

Photon-Driven Chemistry in Coadsorbed N₂O and CO on Pt(111)

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The ultraviolet photon-driven chemistry of coadsorbed nitrous oxide and carbon monoxide on Pt(111) at 47 K has been investigated by X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and temperature-programmed desorption. Evidence is presented for the formation of CO₂ from photoexcited N₂O reacting with CO. The results depend on the order of adsorption. When N₂O is adsorbed on a monolayer of CO at 47 K, the photon-driven production of CO₂ is not detectable. For dosing in the opposite order, reaction induced by photons is easily detected and, when CO is dosed on a monolayer of N₂O at 47 K, about 80% of the N₂O is displaced into the second layer.

1. Introduction

Although the photochemistry of metal-adsorbate systems is a relatively new subject, a number of studies have recently demonstrated that photodesorption, photodissociation, and photoinduced reactions between coadsorbed species do occur on metal surfaces.¹⁻³ Substrate-mediated quenching of the electronic excitation of adsorbates is, in many cases, not efficient enough to prevent these reactive processes. Much effort is now being given to the elucidation of the underlying mechanisms and, particularly, distinctions between different excitation paths. From this point of view, knowledge of the effects of coadsorbates is of great interest. Further, photon-driven reactions between coadsorbed species promise novel means of preparing interesting surface species and affecting thermodynamically difficult reactions. Depending on the nature of the coadsorbed species and on the mechanism of the surface photochemistry, the adspecies can decrease or increase the photochemical rate or can even change the photochemical path.⁴⁻¹²

In very interesting work, Ho and co-workers have studied the coadsorption of CO,¹³ H₂,¹⁴ and NO¹⁵ with peroxo-type oxygen species on Pt(111). The coadsorbates were continuously irradiated with a 150-W Xe lamp at a substrate temperature below 100 K. Upon irradiation of ¹³C¹⁸O + ¹⁸O₂, they found isotopically labeled CO₂ formation. After irradiation of coadsorbed H₂ and ¹⁸O₂, they found HREELS evidence for formation of OH and H₂¹⁸O. The results were explained by a reaction of hot oxygen atoms, produced by photodissociated peroxo species, with CO or H(a).

In our previous paper,¹⁶ we have reported the photochemistry of N₂O alone on Pt(111). Upon irradiation with photons of energy exceeding 4.35 eV at 50 K, adsorbed N₂O undergoes both desorption and dissociation with cross sections between 10⁻¹⁹ and 10⁻²⁰ cm². The data are adequately described with a model involving subvacuum hot electrons that are formed by photon absorption in the substrate, are transported to the surface with significant inelastic scattering, and are resonantly attach, transiently, to the adsorbed N₂O and thereby drive the observed chemistry. Building on this work and that of Ho and co-workers,² we were motivated to establish the effects of a coadsorbate, CO, which, by comparison with N₂O, is strongly held, and to search for a photon-driven reaction between these two coadsorbed species.

2. Experimental Section

A standard turbo-pumped ultrahigh vacuum (2.5 × 10⁻¹⁰ Torr) chamber, equipped with XPS, UPS, and TPD capabilities, was used.^{9,16} The Pt(111) sample could be cooled to 47 K by a closed-cycle He cryostat and heated resistively to 1400 K at a controlled rate by a dc power supply and temperature-ramp controller. A heating rate of 4.3 K/s was used for TPD. XP spectra were taken with a hemispherical electron energy analyzer (40-eV pass energy and 0.1-eV step size) and a 300-W Mg Kα source (1253.6 eV). Work function changes were measured by

monitoring the shift of the secondary onset in He I UPS.

The Pt(111) sample was cleaned by Ne⁺ ion sputtering, oxidation, and high-temperature vacuum annealing. The cleanliness of the sample was checked by XPS. N₂O (>99% purity) was used without further purification. In order to discriminate against background CO, ¹³CO (MSD Isotopes; isotopic purity, 99 atom % ¹³C) was used in the coadsorption experiments. The gases were dosed through a 2-μm pinhole doser, the head of which was brought to within 2 mm of the crystal surface by using a linear motion device. This procedure minimizes adsorption on, and desorption from, surfaces other than the front face of the Pt(111) substrate and lends itself to excellent TPD spectra.¹⁷

A 100-W high-pressure Hg-arc lamp was used to irradiate the surface. The light was filtered through a water cell to remove infrared contributions but was, otherwise, the full arc, i.e., broad-ranged emission between 230 and 1000 nm. The power flux to the sample was 100 mW/cm² and the light was incident at 45° off the surface normal. Under these illumination conditions the bulk temperature of the sample rose 5 K.

3. Results and Discussion

N₂O and ¹³CO were examined separately and coadsorbed, with and without UV light, at 47 K. When the adsorption temperature of CO is higher than 60 K, it desorbs between 380 and 580 K, with a peak near 450 K, which shifts slightly to lower temperature with increasing exposure. There is also a small hump around 550 K. These spectra agree with those published by other authors and the saturation coverage corresponds to a fractional coverage of 0.68 molecules of CO per surface Pt atom.¹⁸⁻²² We define this as 1 ML of CO.

