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Recombination of 5-eV $O(^3P)$ atoms with surface-adsorbed NO: Spectra and their dependence on surface material and temperature

O. J. Orient, K. E. Martus, and A. Chutjian
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

E. Murad
Phillips Laboratory, WSSI, Hanscom Air Force Base, Bedford, Massachusetts 01731

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Recombination spectra are measured in the wavelength range 300–850 nm resulting from collisions of 5-eV $O(^3P)$ atoms with NO adsorbed on MgF_2, Ni, and Ti surfaces. The dependence of the chemiluminescence intensity on surface temperature (240–340 K) is measured, and activation energies for desorption of the physisorbed NO obtained. Activation energies as a function of wavelength for each material are also reported. It is found that, with minor variations, the recombination spectra are similar for the three surfaces, and that the emitter is very likely electronically excited NO_2. All three materials exhibit a greater tendency to emit at the lower temperatures. MgF_2 has the greatest tendency to chemiluminesce, followed by Ni then Ti. Also, the activation energies for NO desorption are similar for the surfaces, and are independent of emission wavelength. The results are interpreted as a single mechanism of removal, with increasing T, of physisorbed NO from saturated surfaces of different coverage.

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I. INTRODUCTION

The effect of temperature on the efficiency of surface-catalyzed reactions has been a long-standing subject of study. The internal states of the reactants are generally in an equilibrium distribution determined by the surface temperature. By contrast, the effects of particle translation energy on the efficiency of surface catalysis is an area only recently studied with the development of fast (hyperthermal) neutral sources. Interest has been sparked by the effects of collisions in low-earth orbit (LEO) between spacecraft surfaces and the ambient atmosphere.

Under conditions of LEO, an orbital velocity of 7.8 km/sec translates into a mean collision energy of 5.0 eV for O atoms (which comprises approximately 70% of the atmosphere), and 8.8 eV for N_2 (30% [1]). A combination of high incident energy with low surface temperature (200–280 K) has led to a number of interesting phenomena whose significance extends beyond their LEO origins. Among these are two important effects of surface erosion [2,3], and off-surface optical emission, sometimes referred to as the "shuttle glow" [4–6].

The work described herein addresses the nature of the surface-catalyzed reactions that may be responsible for the chemiluminescent shuttle glow. This glow has been attributed to emission of electronically excited NO_2^* molecules formed in the reaction of surface-adsorbed NO with incoming, fast O atoms [7]. The NO_2^* hypothesis has its genesis in early observations of high background radiation in airglow spectral measurements from rockets [8]. Laboratory work [9–12] has shown that the recombination spectrum of O+NO at thermal energies is quite complex, resembling a continuum. The laboratory measurements have supported the space data, the latter being continua within the instrumental resolution. Shuttle-borne mass spectrometric measurements have indicated that sufficient NO_2 was scattered from shuttle surfaces to account for observations, assuming that most of the observed NO_2 was in an excited state [13]. The implication of the NO_2^* hypothesis in terms of other potential emitters has also been studied [14].

In the first studies of the glow phenomenon [15] spectra were reported for the recombination of 5-eV $O(^3P)$ atoms with (separately) CO and NO, adsorbed at room temperature on an MgF_2 surface. It was clearly shown that the recombination spectra arose from bent $CO_2(\tilde{A})$ and, presumably, bent NO_2^* molecules. That work is extended here in the NO case to study the effects of materials and surface temperature on the glow spectrum and intensity. Measurements are compared with recent laboratory data and spacecraft observations.

II. EXPERIMENTAL ARRANGEMENT

The low-energy atom range of interest (1–100 eV) is a difficult region to access. Conventional "plasma-asher" sources of atomic oxygen attain energies of about 0.2 eV [16], whereas energies of several eV or greater are required for the chemiluminescence and many beam-beam reaction channels to open [15,17].

