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February 23, 1978

Final Report

PHOTODISSOCIATION OF CO_2 AND QUENCHING OF METASTABLES
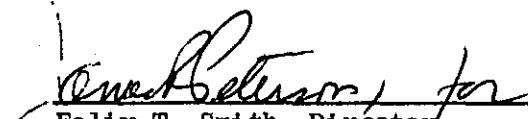

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Prepared for:

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Washington, D.C.   20546

SRI International Project PYU-4725

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CONTENTS

SUMMARY

Work under this contract was conducted to further our understanding of the chemistry of the atmospheres of Mars and Venus. Investigations in four different areas have been carried out. These investigations, and the results obtained, are summarized briefly below.

- CO_2 photodissociation quantum yields were determined in the 1300-1500 $\overset{\text{o}}{\text{A}}$ spectral region by measuring both CO and oxygen atoms. Contrary to earlier studies, which we now believe were affected by heterogeneous processes, the photodissociation yields appear to be unity at wavelengths below 1500 $\overset{\text{o}}{\text{A}}$.

- The $O(^1S)$ quantum yield was determined for CO_2 photodissociation in the 1060-1175 $\overset{\text{o}}{\text{A}}$ spectral region. The measurement resolves the differences between two earlier experiments, and demonstrates that the $O(^1S)$ yield is unity throughout most of the measured region. An anomaly was discovered at 1089 $\overset{\text{o}}{\text{A}}$, the location of a strong Rydberg transition, where the oxygen atom is produced in the ^1D state.

- The pathways for the quenching of $O(^1S)$ by N_2O, CO_2, H_2O, and NO were investigated. Distinction was made between deactivation to $O(^1D)$, to $O(^3P)$, and reaction. The only clear-cut case of reaction was with H_2O; the other quenchers gave various mixtures of $O(^1D)$ and $O(^3P)$. This experiment demonstrates for the first time that $O(^1S)$ reactions differ markedly from $O(^1D)$ reaction not only in terms of quenching rate coefficients, but also in terms of the products formed.

- The source of the Venus nightglow, detected by Venera 9 and 10, was investigated. We followed the observations of Lawrence et al.,

who found that a He-O_2 discharge with added CO_2 produced the emission (the $c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-$ O_2 transition). We were able not only to duplicate their results, but also to show that oxygen atom recombination is the $O_2(c^1\Sigma_u^-)$ source, that CO_2 is not an essential ingredient (N_2 is as effective), and that $O_2(c^1\Sigma_u^-)_{v=0}$ is quenched primarily by $O(^3P)$ in our system. We believe that the difference in the O_2 recombination spectra in the terrestrial and Venusian atmospheres is merely a consequence of the difference in $[M]$ $[O(^3P)]$ at the altitude of emission. We have also found what appears to be a new O_2 band system, although the identity of the transition is not yet evident.

BACKGROUND

Photodissociation of CO_2 is a primary process in the atmospheres of Mars and Venus, and a major goal of the research was to settle some of the ambiguities existing in the literature on this subject. The issue of a photodissociation quantum yield that varied with wavelength, in the wavelength region below 1670 $\overset{o}{A}$, has caused concern for the last several years. We had contributed to these observations[1] by confirming and expanding two earlier studies[2,3] by other investigators. However, there were enough contradictory measurements to make us believe that further resolution of the problem was needed, so we have conducted an additional study in which, for the first time, both CO and oxygen atoms were measured, in real time.

In the high absorption cross-section spectral region below 1200 $\overset{o}{A}$, CO_2 photodissociation can lead to $O(^1S)$ production, and hence is an important source of the 2972 $\overset{o}{A}$ $^1S \rightarrow {}^3P$ emission line in the Mariner spectra of Mars.[4] Previous work, by Lawrence[5] and by Koyano et al.,[6] had indicated high $O(^1S)$ yields at 1100-1140 $\overset{o}{A}$, but those studies produced markedly different results above and below this wavelength region. To resolve these discrepancies, and to ascertain the $O(^1S)$ yield from CO_2 at 1067 $\overset{o}{A}$, which is needed for the work on the $O(^1S)$ product channels, we investigated the 1060-1175 $\overset{o}{A}$ region. Our results agree with parts of each of the two previous studies. However, neither of those studies reported that at the strong absorption band at 1089 $\overset{o}{A}$, which is an intense Rydberg transition, CO_2 dissociates via a $CO + O(^1D)$ pathway; this is an abrupt change from the $CO + O(^1S)$ pathway found elsewhere.