On the other hand, if the adsorption temperature is 47 K, a low-temperature desorption feature starts to develop as soon as the coverage in the high-temperature state exceeds the 0.5 ML

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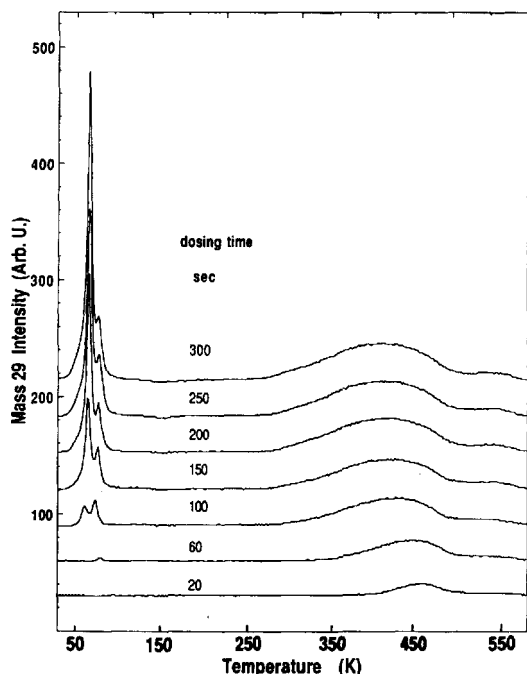


Figure 1. TPD spectra for various CO coverages on clean Pt(111). Adsorption temperature was 47 K.

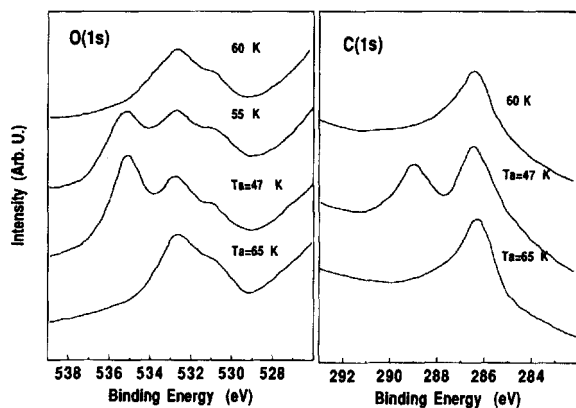


Figure 2. O(1s) and C(1s) XPS of adsorbed CO on Pt(111) at 65 and 47 K.

relative coverage (i.e., half its saturation value). This low-temperature feature splits into two desorption peaks with increasing exposure. The peak temperatures, 59 and 54 K, do not vary with the exposure (Figure 1). The intensity in the low-temperature region (both 54 and 59 K) increases linearly at first but then slows (presumably approaching saturation) for exposures significantly larger than required to saturate the high-temperature desorption state. We assign the high-temperature state to normal chemisorbed CO, with compression features, and the low-temperature peaks to second-layer physisorbed CO. The splitting of this feature might be explained by different orientations of physisorbed molecules or by clusters of CO.

Figure 2 shows the O(1s) and C(1s) XPS spectra of adsorbed CO for equal doses at 60 and 47 K. This exposure exceeds the saturation requirement for the chemisorbed state. In harmony with literature data, the binding energies of chemisorbed CO appear at 532.7 eV with a shoulder at around 531.0 eV for O(1s) and at 286.5 eV for C(1s). The two O(1s) features reflect the presence of on-top and bridge bonded species.^{23,24} When the adsorption was carried out at 47 K, in addition to the peaks originating from the chemisorbed state, new peaks appeared at 535.0 and 289.1 eV for O(1s) and C(1s), respectively. When this surface was warmed in a stepwise manner, the intensities of the

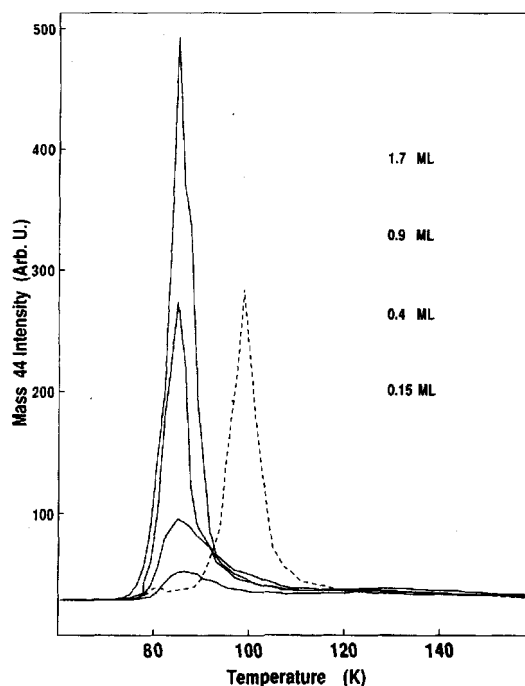


Figure 3. TPD spectra for various N₂O coverages from CO-saturated Pt(111). Dashed curve represent a TPD spectra for 1 ML of coverage from a clean surface.

high binding energy peaks, in harmony with the TPD results, disappeared around 60 K with no increase in the intensity associated with the chemisorbed state. These XPS results are consistent with the assignment of the 54 and 59 K TPD peaks to physisorbed CO.