A new technique had to be developed which would not only access high O-atom energies, but also provide a narrow energy width, specific quantum state, and known beam purity [15,17]. A schematic diagram of the O-atom source that was developed is given in Fig. 1. Briefly, techniques used to produce the ground-state oxygen atoms involve the following steps carried out in a uniform, high-intensity (6 T) solenoidal magnetic field: (a)

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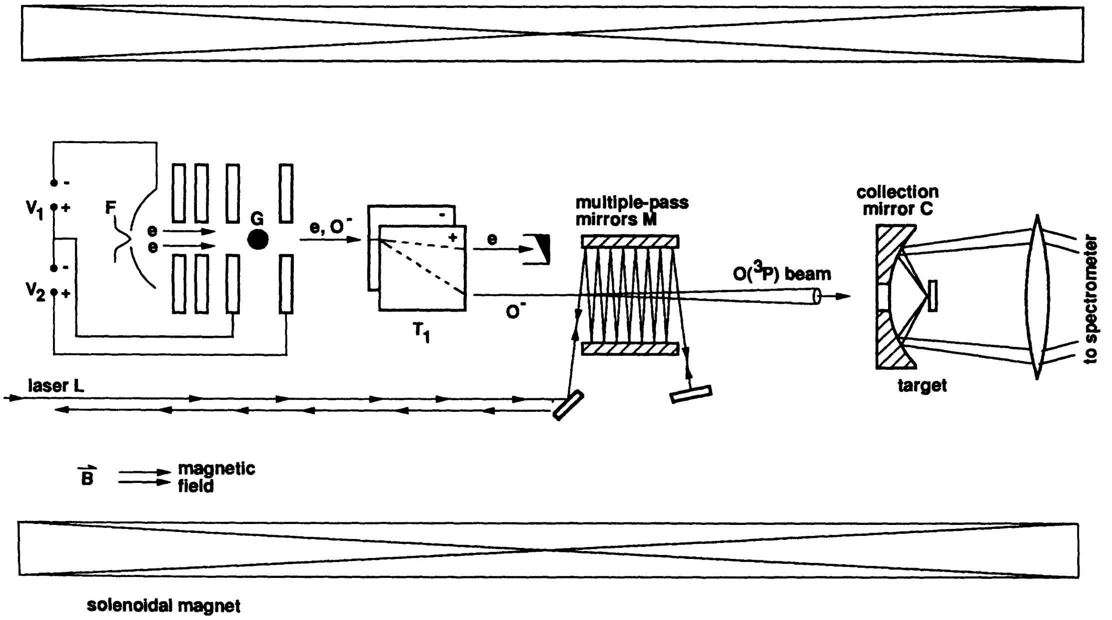

FIG. 1. Schematic diagram of the magnetically confined source used to produce ground-state atomic oxygen. See text for details.

electrons are generated from a spiral wound, 0.015-in.-diam tungsten filament (F). The magnetically confined electrons are extracted at high energy, then decelerated to a final energy of 8 eV at the gas nozzle (G); (b) NO molecules effusing from G dissociatively attach to form $O^-(^2P)$ ions. The confined ions and electrons are then accelerated to the desired final energy (5 eV, say); (c) using a trochoidal deflector (T_1) the faster electrons are separated from the slower ions, and are trapped in a Faraday cup; (d) with a 20-W argon-ion laser (L, using all visible lines) and a multiple-pass mirror assembly (M), the electron are detached from $O^-(^2P)$ to form exclusively $O(^3P)$ atoms [18]. The detachment efficiency is about 15%. Finally, the O^- and O beams are directed to the target, and the undetached O^- beam is reflected by negatively biasing the target. The 95%-transmitting tungsten mesh which covered the target surface to repel the O^- beam was shown not to contribute to the optical emission. The O-atom flux, as obtained from the decrease in O^- flux with the laser "on," is estimated to be $\sim 10^{13}$ atoms/cm^2 sec. Further details on space-charge effects, collection mirror, monochromator, and multichannel scaling techniques may be found in Refs. [15] and [17].