Because $O(^1S)$ is an important metastable species in the atmospheres of the CO_2 planets, we attempted to ascertain the products of its quenching

by CO_2. If the interaction were found to reactive, an additional source of CO and O_2 would exist. The best laboratory source for $O(^1S)$ was found to be the 1302-1306 $\mathring{A}$ photolysis of N_2O.[7] In the course of the study, we also measured the $O(^1S)$ quenching products from N_2O, H_2O, and NO, in all cases differentiating between physical quenching and chemical reaction. These are the first such measurements for $O(^1S)$, although by now there is an extensive literature on the $O(^1D)$ reactions, subsequent to our initial measurements of ten years ago.[8]

The Venus nightglow observations were unexpected in the aeronomy community, since it was considered unlikely that an O_2 system would be the only feature in the visible spectral region, particularly one almost totally unknown in the laboratory. Moreover, the Russians had twice misidentified the emission, first calling it a CO_2 system,[9] and then the CO Fourth-Positive bands.[10] Lawrence et al,[11] identified the emission as the $O_2(c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-)$ system and were able to produce it in the laboratory. We have now extended this work and have obtained information on the $O_2(c^1\Sigma_u^-)$ production mechanism, and loss channel. On the basis of these data, we are able to present a possible explanation for the difference in the O_2 recombination spectra observed in the Venusian and terrestrial atmospheres.

RESULTS

The work on CO_2 photodissociation and on the $O(^1S)$ product channels has either been published[12] or is about to be published, in the _Journal of Chemical Physics._ Abstracts of these papers are presented in the Appendix. Thus, only the work on the Venus nightglow will be discussed here.

The emission observed from Venera 9 and 10 is the 0-v'' progression of the $O_2(c \to X)$ transition.[9] The spectra are far clearer than had ever been seen in the laboratory, the only previous emission spectra having been reported by Degen.[13] He saw only two very weak bands, and 100 hours was required to record them on film. This emission in the Venus nightglow was unexpected, particularly because it appears to emanate in a region where the CO_2 pressure is ~ 1 torr. The estimated $O_2(c^1\Sigma_u^-)$ radiative lifetime is > 100 sec,[14] a time equivalent to 5×10^8 CO_2 collisions.

Lawrence et al.[11] were able to produce a clean $O_2(c-X)$ spectrum by discharging 0.3% O_2 in He, followed by addition of CO_2 downstream. They concluded that the role of CO_2 was unique, and that, even though oxygen atom recombination was assumed to be the source of the $O_2(c^1\Sigma_u^-)$ excitation energy, the CO_2 acted in a "chemical" way, resulting in specific $O_2(c)$ production. To support this argument, they pointed out that oxygen atom recombination in the terrestrial atmosphere, where the CO_2 concentration is negligible, results in production of the $A^3\Sigma_u^+$ state of O_2,[15] not the $c^1\Sigma_u^-$ state.

We have performed experiments in a discharge flow apparatus in which it was possible to observe products in two different flow regimes--in fast flow, with discharge-to-viewing-region times of ~ 3 ms, and in a slow flow, with an aging time of ~ 0.5 sec. Titration ports were

incorporated in the system so that $O(^3P)$ atoms could be produced by means other than O_2 dissociation. The reaction cell was viewed by a high speed transmission grating image tube spectrograph,[16] enabling us to obtain complete spectra in the 4000-8000 Å region in 30 seconds to 4 minutes. Absolute measurements of $O(^3P)$ densities were obtained by NO_2 titration.

Our results differ significantly from those of Lawrence et al.[11] in several ways. We find that it is not necessary to have CO_2 present in order to see the $O_2(c-X)$ transition. This transition is clear and strong in the afterglow of an $He-O_2$ discharge (20 torr He, 30 mtorr O_2). Addition of CO_2 enhances the emission somewhat, and makes the spectrum cleaner by removing emissions from other sources, but the $O_2(c-X)$ band system is present at all times. This observation is quite surprising, since Degen[13] required very long exposures to obtain sufficient intensities for analysis, and Lawrence et al.[11] were unable to observe any c-X bands without CO_2 addition. We, on the other hand, are able to obtain spectra (on film) with 30-second exposures, using the image tube instrument. A spectrum is presented in Fig. 1, which shows the 5000-8000 Å region. The background continuum is the NO_2^* emission that results from the conversion of trace N_2 impurities to NO in the discharge, and subsequent reaction of this NO with $O(^3P)$. The upper spectrum was obtained in the absence of CO_2, whereas the lower spectrum was obtained with 7 torr CO_2. The most prominent feature in the upper spectrum is the $O_2(b\,^1\Sigma_g^+ \to X\,^3\Sigma_g^-)$ band at 7618 Å, also generated by $O(^3P)$ recombination.

The $O_2(c-X)$ bands are prominent in both spectra, but the spectrum taken without CO_2 shows additional features--the OH Meinel system, and three other bands, occurring at 300 ± 10 cm^{-1} to the long wavelength side of the three c-X bands. Even after CO_2 addition, traces of these three new bands remain, but the $O_2(b-X)$ band and the OH Meinel bands are completely extinguished. Spectra taken of the 4500-5500 Å region show a fourth unknown band, at 5212 ± 3 Å.