N₂O adsorbs molecularly at 47 K. Desorption occurs, without decomposition, in two peaks, at 85 and 97 K, which have been assigned to multilayer and monolayer, respectively.¹⁶ The maximum exposure that gave no 85 K peak was used to define 1 ML coverage. The total TPD area grows linearly from submonolayer through multilayer. The low TPD peak temperatures underscore the very weak bonding of N₂O to Pt(111). In this context, it is important to note that the chemisorption energy of CO is much higher than that of N₂O. This will be of significance in the coadsorption experiments described below. Comparing the O(1s) XPS peak intensities obtained after CO and N₂O adsorption at saturation monolayer coverages and using $9.6 \times 10^{14} \text{ cm}^{-2}$ as the chemisorbed monolayer CO coverage on Pt(111),²⁵ we calculate the surface concentration of chemisorbed N₂O to be $(7.0 \pm 0.5) \times 10^{14} \text{ cm}^{-2}$.

3.1. CO Precovered Pt(111). Turning now to coadsorption, Figure 3 shows the desorption of N₂O as a function of N₂O exposure, for 1 ML of CO dosed first. For comparison, desorption of 1 ML N₂O, with no CO, is also shown. Not surprisingly, in the presence of 1 ML of CO, N₂O desorbs with a peak near 85 K, which corresponds to its normal multilayer desorption temperature.¹⁶ Comparing peak areas as a function of exposure shows that N₂O adsorbs with the same sticking coefficient in the presence and the absence of CO. These results show that saturation coverages of chemisorbed CO and N₂O both force additional N₂O into a very weakly held physisorbed multilayer state.

UPS measurements confirm this. Figure 4 presents UPS spectra after 1 ML of N₂O adsorption on clean and 1 ML of CO precovered surfaces. In the latter case, the UPS spectrum of the adsorbed CO was subtracted from that of the coadsorbed CO and N₂O. The UPS peaks, characteristic for 2π , 7σ , 1π , and 4σ molecular levels of N₂O, are all at higher binding energies by 0.4 eV, in the presence of adsorbed CO. In the absence of CO, orbitals associated with the second layer of N₂O are also shifted to higher binding energy, but the shift in the presence of CO is less pro-

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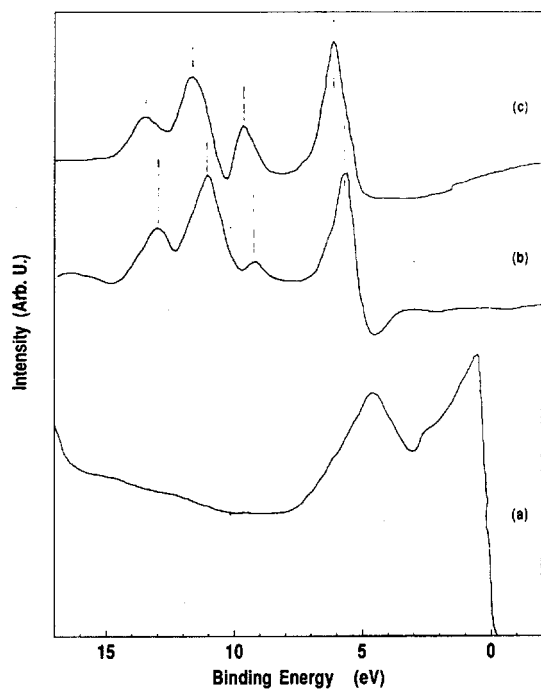


Figure 4. UPS difference spectra of N_2O adsorbed on a clean surface (b) and on CO-covered Pt(111) (c). The spectrum of clean Pt(111) is shown (a).

nounced. Greater final-state screening of N_2O on CO than that of N_2O can itself could account for this. For example, second-layer physisorbed N_2O on CO might reside slightly closer to the metal than N_2O on chemisorbed N_2O . In both cases, as expected,²⁶ the vacuum level is a more appropriate reference for the orbital energies of the second layer of N_2O , whereas the Fermi level is the appropriate reference for the chemisorbed N_2O .

We also measured work function changes for N_2O dosed alone and after CO. With no CO, dosing 1 ML of N_2O lowered the work function by 0.6 eV, while the same dose on 1 ML of CO caused only a slight (0.1 eV) work function drop. With respect to clean Pt(111), adding 1 ML of CO lowered the work function by 0.19 eV; then, adding 1 ML of N_2O (0.1-eV drop) gave a total work function lowering of 0.29 eV.

The photochemistry in these coadsorbed systems is very interesting and can be compared with our previous work.¹⁶ As was pointed out there,¹⁶ N_2O alone, on clean Pt(111), undergoes dissociation and desorption during irradiation with photons having energies exceeding 4.35 eV. Photon-driven dissociation was evident from the postirradiation TPD of N_2 ($T_p = 62$ and 110 K) and the growth, with irradiation time, of O(1s) and N(1s) XPS peaks characteristic of atomic oxygen and molecular nitrogen. Desorption during irradiation was evident in the loss of XPS and UPS intensities and of N_2O TPD peak intensity.