The materials MgF_2, Ni, and Ti were chosen as targets to illustrate possible different tendencies of insulators and conductors to glow, and for their use as spacecraft materials. Surface preparation of these materials involved only ultrasonic cleaning in a solvent bath; followed by heating under vacuum in the target holder to 100 C for 24 h prior to initiating measurements. The target region was differentially pumped with a cryopump to maintain a pressure difference of 4×10^{-4} Pa (3×10^{-6} Torr, source) and 3×10^{-5} Pa (2×10^{-7} Torr, target) during operation. This ensured that no impurities (especially NO from G) could reach the target. Base pressures were 7×10^{-6} Pa (5×10^{-8} Torr) and 7×10^{-8} Pa (5×10^{-10} Torr) at the source and target, respectively.

As in Ref. [15], a small gas jet was used to direct a continuous beam of NO onto each surface. In the present work, a regulated refrigerator using a methanol-water mixture as the heat-exchanger was used to heat or cool the target between temperatures of 240 and 340 K, with regulation to 0.1°. The target temperature was monitored with a chromel-alumel thermocouple attached to the target holder. Chemiluminescence could thus be observed both as a function of material, and as a function of material temperature.

III. CHEMILUMINESCENCE SPECTRA

The observed optical emission was shown in several ways to arise from the surface, and not from two-body, gas-phase reactions or recombinations occurring above the surface.

(a) The time constant for the decay of the emission was found to be an order of magnitude larger than the vacuum system time constant (chamber volume divided by pumping speed) [15].

(b) A separate test carried out herein of replacing the surface with a beam of NO produced no observable two-body, gas-phase emissions.

This last result is consistent with the measured rate constant for the reaction $NO+O\rightarrow NO_2$ of 4.2×10^{-18} cm^3/molecule sec reported by Becker, Groth, and Thran [19]. Under present conditions of NO and O-atom density, this would correspond to $\sim 10^3$ recombinations/cm^3 sec, an amount that would be undetected.

Chemiluminescence spectra were measured for NO adsorbed on MgF_2, Ni, and Ti surfaces bombarded with 5-

eV O(^3P) atoms. Spectra in the wavelength range 300–850 nm are shown in Fig. 2. The region between the vertical dashed lines corresponds to the region of the strong detaching-laser wavelengths. The resolution in these measurements was 10 nm [full width at half maximum (FWHM)], and the surface temperature held at $T=240$ K.

One notes that MgF_2 is the brightest emitter, followed by Ni and Ti. To explain this, we propose that in the present measurements one has saturated, at each T, all available adsorption sites with NO. This is apparent because the recombination intensity for each surface was found to be independent of NO pressure. (However, this coverage may not be unity [20]). The ordering of intensities would seem to imply that the saturated packing density or coverage of adsorbed NO on the MgF_2 surface is the highest, followed by Ni and Ti.

One also notes that the spectra lack any sharp bands, and are featureless (to within the 5% statistical uncertainty of the data) but for several broad undulations. Similar results were found in previously reported work [15]. In order to ensure that the undulations were not due to instrumental artifacts (such as the variation in grating reflectivity with λ for the double-grating monochromator used in this work), a separate measurement of the monochromator transmission was carried out. A blackbody source (quartz halogen lamp) was used, and the wavelength range scanned from 350–850 nm. A smooth continuum emission spectrum was measured, with no undulations.

At the long-wavelength end of the spectra all intensities decrease abruptly at 825–850 nm, well away from the cutoff at 900 nm of the phototube used in this work. Also, the long-wavelength intensities are slightly different than found in the previous work (Fig. 2 of Ref. [15]). The difference probably arose from a new sample of MgF_2 used in the present work that replaced the older, eroded MgF_2 sample used in the first study.

