [3] and CH_3NO_2. For N_2O_3, three peaks at 1898, 1273 and 1184 cm^{-1} are assigned to the $v(NO)$, $v_{as}(NO_2)$ and $v_s(NO_2)$ modes, respectively. Chemisorbed NO_2, in contrast, only shows one peak at 1178 cm^{-1} from the $v_s(NO_2)$ mode (small peaks at 1273
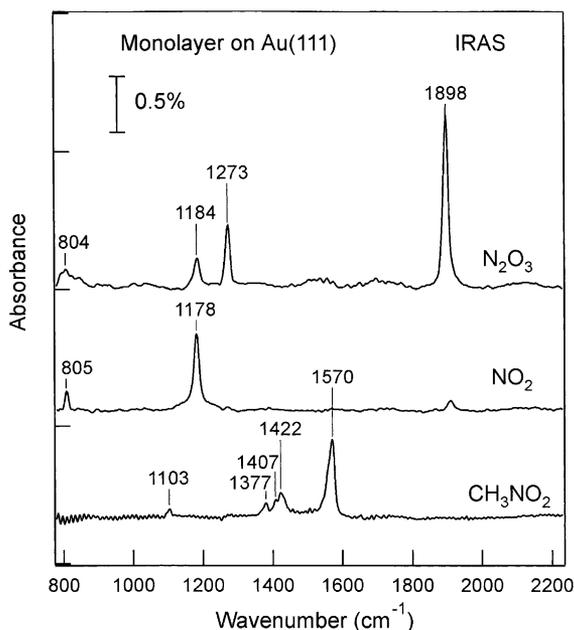

Fig. 3. IRAS spectra of monolayers formed on Au(1 1 1) of (top) monodentate N_2O_3 at 86 K, (middle) bidentate NO_2 at 86 K, and (bottom) CH_3NO_2 at 110 K.

and 1900 cm^{-1} are caused by coadsorption of a small amount of contaminant N_2O_3). Clearly both $v_{as}(NO_2)$ and $v_s(NO_2)$ modes show up in the IRAS spectra of N_2O_3 and CH_3NO_2. This distinct difference from chelating NO_2 along with the surface dipole selection rule will be used below to determine the CH_3NO_2 adsorption geometry and furthermore indicate monodentate bonding to the surface, as shown in Scheme 1.

4. Discussion

The CH_3NO_2 molecules in the gas phase effectively exhibits C_{2v} symmetry because the rotational barrier of the CH_3 group is only 6 cal/mol [7]. Information on the adsorption geometry of CH_3NO_2 at a metal surface can be obtained from a comparison of IR intensities of gas and liquid phase CH_3NO_2 with those of adsorbed CH_3NO_2. In IRAS, a significant change in relative band intensities accompanying adsorption is usually indicative of a preferred orientation for the adsorbate

C_{2v}, bidentate　　　　　　C_S, monodentate　　　　　　C_S, monodentate

Au(1 1 1)　　　　　　Au(1 1 1)　　　　　　Au(1 1 1)
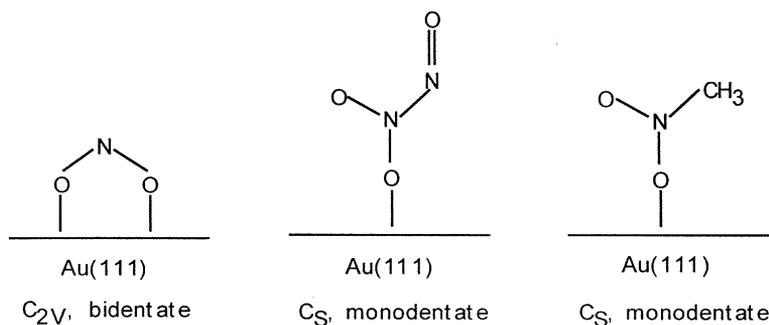
Scheme 1.

because the underlying gold surface imposes a "metal surface selection rule" [11]. This rule states that only vibrations with a dipole moment change perpendicular to the surface can be detected because of the screening effect of the metal valence electrons. Furthermore, based on the known coordination chemistry of CH_3NO_2 and previous surface science studies [10,12,13] bonding to the metal surface most likely involves the oxygen atoms(s). The issue here is whether one or both of the oxygen atoms are utilized. CH_3NO_2 can be either a monodentate ($\eta^1(O)$) or a bidentate ($\eta^2(O)$) ligand in inorganic complexes [8,14,15]. However, because nitromethane is a weak ligand, there is no correlation between the bonding mode and the splitting between the $v_{as}(NO_2)$ and $v_s(NO_2)$ modes, in contrast to the situation for nitrite (NO_2^-) ligands.