Turning to the photochemistry of coadsorbed layers where 1 ML of CO was dosed first, Figure 5 shows the N_2O TPD spectra after different irradiation times. The amount of N_2O desorbed decreases, but very slowly, with increasing irradiation time; there is no change of its desorption temperature; and, at most, only traces of molecular N_2 desorbed. Possible reaction products, in particular CO_2 , were also monitored but not detected. The quantity of CO desorbed was unchanged.

XPS was also used to examine the effects of irradiation on this coadsorption system. Before photolysis, Figure 5 shows a very broad O(1s) feature corresponding to the superposition of the 533.9 and 532.7 eV O(1s) peaks due to N_2O and CO, respectively. After 10 min of irradiation, only the intensity of the N_2O XPS peak decreased, in harmony with the TPD results. There was no indication of a peak developing around 529.7 eV due to atomic oxygen, a peak easily detected when N_2O alone is irradiated.¹⁶

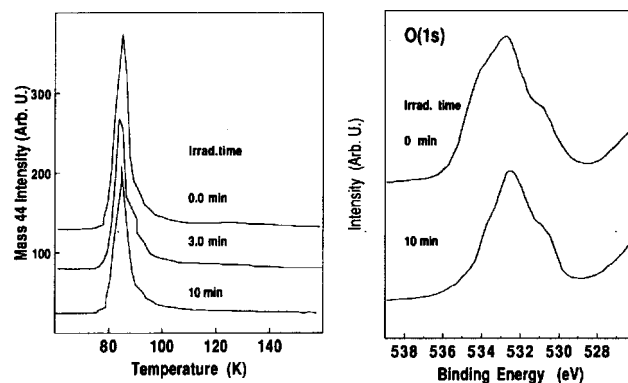


Figure 5. TPD spectra for 1 ML of N_2O adsorbed on CO-saturated Pt(111) as a function of increasing irradiation time (left panel). O(1s) XPS spectra before and after irradiation (right panel).

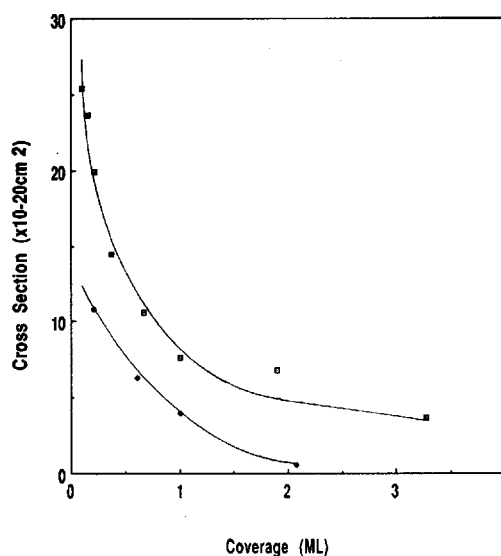


Figure 6. Effective cross section for photon-driven total loss (i.e., desorption and dissociation) of N_2O on clean (upper curve) and on CO-covered (bottom curve) Pt(111) at 50 K.

Time-dependent loss of the parent molecule, as determined by postirradiation TPD, was used as a quantitative measure of the photon-driven rate. Figure 6 shows the cross sections, calculated from the loss of parent molecules as a function of initial N_2O coverage. Results with and without CO coadsorption are shown. In the presence of preadsorbed CO, the cross section for loss of N_2O is significantly lower. It is interesting to note that shifting the upper curve to the left by 1 ML brings the two curves into near coincidence. This suggests that the photon-driven desorption cross section of physisorbed N_2O is about the same from either chemisorbed CO or chemisorbed N_2O .

As discussed in detail for N_2O alone,¹⁶ these results are consistent with a hot electron attachment mechanism like that proposed by Cowin and co-workers²⁷ to describe the photon-driven chemistry of alkyl halides on metals. The rapidly decaying cross section as the multilayers grow is evidence against direct excitation of the adsorbate. Because the work function of the coadsorbed system, 5.5 eV, is greater than the photon energies used here, the hot electron model predicts that electrons, excited in the substrate with energies insufficient to be ejected into the vacuum, drive the observed photochemistry as follows. After their formation by photon absorption in the metal, some fraction of these electrons move toward the surface. As they move, inelastic scattering tends to lower their energy. At the adsorbate-substrate interface, they may pass over, if they have sufficient energy, or tunnel through, if they do not, a potential barrier to attach themselves to neutral N_2O forming transient N_2O^- ions. The desorption and dissociation

