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COMPOSITION, AND THE CHEMISTRY OF THE TERRESTRIAL ATMOSPHERE (Pittsburgh Univ.)

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Studies of the Airglow, the Aurora, the Ion and Neutral Composition

and the Chemistry of the Terrestrial Atmosphere

[Previously: "Helium Geocorona Rocket Experiment"]

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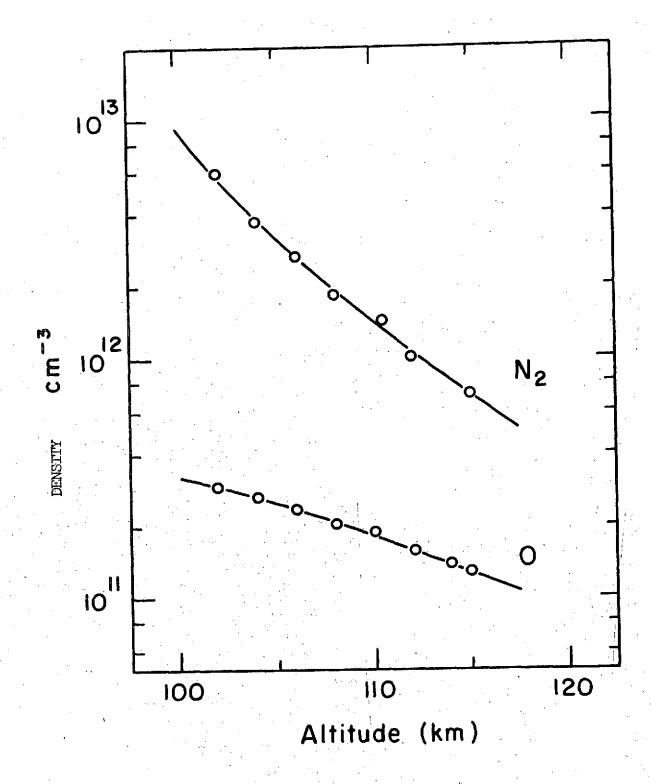
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I. A Report On

Studies of the Airglow, the Aurora, the Ion and Neutral Composition, and the Chemistry of the Terrestrial Atmosphere

A familiar proverb reminds us that "A picture is worth a thousand words!" Figure 1 succintly demonstrates this point for it shows the first altitude profile of atomic oxygen and N₂ in the mesosphere obtained by an optical mass spectrometer [OMS]. This instrument was launched on 14 August 1973 at 11:45 pm MST into the atmosphere above White Sands, N. M. on board Nike-Apache rocket 14.512 UA. This experiment was one of five conducted successfully this year by the University of Pittsburgh aeronomy group:

- (1) Javelin rocket (8.61 UA), 17 July 1973, high altitude (200 - 740 km) OMS and OI λ1304A airglow experiment, Wallops Island, Va.
- (2) Nike-Apache rocket (14.512 UA), 14 August 1973, low altitude (90 115 km) OMS experiment, White Sands, N. M.
- (3) Black Brant V vehicle (AMD-VB-35), January 1974, double-mode mass spectrometer 1304A resonance fluorescence/absorption experiment, and nitric oxide auroral studies, Fort Churchill, Manitoba.
- (4) Nike-Apache rocket (14.526 UA), 21 February 1974, double-mode mass spectrometer and multiple photometer for auroral composition and excitation studies, Fort Churchill, Manitoba.