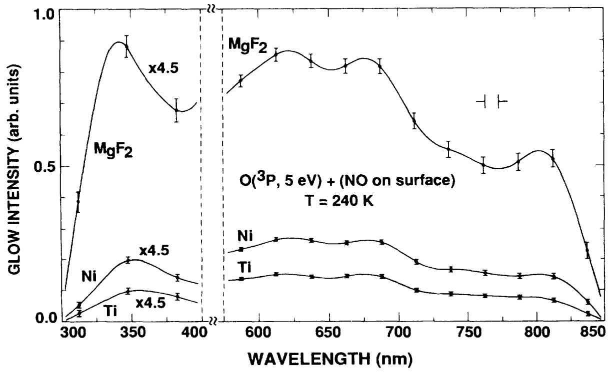

FIG. 2. Glow spectra produced in collisions of 5-eV O atoms with MgF_2, Ni, and Ti surfaces with adsorbed NO. Intensity ratios within and among the spectra may be intercompared. The surface temperature is maintained at $T=240$ K, and the spectral resolution (10 nm, FWHM) is shown. The region between the vertical dashed lines corresponds to the strong detaching-laser wavelengths.

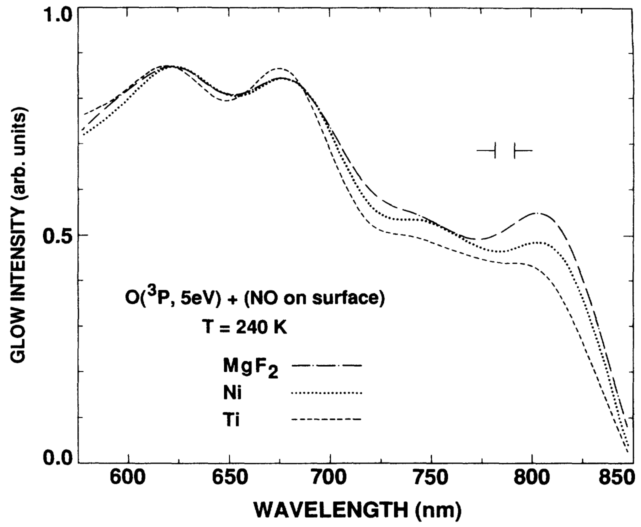

FIG. 3. Superimposed glow spectra of Fig. 2 to show changes in spectral shape for the three surfaces. All data were normalized to the MgF_2 spectrum at $\lambda=622.5$ nm for display.

To compare shapes of the three spectra we show in Fig. 3 a superposition of the spectra normalized to the MgF_2 results at $\lambda=622.5$ nm. Within statistical uncertainty the three spectra are identical in the wavelength range 575–725 nm. Some differences begin to appear in the range 725–825 nm that are slightly larger than the statistical errors in the data. These could arise through differences in the excited-state vibrational populations produced by differing geometries of adsorbed NO on the three surfaces. Further elucidation would have to await mass-spectrometric studies of the nature of the emitting species.

IV. ACTIVATION ENERGIES FOR SURFACE DESORPTION

By varying the temperature of the target surface and monitoring the recombination intensity at a particular wavelength, one can obtain an activation energy E_a for desorption of the NO precursor from the surface.

The glow intensity I relative to a reference intensity I_0 will have a dependence on temperature given by the Arrhenius relation [20]

$$I/I_0=A\exp(E_a/kT)\ , \tag{1}$$

where A is a preexponential factor, E_a is the activation energy for destruction of the adsorbed NO, presumably through desorption into vacuum, and T the absolute temperature. In the three cases studied, the recombination emission was found to decrease with increasing surface temperature. In this respect, the energy E_a does not promote a reaction (in the usual Arrhenius sense), but rather inhibits it, via a reaction channel (desorption) which removes the NO at a rate increasing with T. And hence, the exponential in Eq. (1) is a positive quantity, and the Arrhenius plots have a positive slope.