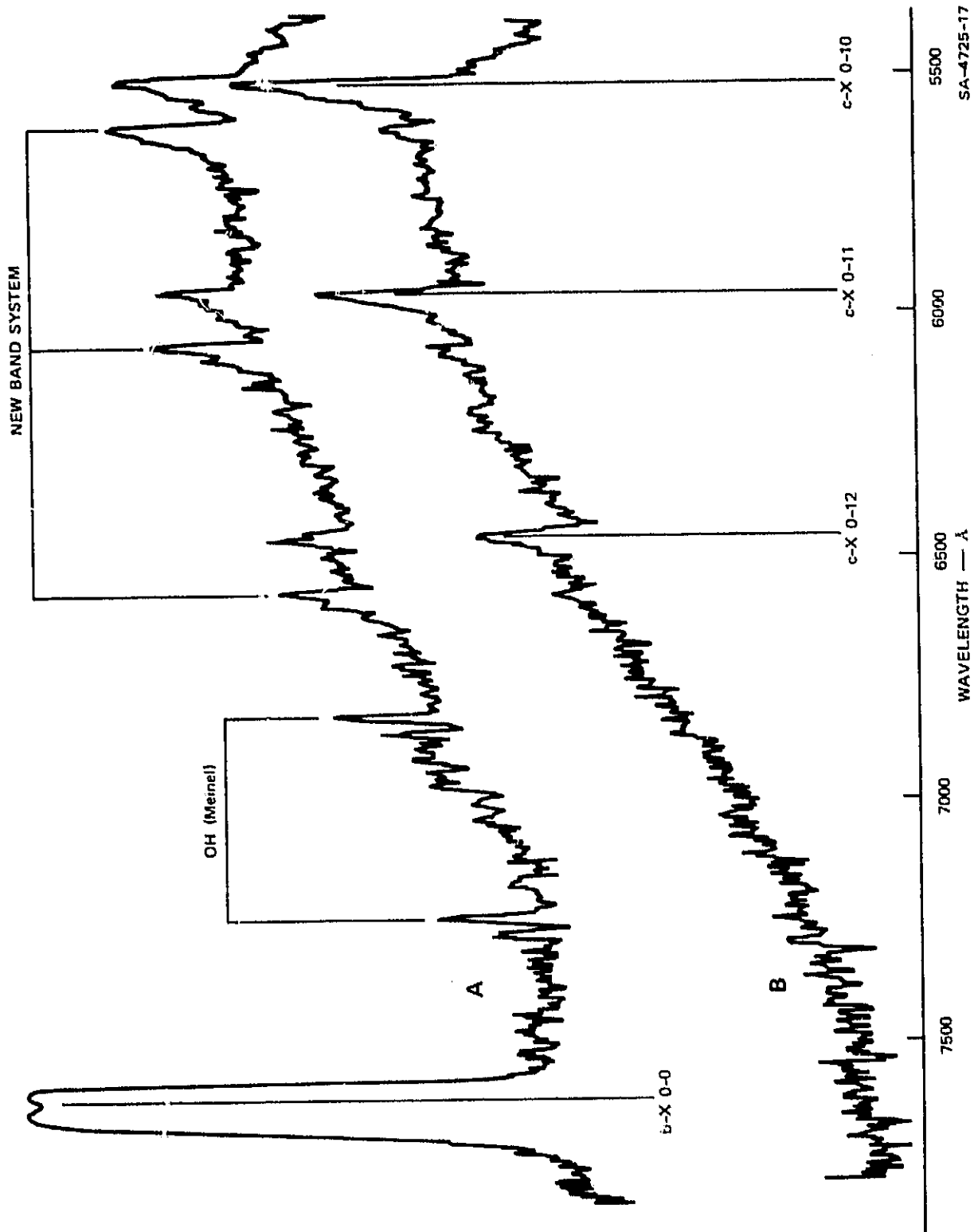Figure 1   Microdensitometer traces of afterglow spectrum, fast-flow system, 20 torr He, 30 mtorr O_2, wavelength range 5300-8000 Å. A. No CO_2. B. 7 torr CO_2.

From the variety of ways in which we have been able to generate the new bands, it is clear that they belong to an O_2 system and are formed by atom recombination. No transitions of the common impurities (CO, CN, C_2, CH, OH, NO) correlate with them. If recombination is the mechanism, then the $A^3\Sigma_u^+$, $c^1\Sigma_u^-$, and $C^3\Delta_u$ states are the only likely candidates for the upper state, and $c^1\Sigma_u^-$ (v=0) is excluded because the ratio of intensities of the new system to the c-X 0-v' system is not constant. Table I gives the observed wavelengths, along with two conceivable indentifications for the system.