Fîgure 1

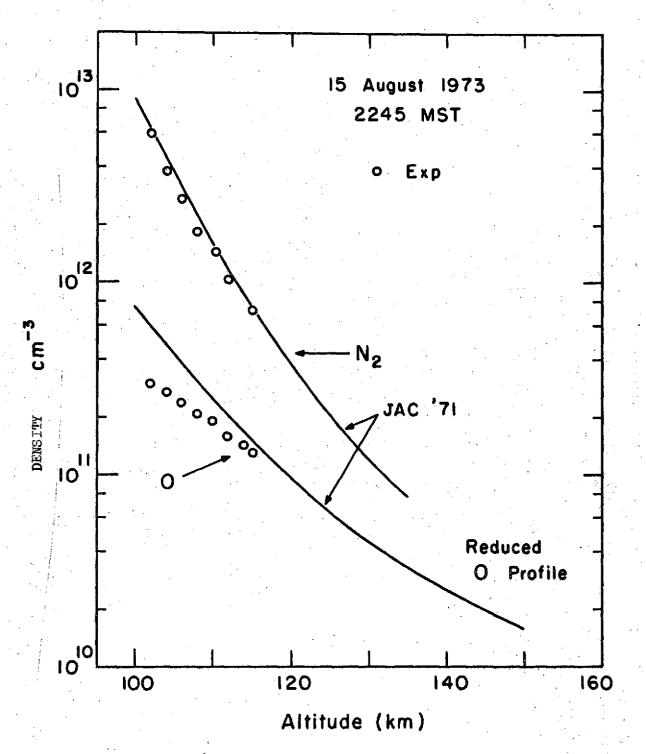


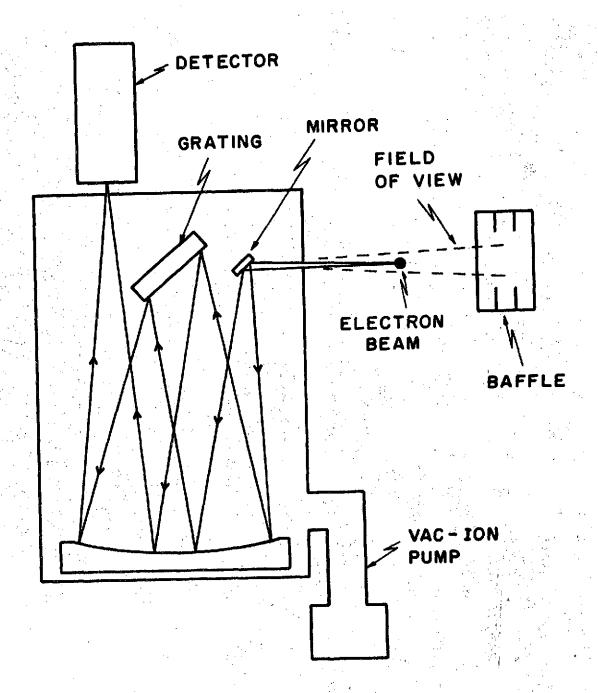
Figure 2

(5) Nike-Apache rocket (14.528 UA), 2 March 1974, double-mode mass spectrometer and multiple photometer for auroral composition and excitation, Fort Churchill, Manitoba.

1. Composition Measurements

The optical mass spectrometer is a new and unique instrument. The OMS combines a laboratory-quality, focused electron gun and a 1/8 - meter UV monochromator (Figure 3) which analyses the gas excited by the electron beam. As the monochromator scans the $\lambda 1200$, 1215, and 1304Å resonance lines by N, H, and O respectively, the energy of the electron beam is switched from 14.5 eV to 75 eV every 20 msec to exploit the difference between direct and dissociative excitation. In the low energy mode the OMS measures the density of the atomic species without interference from the related, parent molecular gases. The 0_2 , N_2 , and H_2 concentrations are then measured separately in the high energy mode. The instrument does not require active pumping of the sampled gas and uses an open end, electron-gun-design with a very large conductance.

This instrument has been further improved to increase its sensitivity so that atomic N, O, or H concentrations as little as 10^5 atoms/cm³ can now be detected at mesospheric altitudes. The modified CMS will be flown as part of Project Alladin from Wallops Island, Va. during the week of 17 June 1974. This complex series of rocket-borne experiments will provide us with the opportunity to cross-compare a variety of techniques for measuring atomic oxygen at



1/2 - METER UV MONOCHROMATOR

Figure 3

mesospheric altitudes and above, and hopefully resolve several vexing problems concerning this highly reactive species. However, only the OMS has the necessary sensitivity and discrimination to measure the N and H concentrations in the D and E regions.

