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Final Report
For the Period December 8, 1972 to July 8, 1974
SRI Project PYU-2372, MP 74-27

CO_2 PHOTODISSOCIATION AND VIBRATIONAL EXCITATION IN THE PLANETARY ATMOSPHERES

By: TOM G. SLANGER

Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

Attention: CHIEF PLANETARY ATMOSPHERES, CODE SL

NASA CONTRACT NASW-2400

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Approved by:

FELIX T. SMITH, *Director*
Molecular Physics Center

CHARLES J. COOK, *Executive Director*
Physical Sciences Division

SUMMARY

The following results have been obtained with the support of this contract:

(1) Measurements on the photodissociation quantum yield of CO_2 in the 1200-1500 Å region show that it is wavelength dependent, and for the six atomic line sources used in this study, the quantum yield varied from 0.2 to 0.8. The data appear to fit the interpretation of stable CO_2 bound states mixed with repulsive or predissociating states, since the low quantum yields coincide with the maximum structure in the CO_2 absorption spectrum.

(2) The first reliable measurements have been made on the efficiency of electronic-to-vibrational energy transfer in the systems $O(^1D)$-CO and $O(^1D)$-N_2, using a uv resonance fluorescence technique. In the former case, 40% of the $O(^1D)$ energy appears in CO vibrations; in the latter case, 33% appears in N_2 vibrations. Recent theoretical estimates on the N_2 reaction are in excellent agreement with the present results. The $O(^1D)$-N_2 interaction is critical in determining the vibrational temperature of the terrestrial upper atmosphere.

(3) The $O(^1D)$-CO_2 interaction was investigated by infrared techniques. Apparent high quenching efficiencies of vibrationally excited CO and CO_2, possibly due to high concentrations of $O(^3P)$ and $O_2(b^1\Sigma_g^+)$ generated in the flash photolysis experiment, prevented observation of the infrared signal. From current experiments on E → V transfer efficiencies, we believe that taking a value of 50% for the fraction of the $O(^1D)$ electronic energy transferred to CO_2 vibrations will not be far wrong.

CONTENTS

INTRODUCTION

The two principal subjects of investigation under this contract are the determination of the CO_2 photodissociation quantum yields at wavelengths from 1200 Å to 1500 Å and the investigation of the efficiency of electronic-to-vibrational energy transfer in the systems $O(^1D) + CO, N_2, CO_2 \rightarrow O(^3P) + CO^{\ddagger}, N_2^{\ddagger}, CO_2^{\ddagger}$.

The study of the CO_2 photodissociation quantum yields is a subject that generates interest in three areas. From a theoretical point of view, the concept of a polyatomic molecule that has energy above the dissociation threshold, and yet does not dissociate, is an intriguing one and requires explanation. From the standpoint of the chemistry of the atmospheres of Mars and Venus, the idea of the possible nondissociation of these atmospheres under solar uv radiation below 1500 Å presents a way to aid in explaining the low observed steady state concentration of CO and oxygen atoms. Lastly, many of the photochemistry studies carried out over the last 15 years have employed CO_2 as an actinometer in the vacuum uv region, and a quantum yield for CO production of unity has generally been assumed. A change in this assumption would have a significant retroactive effect.

The importance of the study of the $O(^1D) + CO_2$ reaction arises from the fact that in the planetary upper atmospheres, most of the absorbed solar radiation results in CO_2 photodissociation, via $CO_2 \xrightarrow{h\nu} CO + O(^1D)$. Because the quenching of $O(^1D)$ by CO_2 takes place on every collision, and the $O(^1D)$ loss is controlled by CO_2 quenching up to very high altitudes [$O(^1D)$ has a 110 sec radiative lifetime], it is important to determine how the 2 eV electronic energy of $O(^1D)$ is distributed among CO_2 degrees of freedom. If the electronic energy appears in rotational or translational modes, then it will contribute significantly to the kinetic

temperature of the atmosphere. If the energy goes into CO_2 vibrations, there is a high probability that it will radiate in the infrared and be lost to space. Up to this time, there has been very little information available on electronic-to-vibrational energy transfer.

The measurements on E → V transfer for $O(^1D)$-CO and $O(^1D)$-N_2 interactions were partially sponsored by this contract. It was important to study at least the former reaction because we had proposed using it as a standard against which to make absolute measurements on the $O(^1D)$-CO_2 system. The $O(^1D)$-N_2 system is, of course, of great relevance to the terrestrial atmosphere. At altitudes above $\sim$ 80 km, it is potentially the dominant source of vibrationally excited N_2 in the atmosphere unless the efficiency of the transfer $O(^1D) + N_2 \rightarrow O(^3P) + N_2^{\ddagger}$ is negligible. Prior to our work, the only two theoretical treatments of the system predicted a transfer efficiency of $\leq$ 5%.

RESULTS

CO_2 Photodissociation Quantum Yields

An article on the work on the CO_2 photodissociation quantum yields is being submitted to the Journal of Chemical Physics, and a copy is included as Appendix A. The principal conclusion is that in the 1200-1500 Å wavelength region, the quantum yield for CO production is not unity but is in fact quite variable. Our measurements were made using six different atomic line sources, some emitting multiple lines, and we found a variation from 0.22 for the OI triplet at ~ 1300 Å to 0.81 at 1236 Å. The data appear to correlate with the structure of the CO_2 absorption spectrum in that where the spectrum shows apparent vibrational structure, as around 1300 Å, the quantum yield is low; where the spectrum is continuous, the quantum yield is high.

