THE NO-NO$_2$ SYSTEM AT LABORATORY SURFACES

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Abstract. Experiments on formation and excitation of NO$_2$ and NO molecules at (and near) laboratory surfaces of varying degrees of characterization are reviewed. On some transition metals NO is desorbed in the B$^2\Pi$ state, from which it radiates the familiar β (B $\rightarrow$ X) bands. In contrast while an ONO intermediate is inferred from isotope interchange measurements on platinum, neither ground-state nor excited NO$_2$ has been found to be desorbed under the relatively limited number of laboratory conditions so far investigated.

Introduction

The spectral and spatial distributions recently measured viewing parallel to shuttle Orbiter's coated SiO$_2$ tiles have been suggested as being due to the pseudo-continuum radiation from NO$_2$ electronically excited at the surface [Swenson et al., 1985]. Experiment data on surface desorption of NO$_2$, and of NO*†, are summarized and briefly discussed here in the context of their relevance to spacecraft glows. Potential curves for the two species, and similar surface-catalyzed recombination information for other small molecules, are in the two accompanying papers by Kofsky and Barrett [these Proceedings].

Fluorescence of NO$_2$ using laser excitation shows that weakly absorbing features decay exponentially (that is, as single isolated states), with radiative lifetimes about 200 µsec [Donnelly and Kaufman, 1977; Cheshnovsky and Amirav, 1984]. In contrast strongly absorbing features decay nonexponentially with a range of lifetimes between 25 and 260 µsec (this is believed to result from Jahn-Teller coupling of the ^{2}B$_2$ state with the ground ^{2}A$_1$ state [Jackels and Davidson, 1976]). Thus desorption velocities close to wall-thermal would fit the few-cm outward extent seen off Orbiter's remote manipulator, and the lack of strong color gradients in the photographs of shuttle glow. As discussed in the review of infrared emission from NO$_2$ by Kofsky and Barrett [these Proceedings], the shift of Orbiter's glow spectrum roughly 1000 cm^{-1} below the yellow-green afterglow that results from the well-characterized NO + O (+ M) reaction could be due to weak bonding of the participating O atom or NO molecule to the insulating surface.

Experiments

Table 1 summarizes experiments on and observations of the NO − NO$_2$ system at laboratory (in one case, instrument) surfaces. Items [7] and [8] refer specifically to N + O recombination on polycrystalline transition metals, and [1] references earlier work on the kinetics of NO on model substrates (which has some bearing on the issue at hand).

NO$_2$ and NO were identified as artefact species in one set of data from a satellite-borne neutral mass spectrometer with Au-NiCr surfaces [Enge-

bretson and Mauersberger, 1979], with the interpretation that NO_2 had been formed by reactions of inflowing O with adsorbed NO and then was desorbed over a characteristic time of ~11 sec; this appears longer than the decay time of the glow that can be inferred from the lag in brightness off one surface as Orbiter was rotated [Banks et al., 1983]. Other reaction mechanisms might also fit these data, and insufficient information is given about the densities of neutral and charged particles within the instrument to rule out gas-phase recombination with other reactive species formed in wall interactions (as in the kinetically complex process deduced by Kenner and Ogryzlo [1984], item [4] of Table 1). Artefacts from both associative and dissociative reactions are of course common features of mass spectra of the upper atmosphere. Note that the equivalent of an energized plasma is present in the instrument; no such stream of ions and electrons (from the induced suprathermal plasma [Papadopoulos, 1984], or the natural ionosphere) was incident on the laboratory recombination surfaces in Table 1.

In contrast under the admittedly limited range of controlled and defined laboratory conditions (items [1-4] of Table 1) no NO_2 has been found to be desorbed. Perhaps more important is the observation that in none of the several flow-tube measurements of the rate coefficient of the NO + O (+ M) reaction (items [6a-e], among others) has wall-catalyzed recombination into excited states been reported as an experiment artefact requiring correction; unlike the transition metals of the experiments tabulated, and like most of shuttle's exposed surfaces, these walls are "dirty" insulators. Isotope interchange experiments on a Pt crystal face are interpreted as showing that an ONO complex forms, but then redissociates before desorbing [Dahlgren and Hemminger, 1982].