Table I

UNIDENTIFIED BANDS

Observed Bandheads	$A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$		$A^3\Sigma_u^+ \rightarrow b^1\Sigma_g^+$	
5212 ± 3 Å	0-11	5220 Å	0-2	5234 Å
5604 ± 2 Å	0-12	5602 Å	0-3	5632 Å
6055 ± 2 Å	0-13	6035 Å	0-4	6085 Å
6572 ± 5 Å	0-14	6531 Å	0-5	6603 Å

Although the 0-12 and perhaps 0-11 A-X bands look like good identifications, the others do not, and as the bands appear to have a constant intensity ratio, it is likely that they have the same upper state and vibrational level. The constant displacement from the c-X bands suggests that the four new bands have a common upper level and the same lower level as their c-X neighbors. This implies a new O_2 state, lying 300 cm^{-1} below the $c^1\Sigma_u^-$ state, a hypothesis difficult to explain on theoretical grounds. More experimentation is required to identify the system.

The two spectra in Fig. 2 show the 4100-4600 Å region, taken in the second order of the transmission grating. It may be seen that the c-X bands are now partially rotationally resolved; the 0-7 band, the same one analyzed by Degen,[13] can be followed out to K = 23. Again, in the absence
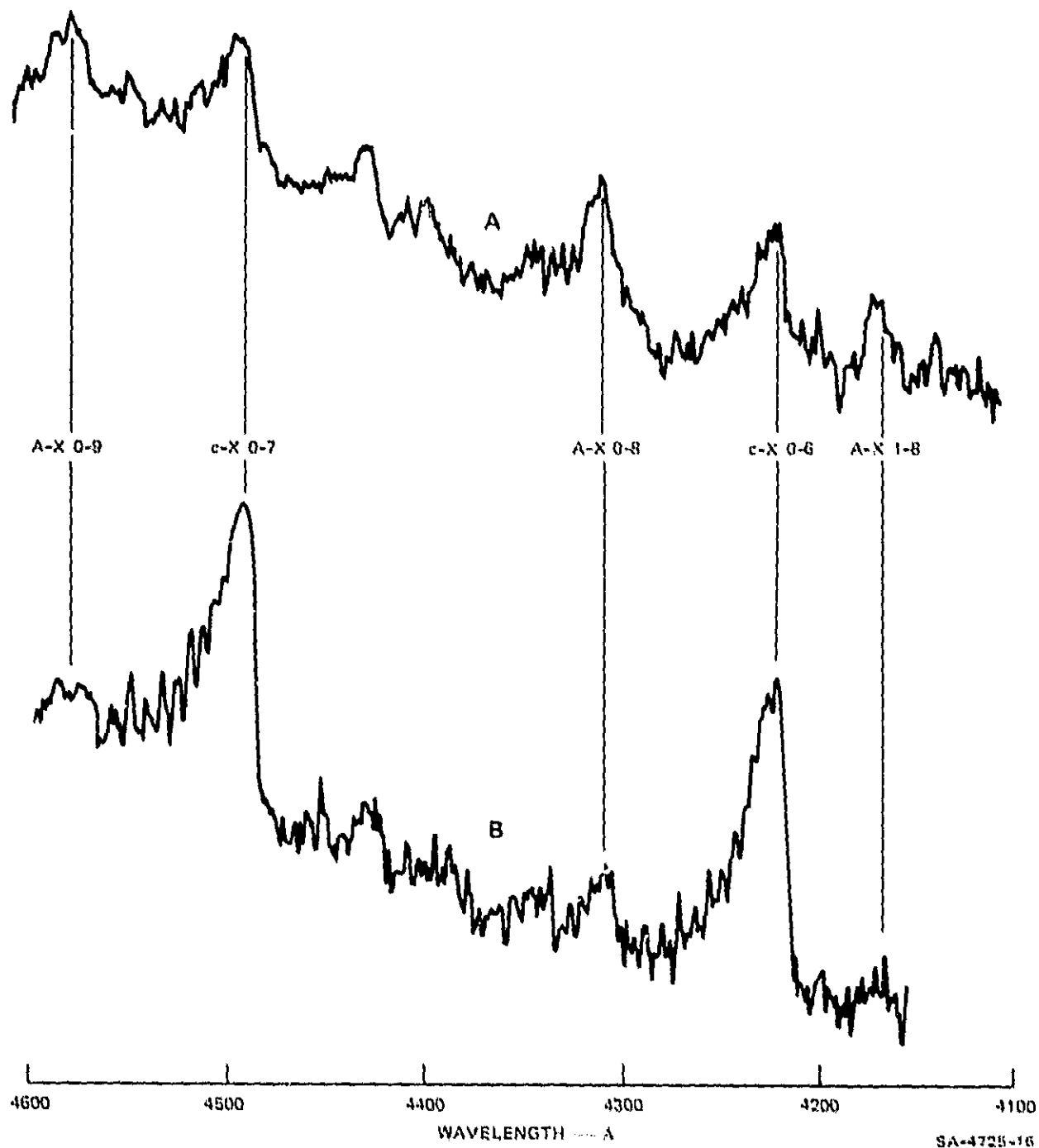
Figure 2   Microdensitometer traces of afterglow spectrum, fast-flow system, 20 torr He, 30 mtorr O_2, wavelength range 4100-4600 Å. A. No CO_2. B. 7 torr CO_2.

of CO_2 the c-X bands are clearly present, and the $A^3\Sigma_u^+ - X^3\Sigma_g^-$ system is also observed. CO_2 addition quenches the A-X system and also reduces the background NO_2 continuum.