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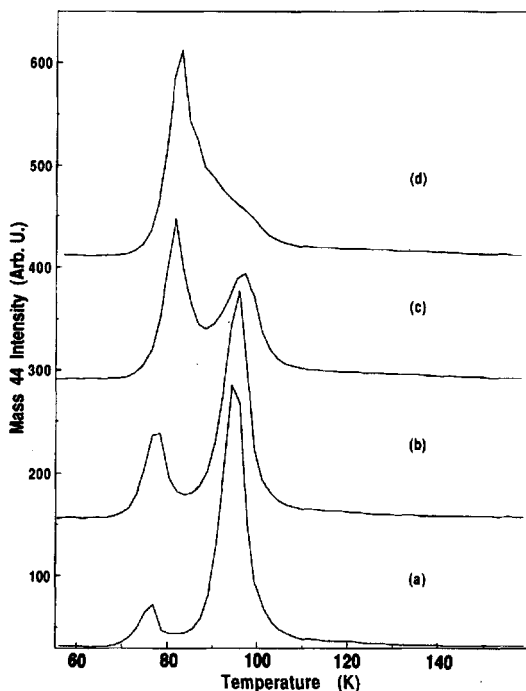


Figure 7. TPD spectra for 1 ML of N₂O at different amounts of CO postdesorbed at 47 K on Pt(111): (a) 0 ML; (b) 0.2 ML; (c) 0.5 ML; (d) 1 ML.

chemistry follows. Compared to N₂O alone on Pt(111), the presence of preadsorbed CO will significantly lengthen the distance between N₂O and Pt, making tunneling less probable. Moreover, as the N₂O-to-Pt distance increases, the positions of all the N₂O orbitals will move toward the vacuum levels, and we expect this to raise the local potential barrier that the hot electron must cross and, thereby, lower the excitation cross section.

3.2. N₂O Precovered Pt(111). We now examine the situation where 1 ML of N₂O was adsorbed first and was followed by various doses of CO. Even before illumination, the TPD spectra are revealing. Figure 7 shows that, with increasing CO exposure, the amount of N₂O desorbing at temperatures characteristic for N₂O bound to Pt drops, while that desorbing with characteristics of multilayer N₂O increases. The total amount of N₂O desorbing remains constant. It seems clear that, for thermodynamic reasons, adsorbing CO is able to restructure the adsorbed layer; because of its stronger bonding to Pt, compared to N₂O, CO is able to move to the Pt and displace some of the N₂O into the second-layer regime.

As the total amount of CO adsorbed increases to 1 ML (based on total TPD peak area), Figure 7d, about 20% of the N₂O still desorbs in the high-temperature desorption state. The main desorption characteristics of CO are not changed by N₂O preadsorption. As expected, based on the TPD of N₂O, there is a distribution of N₂O TPD between the second and the chemisorbed (first) layers.

On the basis of the growth of the CO TPD peak area with exposure, the initial sticking coefficient of CO was independent of N₂O coverage. This means that, even at 47 K where the substrate contributes little thermal energy, the displacement of N₂O by CO occurs readily. The saturation amount of chemisorbed CO, however, decreased with increasing N₂O precoverage and, for 1 ML of preadsorbed N₂O, reached only 80% of the coverage achieved in the absence of N₂O. This change was also observed in XPS as a decrease in the O(1s) peak intensity due to chemisorbed CO. Since XPS involves no thermal heating, it is clear that the displacement process is facile at 47 K. One possible explanation of the drop in chemisorbed CO is that the adsorption energy of CO drops rapidly above a certain total coverage, just as it does for high coverages of CO alone.^{22,23,28} A related

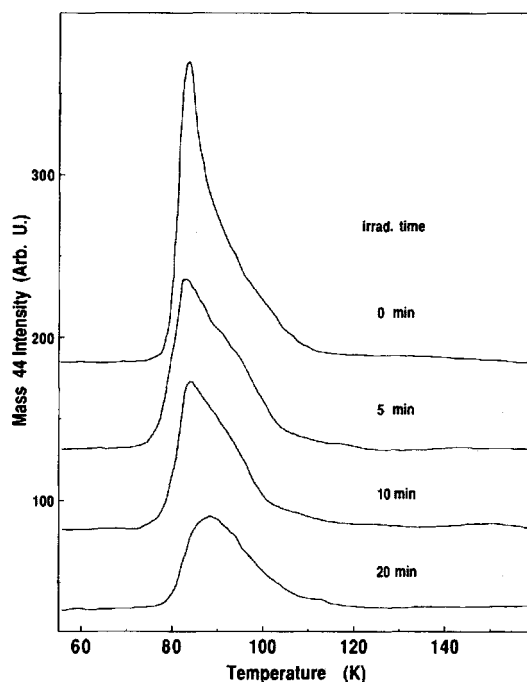


Figure 8. TPD spectra for 1 ML of N₂O as a function of irradiation time. After N₂O adsorption, the surface was saturated with CO.

possibility, but one that focuses on kinetics rather than thermodynamics, is that above a certain total coverage, additional CO must occupy sites that can only be reached by passing a significant kinetic activation barrier that involves motion of the nitrous oxide substrate system. On Pt(111), this may involve the occupation of bridge sites. HREEL spectroscopic measurements would help answer this question but are not available.

For these experiments, which involved no UV irradiation, there was no TPD evidence for the formation of reaction products; in particular, there was no N₂ or CO₂. When the coadsorbed layer was warmed to 150 K, XPS spectra were entirely attributable to adsorbed CO and there was no change in the intensities of C(1s) and that part of the O(1s) attributed to CO.