Shown in Fig. 4 are plots for the MgF_2, Ni, and Ti sur-

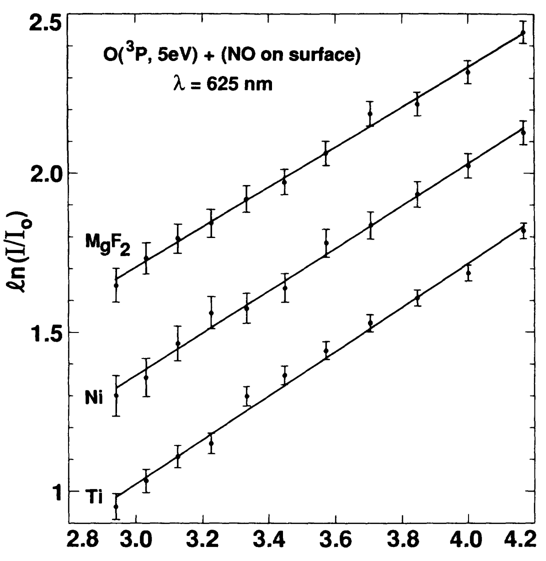

FIG. 4. Arrhenius plots of the dependence of surface-emission intensity vs surface temperature for NO adsorbed on the three materials. Ordering along the vertical axis is arbitrary. The observing wavelength is fixed at 625 nm, and the temperature variation is 240–340 K.

faces in the temperature range $T=240$–340 K, for a fixed wavelength $\lambda=625$ nm. One notes that the slope E_a/kT is very nearly the same for the three surfaces, giving a value of E_a of 0.11 or 0.12 eV. Values of E_a are listed in Table I, along with error limits at the 2σ confidence level.

This result would indicate that there is a commonality to the three surfaces studied. On the one hand, the release of NO_2^* could be taking place from surfaces having a saturated coverage of NO. The substrate is effectively "hidden" from the recombination by the physisorbed NO. On the other hand, the uncharacterized surfaces used in this work may have a common overcoating of, for example, graphitic carbon or the substrate oxide [21].

The magnitude of E_a would indicate the process taking place is destruction of a physisorbed, rather than a stronger-bonded chemisorbed, NO molecule. In its simplest form, one may visualize the adsorbed NO as either (1) a van der Waal's NO dimer, $(NO)_2$, where the pair is physisorbed to one another, and one of the pair chemisorbed to the surface; or (2) as a physisorbed monomer NO, where the attraction is through an image force exerted by polarization of the surface by the NO charge density [20,22]. The magnitude and similarity of E_a for the three surfaces support the conclusion that the bond being broken in the process of NO_2^* formation is a van der Waal's bond. The measured dissociation energy of $(NO)_2$ is 0.12 eV [23] to 0.16 eV [24], in close agreement with the E_a reported here. One notes that surface dimers have been postulated in energy-loss spectroscopy (ELS) and low-energy electron-diffraction (LEED) studies of NO adsorbed on a Pt(111) surface [25].

In addition to measuring E_a at a fixed wavelength, one may examine its dependence on emission wavelength. Any significant variation of E_a with λ would indicate that more than one species was being released from the surface. Measurements of E_a were made at over 70 wavelengths in the range 300–850 nm, and results are shown in Fig. 5. One sees clearly that, to within statistical uncertainty, there is no dependence of E_a with λ for each of the three surfaces. And hence, there is only a single species emitting throughout the spectral range.

Assuming the model of a surface covered to saturation by NO dimers, or even monomers, one may speculate as to whether off-surface emissions in other species might be detected. With the space shuttle in LEO one could expect to observe the flame bands of CO_2 by the reaction $O_{fast}+CO_{ads}$, since CO is a substantial component of the shuttle's thruster exhaust [26]. These emissions were seen in beam-surface and beam-beam collisions [17]. Moreover, CO, like NO, is a weakly polar molecule known to form dimers and clusters [27]. By contrast, one would not expect to see emissions from O_2^*, since the only route to this molecule is via recombination of O_{ads} and incoming O_{fast}.