Project Alladin is a natural extension of our joint efforts with scientists from York University (G. Shephard and R. A. Young) to compare atomic oxygen concentrations inferred from conventional quadrupole mass spectrometer data with the results of a resonance absorption/fluorescence experiment on board the same rocket. This study was carried out successfully this winter at Fort Churchill on board a Black Brant V rocket (AMD-VB-35) launched during January (1974). These experiments will be continued in the fall with the launch of an additional Black Brant V payload weighing nearly 600 lbs. (AMD-VB-34).

The composition data of Figure 1 agrees well with the results obtained by Von Zahn and his collaborators using a liquid helium cooled mass spectrometer. The OMS data is in relatively poor agreement with the atomic oxygen profiles inferred from OGO VI $\lambda5577$ airglow studies. The OT green problem is clearly still very much with us both in the airglow and in the aurora! Figure 2 compares our OMS data with a recent Jacchia model (1971). Both the magnitude and altitude profile for N_2 are in good agreement with the model values; however, the 0 data are not. In order to facillitate a comparison between the OMS results and the Jacchia model, we have reduced the magnitude of the 0 concentration in the model and in Figure 2 by about a factor of 2. The agreement is acceptable near 120 km but the observed 0 density near 100 km is still considerably smaller and the 0 concentration gradient noticeably less than that

predicted by the model atmosphere. Future OMS experiments will help bring these apparent discrepancies into sharper focus, and perhaps explain their origin.

The launch date for the initial test of the OMS instrument at mesospheric altitudes was chosen to coincide with the seasonal minimum predicted on the basis of the OGO VI airglow experiment. Project Alladin will give us an additional opportunity to see whether other OGO VI predictions are borne out under quite geophysical circumstances.

2. Auroral Studies

Four rocket experiments involving complex payloads were carried out at the Churchill Research Range during January and February 1974. The first vehicle, a Black Brant V, was prepared in collaboration with York University and was launched into a IBC II aurora during January. The University of Pittsburgh contributed a double-mode mass spectrometer in order (1) to continue our studies of nitric oxide enhanced aurora and (2) to compare atomic oxygen concentrations measured by this instrument with similar results obtained using $\lambda 1304\text{Å}$ resonance absorption/fluorescence techniques. Both instruments performed flaw-lessly throughout the flight and a detailed analysis of the results is currently underway. A followup experiment has been planned and will be flown from Fort Churchill on board Black Brant V vehicle

This year was notable in several respects. It began, for example, with the first successful OMS experiment. It moved on to the successful execution of a two-payload, three-rocket mission to the auroral zone.

And it concludes with active participation in Project Alladin. The auroral mission deserves special comment. In previous reports and proposals we had lamented the fact that progress in auroral physics was being impeded by the one experiment per year philosophy, and that a more effective approach would be (1) to construct two different, but complementary, payloads, (2) take them both to Churchill and launch them into suitable aurora, (3) recover both payloads, (4) repair them in the field and then (5) refly the payload that promised the greatest potential dividends based on an "in situ" review of what was learned on the first two flights. This new approach is actually more economical over the long run and makes good scientific sense. A mission of this kind was approved for the February 1974 auroral campaign.

In spite of the severe conditions that prevail at Churchill during the winter months we were able to refurbish and recalibrate completely a recovered payload (14.526 UA) in two days amply demonstrating the feasibility of this modes operandi when the operation is in the hands of an experienced group of scientific, vehicle and telemetry personnel. The breakup of Nike-Apache rocket 14.527 UA, although very unfortunate, does not in any way diminish this tactical accomplishment. Each vehicle was in fact launched into a major auroral substerm characterized by auroral forms 50 kR or more in intensity, and the mission was executed precisely as planned. The ultimate fate of 14.527 UA, however, was not what we had hoped for, and its disintegration was particularly painful because it carried our new extreme ultraviolet [EUV] experiment. No data was

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~£7

Figure 4

obtained.