A second way in which our results differ from those of Lawrence et al. is our finding that while CO_2 does enhance the c-X emission, it is not unique in this behavior. We find that N_2 has a similar effect, although it is less effective in decreasing other emissions, so that c-X bands do not appear as isolated as when CO_2 is used. Lawrence et al.[11] have tried to explain what they considered the unique behavior of CO_2 in terms of a chemical effect between the recombining $O(^3P)$ atoms and the CO_2 third body. We conclude that there is no such effect, and that the choice of a third body is arbitrary. From the spectra in Figs. 1 and 2, we have obtained a measure of the effect of CO_2 addition on the 0-6 and 0-7 c-X band intensities, shown in Fig. 3. A doubling of the intensities is observed over the CO_2 pressure range used, which is just the increase to be expected if the addition of CO_2 merely speeds up the $O(^3P)$ recombination rate. This increase requires that CO_2 be three times as effective a third body as He [typical for several $O(^3P)$ recombination systems[17,18]], and that CO_2 be a poor quencher for $O_2(c^1\Sigma_u^-)$, which follows from the appearance of the O_2(c-X) systems at the CO_2 pressures in the Venus atmosphere and in the laboratory. Note that at the CO_2 pressure used in Fig. 1, the $O_2(b^1\Sigma_g^+)$ state is entirely quenched. As the rate coefficient[19] for this reaction is a moderate 4×10^{-13} $cm^3 molec^{-1} sec^{-1}$, and this state is probably produced at a comparable rate to the $O_2(c^1\Sigma_u^-)$ state, the quenching of $O_2(c^1\Sigma_u^-)$ by CO_2 is clearly inefficient.