Finally, one may examine the energy balance in this process, and calculate the threshold O-atom energy for the glow process, taking the emitting species to be electronically excited NO_2. One has the energy-balance equation given by

$$T_{\text{c.m.}}+D(\text{NO—O})=E_{\text{phot}}+T_{\text{exit}}+E_a\ , \tag{2}$$

where $T_{\text{c.m.}}$ is the center-of-mass energy of the O-atom beam, $D(\text{NO—O})$ the bond energy of NO_2 (3.11 eV), E_{phot} the maximum photon energy released (4.13 eV, or 300 nm), E_a the desorption energy (0.12 eV), and T_{exit} the kinetic energy of the NO_2^* as it leaves the surface (~ 1.5 eV [7]). Not included in the right-hand side of Eq. (2) is a term representing the loss of energy to the surface in the form of heat. From these values one calculates that the minimum required energy for the glow process to occur is $T_{\text{c.m.}} \sim 2.6$ eV. This is consistent with a value of 3–4 eV observed in the present work. The remaining difference may be due to O-atom energy lost to surface heating.

Another result of Eq. (2) follows from the fact that for

TABLE I. Summary of activation energies E_a for surface desorption of the emitting species. Errors are stated at the 98% (2σ) confidence level.

Material	MgF$_2$	Nickel	Titanium
Activation energy E_a (eV)	0.12±0.01	0.12±0.01	0.11±0.01

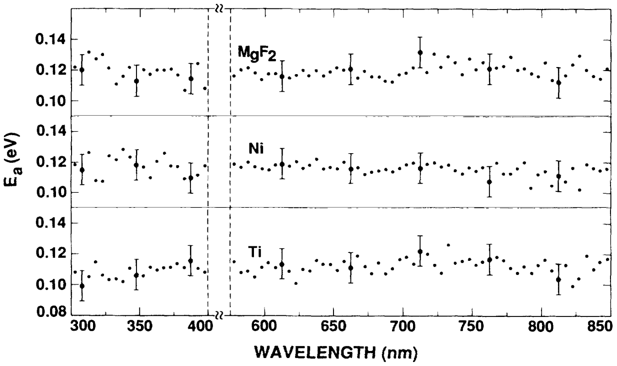

FIG. 5. Results of activation energies E_a vs emission wavelength for destruction of adsorbed NO. Each data point for the three materials is a separate Arrhenius plot. The atom energy is 5 eV.

fixed $T_{\text{c.m.}}$ the sum $E_{\text{phot}}+T_{\text{exit}}$ must be constant. And hence NO_2^* that is ejected from the surface with greater velocity (larger T_{exit}) will have an emission threshold shifted to lower energies (smaller E_{phot}). For a given NO_2^* lifetime, a threshold at lower energies will be observed in the fast-moving emitters further from the target surface. This consequence could be tested with a laboratory or shuttle-borne experiment with spatial as well as spectral resolution.

V. COMPARISONS WITH OTHER EXPERIMENTS

It is interesting to note that, of the materials tested, MgF_2 was also found to be one of the brightest emitters in exposures to ground-state, 5-eV atomic oxygen in LEO, as measured aboard shuttle mission STS 41-D [28].

One may also compare the present emission spectra for the three surfaces (Fig. 3) with a glow spectrum recently measured on shuttle emission STS 38 [29]. From the comparison given in Fig. 6 one sees reasonable agreement between the spectra at wavelengths λ less than ~640 nm. At longer wavelengths, the shuttle-observed intensity exceeds that from NO_2^* alone. Three possible explanations for this difference arise: (a) the actual shuttle surface is coated with additional materials (CO, H_2O, hydrazine, etc.) which may chemiluminesce at $\lambda > 640$ nm; (b) the surface viewed [29] was shuttle tile, which is a porous, ceramic material, quite different than the MgF_2, Ni, and Ti studied herein (the emission characteristics of NO_2^* from a tile surface could be quite different, due to a changing vibrational-electronic population of the excited state); and (c) particles other than O atoms are striking the surface. These could include fast (8.8 eV) molecular nitrogen, or O^+ and NO^+ ions. It is very likely that the emitting species partly responsible for the shuttle emissions is electronically excited NO_2 (as surmised in an earlier model [6,7]), since that emission is known to be continuous, and falls in the present spectral range [9–12]. However, a firm conclusion must await surface mass-spectrometric studies, as well as studies of the chemiluminescence spectra of other surface-adsorbed species to account for the $\lambda > 640$ nm portion of the emission.