The strongest vibrational peaks in the IRAS spectrum of CH_3NO_2 are due to the vibrational modes of the NO_2 group, $v_{as}(NO_2)$ and $v_s(NO_2)$. The dynamic dipoles of these two modes are perpendicular to each other like those in NO_2 [2,3], N_2O_3 [3] and N_2O_4 [3,16]. IR spectra of CH_3NO_2 and CD_3NO_2 in annealed polycrystalline films at 78 K showed an intensity (peak height) ratio for $v_{as}(NO_2)/v_s(NO_2)$ of about 1.1–1.4 [17]. This is about the same ratio as in the gas phase IR spectra [18]. However, in the IRAS spectra of the CH_3NO_2 monolayer shown in Figs. 2 and 3, the ratio $v_{as}(NO_2)/v_s(NO_2)$ is 5–8 and this ratio does not change much for submonolayer or multilayer coverages. This means that adsorbed CH_3NO_2 is oriented and some aspects of the orientation of

CH_3NO_2 do not change substantially over this range of coverages.

Seven possible bonding geometries of CH_3NO_2 adsorbed on Au(1 1 1) were discussed previously [4]. Here we just consider two of the most plausible adsorption geometries for CH_3NO_2 i.e., either monodentate and bidentate coordination for a species adsorbed upright with respect to the surface. Only adsorption geometries with the C–N bond strongly tilted from the surface normal can explain the intensities in the IRAS spectra. Furthermore, this tilt angle is so large that one should reasonably consider that CH_3NO_2 must be bonded to the surface in a monodentate coordination, as shown in Scheme 1. If CH_3NO_2 was bonded in an O,O'-bidentate geometry with C_{2v} symmetry, the intensity of the $v_s(NO_2)$ mode would be enhanced while the $v_{as}(NO_2)$ mode would not be seen because of the surface selection rule. Tilting the molecular plane away from the normal would reduce the symmetry to C_s, allowing the $v_{as}(NO_2)$ mode to be "dipole allowed", but the $v_{as}(NO_2)$ mode would still be heavily screened for small tilt angles and we would expect a much smaller $v_{as}(NO_2)/v_s(NO_2)$ ratio. For example, a tilted $HCOO^-$ species adsorbed on Pt(1 1 0) has been identified in this manner [19].

Further support for our assignment of the orientation of adsorbed CH_3NO_2 is gained by comparisons to spectra shown in Fig. 3 of an adsorbed monolayer of N_2O_3 (ON–NO_2) on Au(1 1 1). The orientation of this species was determined previously to be an upright configuration with C_s symmetry with monodentate coordination using

one oxygen atom [3]. Similar to the IRAS spectrum of adsorbed CH_3NO_2, the IRAS spectrum of adsorbed N_2O_3 has both $v_{as}(NO_2)$ and $v_s(NO_2)$ peaks, with a larger $v_{as}(NO_2)$ peak than that of $v_s(NO_2)$. Also, a monodentate N_2O_4 (O_2N–NO_2) species has been identified near monolayer coverages on oxygen-covered Au(1 1 1) [20] by observation using HREELS of both $v_s(NO_2)$ and $v_{as}(NO_2)$ peaks. On graphite, where N_2O_4 [21] was found to be molecularly adsorbed on the surface with a bidentate geometry at 90 K, HREELS spectra show a strong $v_s(NO_2)$ peak and no $v_{as}(NO_2)$ peak due to the surface selection rule. On gold foil, changes in the orientation of N_2O_4 [16] in physisorbed multilayers with surface temperature were characterized by the $v_{as}(NO_2)/v_{as}(NO_2)$ ratio in a manner consistent with our description above.

Some additional information on bonding that supports the above assignments comes from comparisons to the TPD data for NO_2 and N_2O_3. The low CH_3NO_2 desorption temperature of 177 K and concomitant small value of E_d of 10.5 kcal/mol indicates that the bonding interaction between CH_3NO_2 and Au(1 1 1) is quite weak (the value for E_d is equal to the adsorption energy because weak molecular adsorption is not activated typically). Chelating NO_2 on the Au(1 1 1) surface has an adsorption energy of 14 kcal/mol [3], while monodentate N_2O_4 adsorbed on oxygen-precovered Au(1 1 1) has an adsorption energy of 10 kcal/mol [20]. Furthermore, monodentate NO_2 coadsorbed with N_2O_3 and N_2O_4 on Au(1 1 1) also has an adsorption energy of 11 kcal/mol [20]. Thus, the assignment of monodentate coordination for CH_3NO_2 adsorbed on Au(1 1 1) is consistent with the adsorption energies for these other related species. Because the oxygen lone pair electrons are responsible for dative bonding to Au, we would not expect the adsorption energy to change much due to the presence of the CH_3 group in CH_3NO_2 compared to these other adsorbates, and this is apparently the case.

5. Conclusions

CH_3NO_2 adsorbs molecularly on Au(1 1 1) very weakly with an adsorption energy of 10.5 kcal/mol. Analysis of the vibrational spectra from IRAS shows that CH_3NO_2 is bonded upright on the Au(1 1 1) surface with the C–N bond strongly tilted away from the surface normal. Furthermore, the large tilt angle and the adsorption bond energy is consistent with monodentate coordination of CH_3NO_2 on Au(1 1 1). The Au(1 1 1) surface does not sufficiently activate CH_3NO_2 for isomerization or dissociation to occur under UHV conditions, and thus activation energies for either of these processes on Au(1 1 1) exceed 10.5 kcal/mol.

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