The impact of this development was felt acutely because at the same time we had been making outstanding progress at measuring the absolute cross sections for exciting auroral EUV feature in our complementary laboratory program. Figures 4 and 5 of this report show some typical EUV spectra in the 900Å and 1010Å region produced by electron impact excitation of N2. The laboratory spectrum is complex and the EUV features are quite bright; the same is likely to be true in a well-developed auroral storm. Although we were disappointed by the untimely demise of 14.527 UA, the data of Figures 4 and 5 show that the experiment was and still is a very good one! We are planning to return to Churchill this winter in a continuing quest for this elusive prize: the measurement of the intensity and altitude distribution of auroral EUV radiation in the spectral range 500Å to 1300Å.

The 1974 auroral expedition was an outstanding success overall because two rockets were launched usccessfully into auroras that were ideal for the continuance of our studies of nitric oxide enhancements at northern latitudes. Nike-Apache payload 14.526 UA was launched into an intense magnetospheric storm in which the OI green line (λ 5577A) reached an intensity of nearly 100 kR and the H component of the earth's magnetic field exhibited a negative bay in excess of 600 gammas. Enhanced NO concentrations (~ 2 x 109 NO/cm³) were encountered. The buildup was similar in magnitude to earlier nitric oxide results obtained in a comparable IBC II aurora (see Figure 6). Characteristically perturbed ion profiles (large NO † /0 $_{0}$

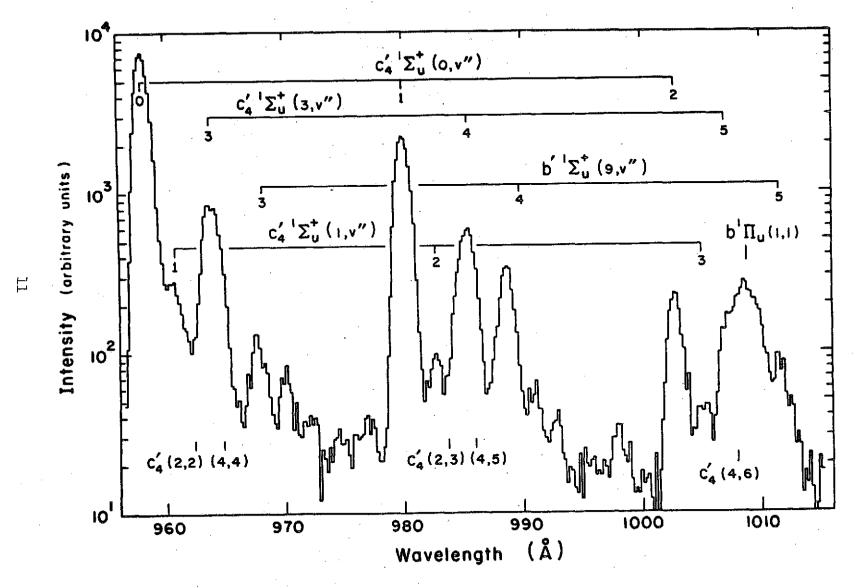


Figure 5

ratios) were also observed. Flight 14.528 UA was launched into an aurora approximately as bright, but not as active magnetically, and with a shorter integration time. In this case comparatively little NO was observed. These flights further delineate a trend that we had noted earlier; namely, the magnitude of the NO enhancement is in proportion to the total energy deposited in the region through which the rocket passes. And, if we distinguish between the energy deposited by precipitating electrons versus the energy dissipated in the ionosphere by the auroral electrojet via Joule heating and other related electric field phenomena, these flights clealy show that the energy associated with the electrojet and with the perturbation of the earth's magnetic field is by far the most important factor.

Figure 7 presents some preliminary data showing this general trend. It is clear that the NO buildup is directly proportional to $\int\Delta H^2$ $^{\circ}\Delta t$; this quantity is a measure of the total energy deposited by Joule heating. The 1974 winter campaign to Churchill has provided data that will allow us to separate quantitatively the two components leading to NO enhancements. Equally important, our results stress the importance of having adequate magnetographic coverage. This point has been made privately to the Air Force Cambridge research group responsible for their auroral studies [Project Icecap]. Even they are convinced now that large NO enhancements do in fact occur (an advance over their attitude one year ago). But like ourselves, they are not sure how this remarkable production feat is accomplished so efficiently.