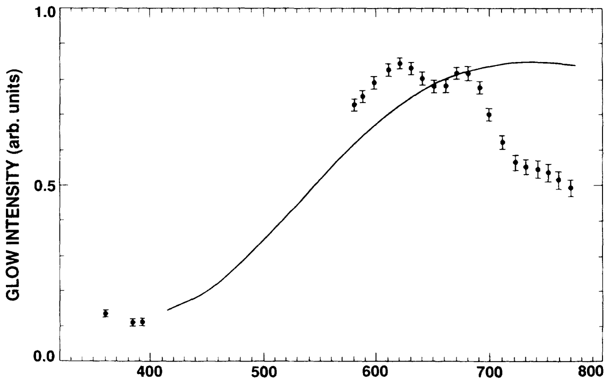

FIG. 6. Comparison of the present glow spectrum (●) with recent shuttle observations (——) [29]. Present data are for NO adsorbed on a surface at $T=240$ K. Data are normalized at $\lambda=650$ nm.

We point out that a recombination spectrum has been obtained with a very different source of O atoms [30]. The source used was pulsed, with a peak pulse density of 4×10^{13} atoms/cm^3, about 5–6 orders of magnitude greater than that of either of the present continuous source or densities present in LEO ($\sim10^8$ atoms/cm^3). This source is also known to contain metastable atoms with energies as high as 12.75 eV ($4d\ ^5D_0$ O atoms) [31]. While a comparison between the two data is not meaningful, spectral results with the pulsed source indicate a faster drop in the glow intensity at $\lambda < 620$ nm than either present or shuttle results. Relative to present results, the peak intensity is at longer wavelengths (~690 nm), followed by a slower decrease towards 780 nm.

In terms of activation energies, the only other measurement with which to compare the present results is obtained again from a LEO analysis of Swenson, Mende, and Llewellyn [32]. Estimating glow intensities and surface temperatures of various spacecraft, they derived an analogous "orbital" Arrhenius plot. Their resulting activation energy was $E_a=0.14\pm0.02$ eV, in remarkably good agreement with present results. This would again indicate that the same phenomenon was being encountered both in the laboratory and LEO.

VI. CONCLUSIONS

The results of the present measurements can be summarized as follows.

(a) The MgF_2 surface has the greatest tendency to chemiluminesce, followed by Ni and Ti. This ordering is very likely due to the fact that the packing density (saturated surface coverage) of NO on the insulating MgF_2 surface is the greatest.

(b) The chemiluminescence spectra are similar for the three surfaces, with minor variations probably due to differences in vibrational excitation of the excited electronic states.

(c) All three materials exhibit a greater tendency to glow at lower temperatures. This is again a reflection of greater packing densities of surface-adsorbed NO at the lower temperatures for each surface. As one heats the surface more NO is lost by desorption, and hence the chemiluminescence diminishes.

(d) The activation energies for NO desorption are similar for the three surfaces. This indicates that the desorption is dominated by a release of NO from a common backdrop which may be either a NO dimer or monomer physisorbed to the surface.

(e) The activation energy for each surface is independent of the emission wavelength. And hence the same species is emitting throughout the wavelength range.

(f) The present glow spectrum closely resembles that observed on the shuttle in LEO. One may conclude that the laboratory results simulate LEO results, and that the emitter is very likely NO_2^* in excited electronic-vibrational levels. The agreement in activation energies of the present data with LEO observations also confirms the fact that the same phenomenon is being measured in the two experiments.

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