A critical test to demonstrate that $O_2(c^1\Sigma_u^-)$ production is a recombination process $[O(^3P) + O(^3P) + M \rightarrow O_2(c^1\Sigma_u^-) + M]$ is to make $O(^3P)$ in the absence of O_2. The classical way is to titrate the $N(^4S)$ atoms from a N_2 discharge with NO, converting the N atoms to $O(^3P)$. Lawrence et al.[11] did not do this, as they believed they had evidence[20] that N_2
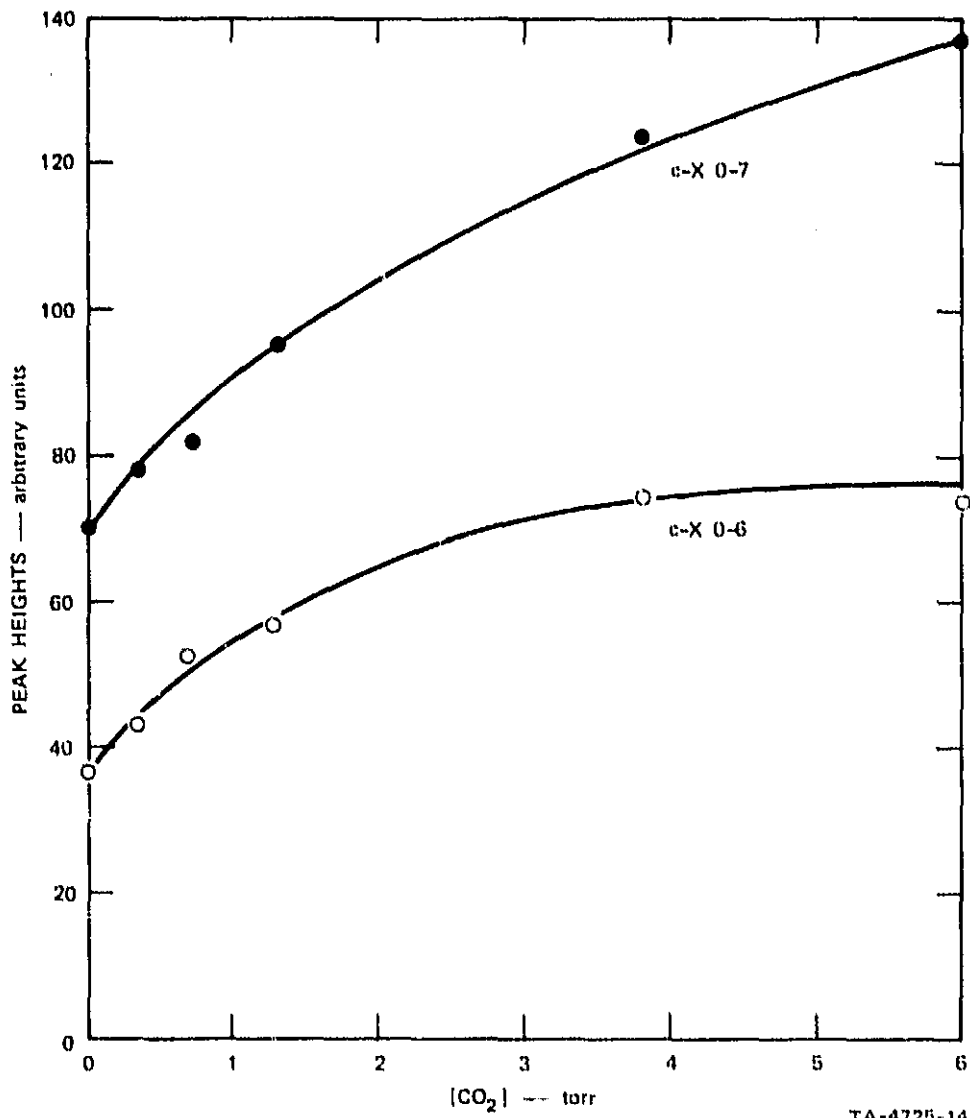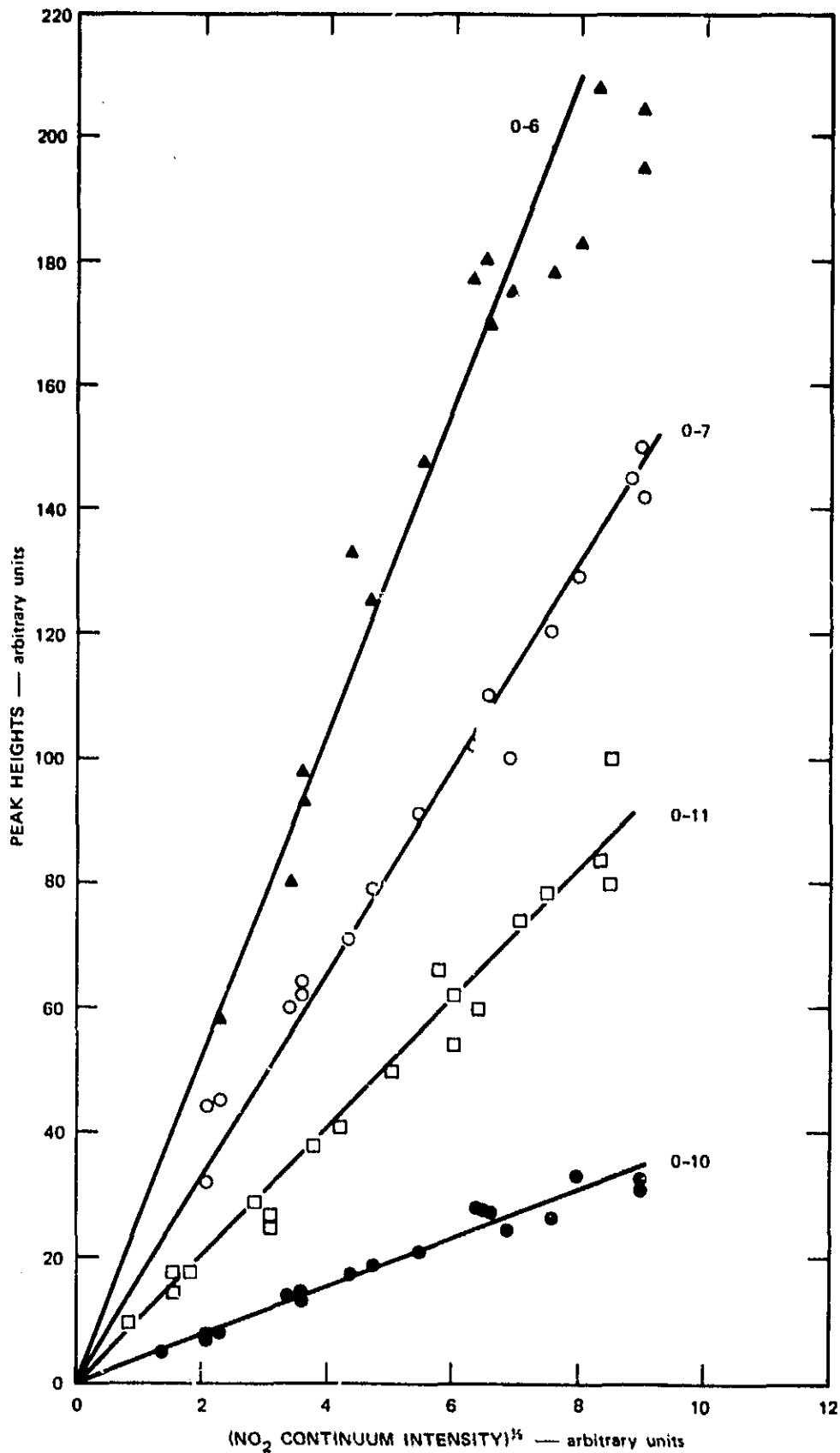
TA-4725-14