Our laboratory program has, however, suggested a partial explanation of this phenomena. Our findings are summarized in the

following abstract of a paper that we presented at the Washington meeting of the AGU (Spring 1974).

Comment on the Production of N(2D) Atoms by Photoabsorption Processes and by Electron-Impact Excitation of N2. Laboratory studies on the production of extreme ultraviolet radiation by electron-impact excitation of No show that $N(^2D)$ atoms are produced very efficiently by the predissociation of N $_{\!\!\!2}$ Rydberg and valence states with $^1\pi_{\!_{\scriptstyle \it U}}$ symmetry. This dissociation process involves a nonradiative transition to the C' $^3\Pi_{_{\rm U}}$ continuum: e + N $_2$ \rightarrow N $_2(^1\Pi_{_{\rm U}})$ + e followed by $N_2(^1\Pi_u) \rightarrow N_2(C'^3\Pi_u) \rightarrow N(^2D) + N(^4S)$. Under auroral conditions these predissociating ${}^{1}\Pi_{_{11}}$ states are populated by electron-impact at a rate comparable to the ${\rm N_2}^+$ ionization rate. Thus, the total N(2D) population rate from dissociative excitation, from dissociative recombination of NO⁺ ions, and from ion molecule reactions could be as much as 50 - 100 times the $\lambda 3914$ volume emission rate. This excitation rate would suffice to account for the large N(2D) concentrations observed recently by Rusch and Sharp in an IBC I aurora, and for the production of unusually large nitric oxide densities in some auroral forms as a result of the $[N(^2D) + 0_2]$ quenching reaction. Under daytime conditions these same $N_2({}^1\Pi_{_{{\bf U}}})$ states are populated by absorption of solar photons and the N(2D) production rate from this process is shown to be comparable to that from photoelectron impact and from the dissociation