This coadsorbed system shows very interesting photochemistry, distinctively different from that found when CO was adsorbed first. As before, irradiation caused a decrease in the TPD area of parent N₂O molecules and the total cross section for loss of N₂O decreased with increasing CO exposure. For 1 ML of CO dosed after 1 ML of N₂O, the cross section [(6.5 ± 0.5) × 10⁻²⁰ cm²] lies between those obtained on CO-free and on CO-precovered surfaces.

Distinctly differing from Figure 7, Figure 8 shows, for various irradiation times, the postirradiation TPD of mass 44 for 1 ML of CO dosed on 1 ML of N₂O (Figures 7d and 8 (0 min) are identical). As expected, the N₂O TPD peak area decreases with increasing photon fluence. Analysis of the product distribution after irradiation shows that both desorption and reaction of N₂O occurred. Before discussing the reaction chemistry, we emphasize that irradiation of CO alone on Pt(111), with the full arc of the mercury lamp, causes no detectable change in either the amounts or the positions of TPD and XPS features of CO. (A more sensitive test involving CO₂ is described below.) By contrast, when CO was dosed onto N₂O-covered Pt(111) at 47 K, irradiation led to a lower CO TPD area (10% decrease for long irradiation times) and drove a surface reaction to form CO₂. Figure 9c-f displays postirradiation ¹³CO₂ desorption curves, all of which have a peak at 85 K. The amount of ¹³CO₂ formed increased with increasing irradiation time (0–20 min). After extended photolysis (20 min) a second, higher temperature ¹³O₂ desorption peak (*T_p* = 285 K) appeared.

These results clearly point to photon-driven processes that lead to carbon dioxide, a product that was not observed when CO was adsorbed first. While the use of ¹³CO helps discriminate against background reactions, we also performed the following blank

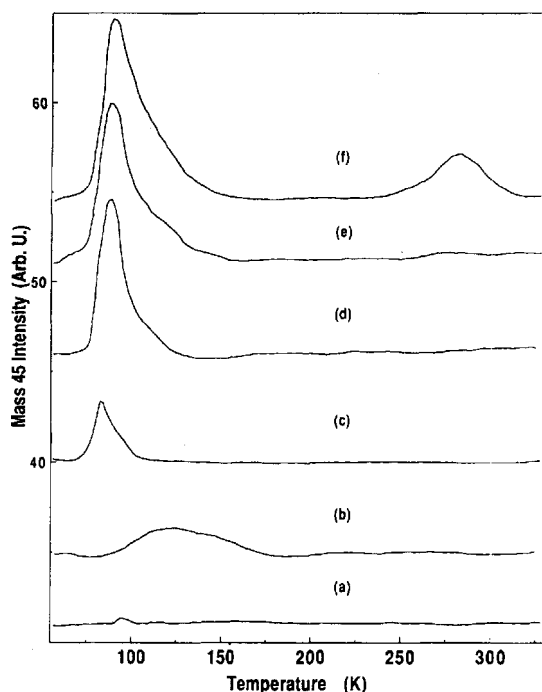


Figure 9. TPD spectra at mass 45, $^{13}\text{CO}_2$, after irradiation of the N_2O + ^{13}CO system for different irradiation times: (c) 0 min; (d) 5 min; (e) 10 min; (f) 20 min. (a) 1 ML of N_2O irradiated for 10 min without CO coadsorption. (b) 1 ML of ^{13}CO irradiated for 20 min without N_2O coadsorption.

experiments. N_2O , 1 ML was irradiated for 20 min without CO adsorption (Figure 9a); there was no TPD peak at 45 amu. In another test, 1 ML of ^{13}CO was introduced at 47 K and irradiated for 20 min. The 45 amu TPD signal, Figure 9b, between 85 and 110 K was significantly less, and appeared at different temperatures, than after N_2O -CO irradiation. When the N_2O -CO coadsorbed system was kept in the dark for 20 min at 47 K, the subsequent TPD run showed a small 45 amu peak with $T_p = 85$ K (Figure 9c). These amounts of $^{13}\text{CO}_2$ are of unknown origin but are small compared to the amounts found after photolysis.

Thus, we are confident that both the low- and high-temperature peaks in Figure 9d-f are dominated by photon-driven processes that lead to carbon dioxide. The high-temperature peak is easy to assign because it appears in a region where carbon dioxide is known to form by a thermally activated reaction between adsorbed CO and O (atomic oxygen) on Pt(111).²⁹⁻³¹ The picture emerging is that, for illumination times of 20 min, O atoms are produced in significant concentrations and these react and desorb as CO_2 in subsequent TPD, i.e., a reaction-limited process involving adsorbed O and CO. The low-temperature desorption of CO_2 is even more interesting because it is formed during irradiation at 47 K (see below).