Figure 3 $O_2(c^1\Sigma_u^- - X^3\Sigma_g^-)$ 0-6 and 0-7 band emission
intensities as a function of added CO_2, fast-
flow system, 20 torr He, 30 mtorr O_2.

destroyed $O_2(c^1\Sigma_u^-)$. Once we had shown that this is not the case, we attempted to make $O_2(c^1\Sigma_u^-)$ by the above titration technique, and were completely successful. The same spectrum was observed, including the four new bands (even with 20 torr N_2). Thus, it is clear that $O(^3P)$ recombination is involved, and that the bands do not come directly from ambient O_2. The titrated N_2 source is advantageous in that it is possible to add just enough NO to convert all the $N(^4S)$, without any excess, which alleviates the problem of the NO_2^+ background found in the O_2 spectra. On the other hand, NO(β) bands may appear if mixing is poor.

In order to understand the $O_2(c^1\Sigma_u^-)$ loss process in our system, measurements have been made on the dependence of the $O_2(c-X)$ intensities on the $O(^3P)$ concentration. We have obtained the relationship between the $O_2(c-X)$ intensities and the background NO_2 continuum intensities, as shown in Fig. 4. The dependence for each of the four bands is clearly quadratic; that is, the continuum intensity is proportional to the square of the $c-X$ intensity. It is to be expected, and our results so indicate, that the continuum intensity is also proportional to the square of the $O(^3P)$ density. This is because the $O(^3P)$ formation rate in the discharge is presumably proportional to the rate of the reaction making NO, so that doubling the $O(^3P)$ production rate quadruples the NO_2^+ production rate.

With the continuum intensity proportional to $[O(^3P)]^2$, and also to the square of the $c-X$ intensity, then it follows that the $c-X$ intensity is proportional to the first power of $[O(^3P)]$. This indicates that the primary loss mechanism of $O_2(c^1\Sigma_u^-)$ in our system is by $O(^3P)$ quenching (O_3 quenching is a less likely possibility), since the production rate (recombination) is proportional to $[O(^3P)]^2$, and the steady state $O_2(c-X)$ intensity is proportional to (production) (loss). A confirmation of this conclusion comes from spectra taken at different discharge power levels (and thus different $O(^3P)$ densities), which show that the clearest $O_2(c-X)$ spectra are those taken at minimum $[O(^3P)]$, demonstrating that the $O_2(c-X)$ dependence on $O(^3P)$ is of a lower order than that of the other emissions,

Figure 4 $O_2(c^1\Sigma_u^- - X^3\Sigma_g^-)$ 0-6, 0-7, 0-10, and 0-11 band
emission intensities as a function of
$(NO_2$ continuum intensity$)^{\frac{1}{2}}$, resulting from
varying discharge microwave power.

In the O_2(A-X) system, on the other hand,[21] the intensity is proportional to $[O(^3P)]^2$, an indication that $O(^3P)$ quenching is not the major loss of $O_2(A^3\Sigma_u^+)$. We also find this to be true for the new band system.

CONCLUSIONS

Our conclusions concerning the source of $O_2(c^1\Sigma_u^-)$ in an $O(^3P)$ afterglow system can be summarized as follows:

(1) $O_2(c^1\Sigma_u^-)$ is generated by $O(^3P)$ recombination, and its emissions can be seen in any system where the recombination rate is sufficiently high; with our detection system the combination of $[O(^3P)] \gtrsim 3$ mtorr and $P \gtrsim 15$ torr is sufficient.

(2) The identity of the third body is not very important, but the use of CO_2 results in a clean spectrum.

(3) It appears that CO_2 and N_2 are very ineffective quenchers of $O_2(c^1\Sigma_u^-)_{v=0}$, and that quenching in our system is controlled by $O(^3P)$.

It is now difficult to understand why the $O_2(c-X)$ system had not been studied and characterized decades ago. We have produced it in a fast-flow system, in a slow-flow system, from $O(^3P)$ atoms, from titrated N atoms, in an He buffer, in an Ar buffer, and in pure N_2. It is, in fact, easier to produce than the well-known $O_2(A-X)$ system.

The visible region also contains what appears to be a new band system, probably in O_2, although we have not yet been able to specify the transition.