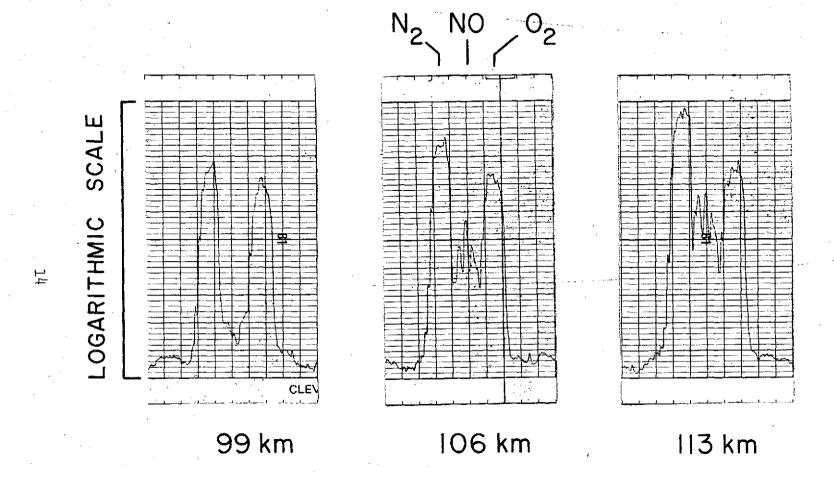


Figure 6

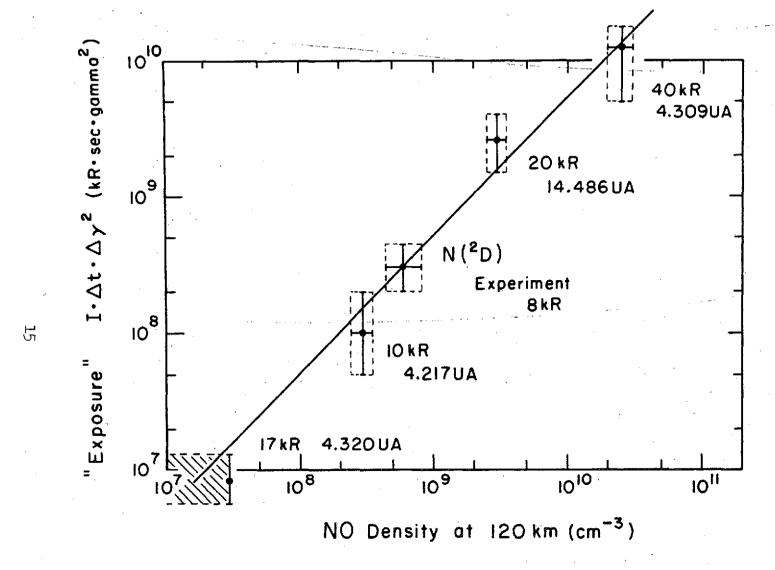


Figure 7

recombination of NO⁺ ions.

Once again in this work we have a very good example of the remarkable effectiveness of complementary laboratory and rocket-borne programs.

These developments have prompted us to formulate an ambitious set of plans for our return to the auroral zone this winter. The measurement of auroral EUV fluxes and the assessment of the role of these photons in a variety of photoionization and photodissociation processes (e.g., the excitation of $O(^1S)$ atoms and the green line) is a major goal. Further work on the excitation and ultimate fate of $N(^2D)$ atoms in the aurora, on the role of joule heating, and on the possibility that plasma instabilities (anomalous resistivity) may be involved are also high on our list of major projects. Our nitric oxide studies will be expanded further to include an investigation of the so-called auroral mystery feature which is observed occasionally at $\lambda 2150\text{Å}$. This band has been observed by rocket-borne and satillite (OGO-IV) spectrometer, but not in every aurora. It is commonly believed that this emission feature is actually the (1,0) gamma band of NO excited by the deactivation of metastable $N_2(\text{A}^3\Sigma_u^+)$ molecules,

$$N_2(A^3\Sigma_u^+) + NO \rightarrow NO(A^2\Sigma) + N_2$$

$$(1)$$
 $NO(A^2\Sigma) \rightarrow NO + hy \qquad (\lambda 2150)$

The critical experiment, in which the three principal actors in the drama $[N_2(A^3\Sigma_u^{\ \ \ }),\ NO,\$ and the intensity of the 2150A feature] are

measured simultaneously and Reaction (1) verified, has yet to be performed. If this reaction sequence could be verified, then the OGO IV spectrometer data could be used to study the morphology of nitric oxide aurora. This development would lead to a much clearer picture of the scope of the whole NO phenomena as well as give a new meaning and significance to unused OGO data. Thus the 1975 auroral campaign has impressive potential.

3. New and Bizarre Developments of Aeronomic Importance

One of the charms and ultimate frustrations of aeronomy is the regularity with which "established" theories become causualties of new experimental advances. In the jargon of the young, this is an endeavor that requires "staying loose". Figure 8 illustrates this point.

Figure 8 shows the vacuum ultraviolet spectrum of a recombining plasma in which vibrationally excited ${\rm CO}_2^+$ ions predominate; this is the first measurement of its kind. Our results indicate strong excitation of the CO fourth positive system (A¹ $\Pi \to X^1\Sigma$) due to the dissociative recombination process:

$$co_2^+ + e \rightarrow co(A^1\pi) + o$$
 (2)

It is important to note that only the v'=0 and 1 levels of the $A^1\Pi$ state can be populated if the recombining CO_2^+ ions are in thermal equilibrium at 300°K. It is quite clear from the data shown in Figure 8 and from other spectra that we have obtained, that $A^1\Pi$