One piece of evidence that $^{13}\text{CO}_2$ is formed during illumination is shown in Figure 10. Here, the 45-amu signal was monitored during irradiation. When the optical shutter was opened at $t = 20$ s, a sudden jump in the $^{13}\text{CO}_2$ signal was observed. With time, the signal slowly decayed and, at $t = 120$ s, the beam was blocked and the $^{13}\text{CO}_2$ signal immediately disappeared. When the shutter was reopened, the formation of $^{13}\text{CO}_2$ promptly took up where it left off. This result indicates that the $^{13}\text{CO}_2$ signal is due to a photoinduced reaction on the surface. The decay of the CO_2 desorption follows the same time dependence as the loss of N_2O (Figure 8). Figure 10 (bottom curve) shows the result with only ^{13}CO adsorbed (saturation). There is a small time-independent signal at mass 45 during irradiation. The origin of this low 45-amu signal is unknown. It was always present during illumination, even without any adsorption.

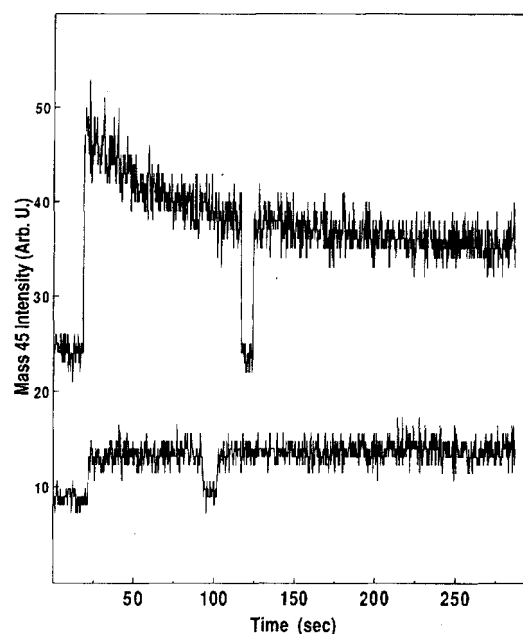


Figure 10. Isothermal scan of $^{13}\text{CO}_2$ photoproduct from photoinduced reaction of N_2O and ^{13}CO at 47 K. The bottom curve shows the $^{13}\text{CO}_2$ level for irradiation of ^{13}CO without N_2O coadsorption.

We conclude that the low-temperature desorption peak for $^{13}\text{CO}_2$, and its formation and partial desorption during irradiation, is dominated by a photoinduced reaction between N_2O and ^{13}CO at 47 K. Control experiments showed that after adsorption of CO_2 at 47 K, weakly chemisorbed CO_2 and condensed multilayer CO_2 desorb with $T_p = 95$ and 85 K, respectively, from clean Pt(111). The $^{13}\text{CO}_2$ desorbing after irradiation appears at 85 K in TPD, indicating that it is bound in the multilayer region. We take this to imply that the photochemically formed carbon dioxide is adsorbed on top of other surface species. The quantity of this kind of CO_2 is too small to be detected by XPS, i.e., the O(1s) for CO_2 at 534 eV³² and for N_2O at 533.9 eV are overlapped and the C(1s) signal is too small to distinguish it from the background. Based on the total change of the XPS intensities, a significant fraction of the $^{13}\text{CO}_2$ formed leaves the surface during irradiation. The ratio between photoinduced desorption and photoinduced reaction can be estimated from the total losses of N_2O and CO. We calculate, on the basis of 10-min irradiation results for 1 ML of CO dosed on 1 ML of N_2O , that 70% of the total loss of N_2O is through desorption and 30% through reaction to form CO_2 .

Compared to this case, the absolute amount of photoinduced formation of CO_2 was higher (by 20%) when less N_2O and CO were dosed (0.5 ML of N_2O and thereafter 0.5 ML of CO as in Figure 11a). If even less CO was dosed, the rate of carbon dioxide production decreased (Figure 11b). In these two cases, most of the N_2O is bonded to the surface as demonstrated by the 28-amu TPD (cracking fragment of N_2O) in Figure 12. This figure shows 28- and 45-amu TPD spectra before (dashed curves) and after irradiation of 0.5 ML of N_2O and 0.5 ML of CO (same scaling factor). After irradiation, a significant amount of N_2 was observed with $T_p = 62$ K. Compared with this, only a small amount of carbon dioxide was detected. This result confirms that most of the $^{13}\text{CO}_2$ formed leaves the surface during irradiation.

We now propose pathways that can account for the photon-driven carbon dioxide formation. The initial step of the photochemistry of coadsorbed N_2O and CO on Pt(111) at 47 K is attributed to substrate-excited electron attachment to nitrous oxide molecules bound directly to the Pt, a process described in previous work.¹⁶ The cross section for loss of nitrous oxide drops when a spacer layer of CO is present, because the substrate electrons tunnel into the second layer with difficulty. Reaction to form $^{13}\text{CO}_2$ is even more strongly dependent on the close proximity of