The total absence of the $O_2(c-X)$ emission in the terrestrial airglow, and its presence in the Venus atmosphere can be explained by the difference in pressures. In the respective emitting regions, the $O(^3P)$ densities are similar,[22,23] on the order of 10^{11} atoms/cm^3. However, the total pressure in the Venus atmosphere is ~ 1 torr CO_2, whereas in the earth's atmosphere it is close to 1 mtorr, mainly N_2. Thus, the ratio $[M]/[O(^3P)]$ is $\sim 10^2$ in the terrestrial atmosphere at the emission peak (100 km), and $\sim 10^5$ in the Venus atmosphere.

The differences in the two systems can most likely be explained on the basis of laboratory observations. In atom recombination, a molecule is stabilized by removal of small increments of energy by a third body. Thus, molecules in high vibrational levels are initially formed. This is abundantly clear in the atmospheric spectra of the $O_2(A-X)$ emission, where only high vibrational levels are detected,[15] and also in the laboratory spectra,[24] where even at pressures of ~ 10 torr O_2 or N_2, high levels still predominate. On the other hand, both in the Venus atmosphere and in the laboratory, only $v'=0$ levels of the $O_2(c^1\Sigma_u^-)$ state are seen. Since the state is initially formed in high vibrational levels, vibrational relaxation must be very rapid. However, in the earth's atmosphere, the N_2 pressure is quite low, and in any case, N_2 may not be a very good vibrational deactivator for $O_2(c^1\Sigma_u^-)$, compared to CO_2. Furthermore, the $[M]/[O(^3P)]$ ratio is relatively low, so that if $O_2(c^1\Sigma_u^-)$ is rapidly quenched by $O(^3P)$, as our results indicate, it is likely that $O(^3P)$ quenching predominates over N_2 vibrational relaxation. Thus, one cannot see emission from $O_2(c^1\Sigma_u^-)$ in the 4000-6500 Å region in the terrestrial atmosphere (as in the Venus atmosphere) because the molecule has little chance of getting down to $v'=0$. Emission from higher vibrational levels, which occurs in the 3000-4000 Å region, is not prevented, but then it is intermingled with the $O_2(A-X)$ emission.

On the other hand, in the Venus atmosphere, with a much higher $[M]/[O(^3P)]$ ratio, vibrational relaxation of $O_2(c^1\Sigma_u^-)$ is faster than $O(^3P)$ quenching (the CO_2 pressure is within an order of magnitude of that in our laboratory measurements), so that the molecules are driven down to $v'=0$. Furthermore, Fig. 2 indicates that $O_2(A^3\Sigma_u^+)$ is quenched by CO_2, although no systematic measurements on this point exist; thus, it is to be expected that $O_2(A-X)$ emission will not be observed on Venus.

We feel that the different $[M]/[O(^3P)]$ ratio in the two atmospheres is the predominant reason for the difference in the recombination emissions. Detailed kinetics measurements are still needed to prove our arguments.

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APPENDIX

Abstracts of Publications Resulting From Contract NASW-2840

CO$_2$ PHOTODISSOCIATION, 1060-1175 Å

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ABSTRACT

The relative O(^{1}S) quantum yield from CO$_2$ photolysis between 1060 Å and 1175 Å has been measured, to sort out the discrepancies between two prior publications on the subject. Whereas the yield is near unity over a considerable portion of the spectral region, there is an abrupt dip to $\phi_{O(^1S)} \leq 0.15$, centered at 1089 Å. As this wavelength is also the location of a very strong Rydberg transition in CO$_2$, it appears that the low quantum yield is associated with excitation of the upper level of this transition, the $^1\Pi_u$ state. The O(^{1}D) yield at this wavelength was found to have a minimum value of 0.65 ± 0.1. In conjuction with the lack of any observable fluorescence it is concluded that dissociation on the O(^{1}S) + CO and O(^{1}D) + CO surfaces probably accounts for all the input energy.

O(^{1}S) INTERACTIONS--THE PRODUCT CHANNELS

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ABSTRACT

The first measurements are reported of the reaction pathways for the interaction between oxygen atoms in the 4.19 eV ^{1}S state, and four molecules, N_2O, CO_2, H_2O, and NO. Distinction is made between three possible paths--quenching to O(^{1}D), quenching to O(^{3}P), and chemical reaction. With N_2O, the most reasonable interpretation of the data indicates that there is no reaction, in sharp contrast with the interaction between O(^{1}D) and N_2O, which proceeds entirely by reaction. Similarly, there is no reaction with CO_2. With H_2O, the reactive pathway is the dominant one, although electronic quenching is not negligible. With NO, O(^{1}D) is the preferred product.

CO$_2$ PHOTOLYSIS REVISITED

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ABSTRACT

Measurements have been made of the absolute oxygen atom yields from CO$_2$ photolysis at 1470 $\overset{o}{A}$ and 1302-06 $\overset{o}{A}$; in both cases the yield is unity. The CO generation rates have also been measured in these two wavelength regions, and they are proportional to the oxygen atom generation rates; by implication, the CO quantum yields are thus also unity. The CO deficiencies observed in earlier work on this subject are probably caused by heterogeneous processes.