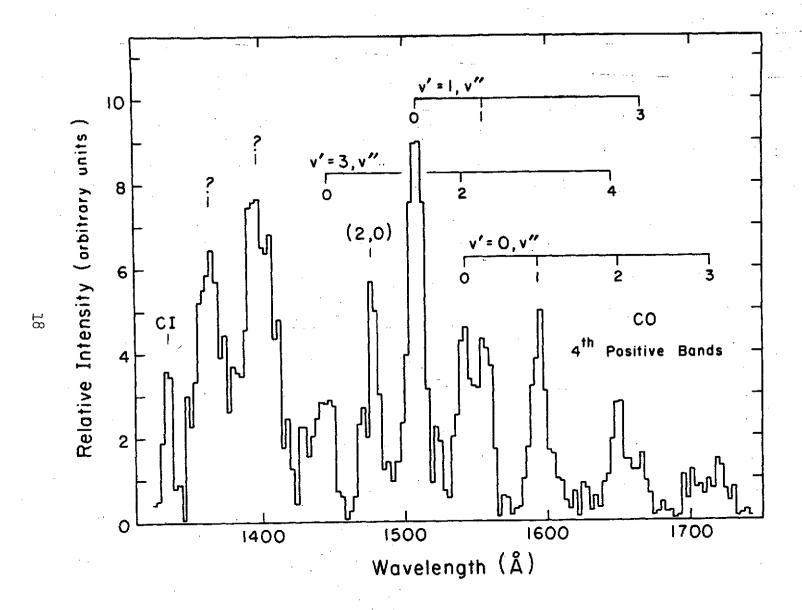


Figure 8

vibrational levels up to at least v' = 5 are in fact being populated. Complementary electron heating experiments have shown conclusively that process (2) is exciting all of these levels (Gutcheck and Zipf, 1973).

The implications of the results are quite clear: ${\rm CO_2}^+$ laboratory plasmas, which had previously been thought to be equilibrated at 300°K, are in fact vibrationally very hot. This finding raises serious questions about previous total recombination-coefficient measurements involving the important atmospheric ions ${\rm O_2}^+$, ${\rm NO}^+$, and ${\rm N_2}^+$. Were these plasmas also vibrationally hot? Can these laboratory results be used now in the analysis of ionospheric data without reservation? Does, in fact, the nominal factor of 2 - 3 agreement achieved by aeronomists when they model daytime ion composition data, really tell us that our own ionosphere, as well as that of Venus has a substantial population of vibrationally excited ions?

Our preliminary data contain another striking result. Figure 8 shows a very intense spectral feature near 1400Å which does not appear conspicuously in electron impact excitation of CO or $\rm CO_2$ (Mumma and Zipf, 1972; Mamma et al., 1973). This is the first laboratory observation of the so-called "mystery" spectral feature at $\lambda 1400$ Å that appears so strikingly in the Venus airglow spectra obtained by Rottman and Moos (JGR 78, 8033, 1973). We have been able to show (Unger and Zipf, 1974) that the 1400Å feature is produced by the dissociative recombination of vibrationally excited $\rm CO_2^+$ ions. However, at this time we do not know what specific quantum transition is involved.

Our experiment provides virtually conclusive evidence for the

presence of substantial concentrations of vibrationally excited CO_2^{-1} ions in the Venus ionosphere. The Mars data in the same wavelength region shows a complete absence of this VUV feature implying a relatively cool ionosphere (and CO_2^{-1} plasma) [Moos, 1974]. It is not clear at this point why the Venus atmosphere is capable of sustaining a vibrationally hot ionosphere while Mars does not or can not.

What about our own ionosphere? Could it be that some of the so-called anomalies in the ion chemistry of the aurora and of other disturbed atmosphere phenomena are really consequences of vibrationally excited ions? Laboratory results of the caliber of those shown in Figure 8 stir the geophysical pot in a profound manner. They remind us that in spite of our best efforts, some popular ionospheric theories, like the smile of the Cheshire Cat, will ultimately fade away. Our oversimplified models of a planetary ionosphere are in need of an overhaul, a major goal of our research program.

The data for Figure 8 was obtained in a plasma spectroscopy experiment carried out recently by our group. These results have already influenced our plans for Churchill next winter. In effect early access to this kind of knowledge gives our rocket program a significant competitive edge - we know where the future action is going to be thanks to the symbictic relationship that exists between both efforts and we are aware of the techniques needed to study these problems using rocket-borne instrumentation. It is to the credit of the National Aeronautics and Space Administration that the effectiveness of the approach was recognized and the effort nurtured.

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