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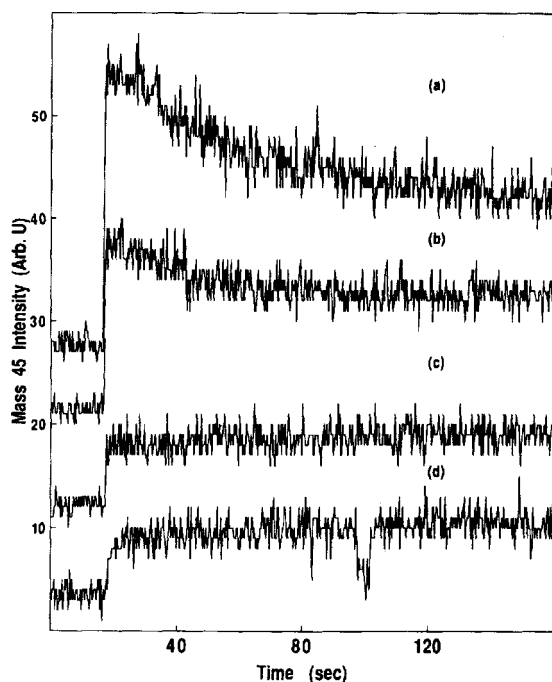


Figure 11. Isothermal scan of ¹³CO₂ from photoinduced reaction of N₂O and ¹³CO at 47 K: (a) 0.5 ML of N₂O and 0.5 ML of ¹³CO; (b) 0.5 ML of N₂O and 0.2 ML of ¹³CO; (c) 0.5 ML of N₂O and 0.0 ML of ¹³CO; (d) background level at 45 amu during illumination without any adsorbates.

N₂O to the surface; when CO is dosed first, this reaction is negligible. We ascribe the observed carbon dioxide to a concerted reaction between chemisorbed N₂O⁻, formed transiently by electron attachment, and chemisorbed CO. It is possible that dissociation of the temporary anion occurs before the reaction. This kind of hot oxygen atom reaction was proposed for the CO + O₂ and H₂ + O₂ photosystems;^{13,14} the primary step would be the formation of a hot oxygen atom (with high translation energy), which reacts with neighboring adsorbed CO. We favor the concerted reaction outlined above because, if formed, hot oxygen atoms should not only react with CO but, at least some of them, should also attach strongly and readily to the Pt surface. Our calculations indicate that O atoms do not appear until 55% of 1 ML of N₂O has been removed. If they attach to Pt, then the reaction with CO to form CO₂ requires thermal activation and would be observed around 280 K as shown in Figure 9f. We do not see this high-temperature form of carbon dioxide until much of the nitrous oxide and carbon monoxide have undergone reaction and there are numerous surface sites available. An alternative to the concerted reaction scheme described above would involve quenching of the anion to a vibrationally excited ground state, which then reacts, in concerted fashion, with neighboring CO. In any case, the newly formed CO₂ must have, or acquire, enough energy to desorb with high probability.

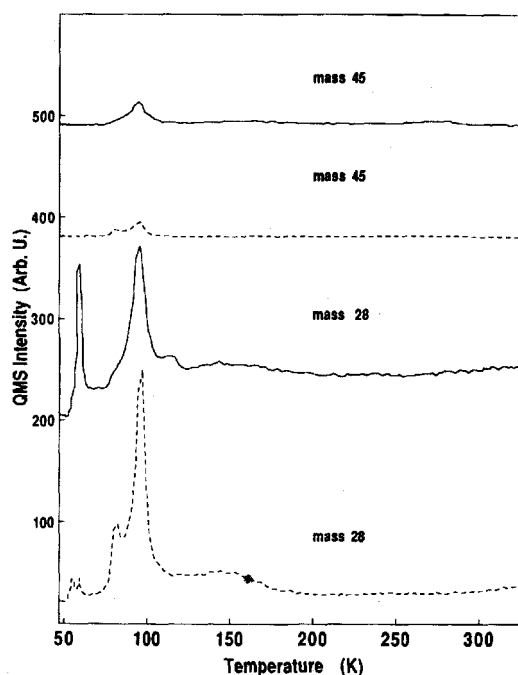


Figure 12. TPD spectra at masses 28 and 45 before (dashed curve) and after (solid curve) irradiation of 0.5 ML of N₂O and 0.5 ML of CO. Irradiation was 10 min at 47 K.

4. Summary

The work reported here can be summarized as follows:

1. Without irradiation, the TPD spectra show that postdosed CO displaces up to 0.80 ML of N₂O away from the Pt surface into a physisorbed configuration. Postdosed N₂O does not displace CO.
2. When 1 ML of N₂O is dosed first and ¹³CO is coadsorbed, UV irradiation, with an unfiltered Hg arc, leads to the production of ¹³CO₂, much of which desorbs during irradiation. That which is retained desorbs at 85 K in subsequent TPD, just as physisorbed multilayer CO₂.
3. When the order of adsorption is reversed and 1 ML of CO is dosed first, no photon-driven production of carbon dioxide is observed.
4. Regardless of the order of adsorption, there is photon-driven desorption of N₂O, but the cross section is higher for nitrous oxide bound to Pt than it is for nitrous oxide separated from Pt by a layer of CO.
5. All of the photon-driven chemistry is consistent with excitation via substrate-mediated electron attachment to chemisorbed nitrous oxide, a process described in our earlier work.¹⁶
6. The preferred pathway to the formation of CO₂ involves a concerted reaction between excited nitrous oxide, perhaps N₂O⁻, and neighboring carbon monoxide.

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