Comments

The adsorption energy of NO on metallic surfaces has been reported to be in the range of 20-30 kcal/mol or about 1 eV, and the NO-O bond energy is 3.1 eV. In the gas phase the chemiluminescent reaction rate of NO with O increases strongly with decreasing (high) temperature [Golomb and Brown, 1975]; this indicates that there is no activation barrier that needs to be lowered by a surface interaction, and that the rate for 5-eV oxygen atoms will be very low. The relevance of the kinetic energy of the air particles impacting spacecraft surfaces is discussed in the accompanying Kofsky and Barrett presentation [these Proceedings].

At reasonably low temperatures, 300-400 K, NO desorbs from some metal surfaces; and NO adsorbs dissociatively at 300 K on silicon (111). From these results on clean model substrates we may infer that for a given material there may be only a narrow range of temperatures—if any— under which NO combines with O to produce desorbed (excited) NO_2. Different mean adsorption energies of the reaction participants on real surfaces would imply different spectrum distributions in the pseudo-continuum from NO_2. The failure of N and O to recombine to NO* on teflon at room temperature [Caubet et al., 1984] and the low recombination rate of N on teflon [Evenson and Burch, 1966] are reflected in the minimal glow off polyethylene in shuttle experiments [Mende et al., 1985], in that it suggests that these saturated polymers lack sites at which reactants can adsorb to form complexes whose fragments desorb with internal excitation (if in molecular form at all); further, these observations support the interpretation that spacecraft glow results (principally) from surface-catalyzed recombination of air species.

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TABLE 1. NO − NO$_2$ ON-SURFACE EXPERIMENTS

Ref.[†]	Conditions	Surface/Temp.	Gas Flow	Measurements
1*	High vacuum	Si 111 (7 x 7)/ 300-1300 K	Adsorption of NO	EELS, LEED, Auger. NO is adsorbed dissociatively.
2	High vacuum	Stepped Pd 111/ 160-600 K	Adsorption of NO (O$_2$)	TPD, LEED, Auger, mass spectroscopy. N$_2$, NO, N$_2$O, but no NO$_2$ desorbs; O$_2$ saturates adsorption-specific sites.
3	High vacuum coadsorption, isotope exchange	Pt 111/ 120-1000 K	Adsorption of NO$_2$, NO, ^{16}O$_2$, ^{18}O$_2$	TPD, LEED, Auger, mass spectroscopy. ONO intermediate on surface but doesn't desorb.
4	Flow tube, microwave discharge source	Nickel mesh/300 K	O onto mesh, NO (or NO$_2$) downstream or upstream	Spectrometry, photometry. O$_2$* precursor of O$_3$[†] forms on surface, but not NO$_2$*.
5	Inside Nier neutral mass spectrometer on spinning spacecraft	Gold, Nichrome 300-400 K; ionization by 25, 75 eV electrons	Ram atmosphere at 300 to 800 km altitude	Mass spectrometry. NO$_2^+$, NO$^+$, O$^+$ (N$^+$, N$_2^+$, O$_2^+$)
6a-e	NO + O recombination, ∼5 laboratories	Principally glass/300 K	NO, O (O$_2$, O$_2$*)	Spectrometry of product NO$_2$ from gas phase.
7	Flow tube, microwave discharge source	Nickel/ 300 K (No glow off teflon)	N, O onto surface	Optical spectroscopy. γ, β, δ bands of NO in gas; only β bands from surface, non-statistical T$_v$.
8	Flow tube, as [7]	Ni, Co, Ag/ 300 K	N, O onto surface	Optical spectroscopy. N$_2$ 1P, NO β bands.

[†]Identified in brackets in the list of references.
*Also references other papers on surface kinetics of NO (only).