These results are in accord with the conclusions of Inn[1] and of Sach[2] that not all photons absorbed at < 1600 Å lead to dissociation. This finding implies one or several metastable CO_2 states that do not predissociate under the experimental conditions but lose their energy through collisions or by radiation. If this is the case, the chemistry of these states should be studied, for among other effects, they could be important intermediates in the planetary atmospheres.

The work we have done so far on the photodissociation quantum yields seems to confirm that there are non-unity yields, as we had shown in preliminary experiments. The next stage is to make more detailed investigations, studying the entire spectral region between ~ 1100 Å and 1650 Å in an attempt to obtain a good correlation between dissociation yield and absorption cross sections. This would be a decided improvement over what we have so far been able to do, in that we have been limited to strong atomic line sources, which are of course scattered randomly throughout the spectral region. It is certainly possible to

construct a strong continuum lamp that will allow measurements to be made with 5-10 Å resolution over the 500 Å spectral range. From these data, we should ideally be able to separate the bound nondissociating states from the underlying continuum, which would be of great importance in furthering our understanding of the higher CO_2 excited states.

Electronic-to-Vibrational Energy Transfer

The work on the $O(^1D)$-N_2 and $O(^1D)$-CO E → V transfer has been published in the Journal of Chemical Physics [60, 468 (1974)]. The results indicated that the reaction

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2^{\ddagger} \qquad (1)$$

takes place with the conversion of 33% of the 2 eV energy of $O(^1D)$ to N_2 vibrational energy. This system has been under theoretical study by John Tully[3] of Bell Laboratories. Using an RRKM approach, he obtained a value of 30 ± 10% for the transfer efficiency, contradicting the value of ≤ 5% obtained by Fisher and Bauer,[4] and by Delos,[5] who used a curve-crossing model. We are very pleased with the good agreement between our value and Tully's. The relatively high efficiency indicates that, for the atmospheric problem, the $O(^1D)$-N_2 interaction is the principal determining factor for any disequilibrium between the kinetic and vibrational temperatures.

For the reaction

$$O(^1D) + CO \rightarrow O(^3P) + CO^{\ddagger} \qquad (2)$$

we find an E → V transfer efficiency of 40%, a figure with which Tully, in a private communication, is in accord. Although this reaction is unlikely to be of atmospheric importance, the details of the $O(^1D)$-CO interaction are important in obtaining a better understanding of intramolecular processes in CO_2.

Infrared Measurements on $O(^1D)$-Quenching Systems

As explained above, the measurements on the system $O(^1D)$-CO were undertaken to obtain an absolute standard against which to determine the transfer efficiency for the $O(^1D)$-CO_2 reaction. The $CO^{\ddagger}$ radiates at 4.7 μ, whereas the CO_2 ν_3 fundamental is at 4.3 μ. These wavelengths are close enough to permit direct comparision between the intensities of ir emission from the two systems. Thus, it was first necessary to observe infrared radiation from the $O(^1D)$-CO system before radiation from the $O(^1D)$-CO_2 system could be adequately interpreted.

Since we had determined that the $O(^1D)$-CO transfer efficiency was 40%, it seemed clear that with a reasonably intense flash lamp source, it should not be difficult to observe the 4.7 μ CO fundamental. Unfortunately this was not the case, and the reasons are still not clear.

Basically, it was ascertained that the flash lamp intensity distribution was such that approximately 5×10^{15} quanta/flash were available below 1550 Å, so that when O_2 was used as the source of $O(^1D)$, it was possible to produce more than 10^{16} CO(v=1) molecules/flash from the $E \rightarrow V$ transfer in the $O(^1D)$-CO system. Such a concentration should have been detected with a signal/noise ratio of ~ 100, without using signal averaging techniques. Although cw measurements demonstrated the high sensitivity of the ir detection system, we were never able to observe a signal associated with either the $O(^1D)$-CO or the $O(^1D)$-CO_2 interactions, even with signal averaging. In Appendix C, the experiments are described in detail, reasons suggested for the negative results, and recommendations indicated for possible subsequent experiments to clarify the situation.

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APPENDIX A

THE PHOTODISSOCIATION QUANTUM YIELDS OF CO_2 BETWEEN 1200 Å AND 1500 Å †

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Abstract

Measurements of the photodissociation quantum yield of CO_2 have been carried out using various atomic line sources between 1200 Å and 1500 Å. The production of CO was monitored by resonance fluorescence, and the results indicate that where the CO_2 absorption spectrum is continuous, the CO quantum yield is high, but where there is structure, the yield is low. At the commonly employed 1236 Å resonance line, the CO quantum yield is 0.85 ±0.17, relative to the absolute value at 1470 Å of 0.75 obtained by Inn. On the same scale, the other values are: 1216 Å, 0.57 ±0.11; 1302-1306 Å, 0.21 ±0.07; ~ 1390 Å, 0.46 ±0.05; 1492-1495 Å, 0.58 ±0.06. The CO_2 pressures employed were in the range 0.4-4.0 torr. If these same quantum yields are valid at the pressures of the Mars and Venus atmospheres, the CO and O atom production rates are less than presently assumed.

INTRODUCTION

Photodissociation of CO_2 has often been used as an actinometer in the vacuum-uv spectral region, since it has been generally believed that dissociation between 1200 Å and 1650 Å leads to a single set of products, CO and $O(^1D)$, with a quantum yield of unity. This conclusion is based on various measurements[1] carried out over the last 15 years, principally at the two convenient rare gas resonance lines, Xe 1470 Å and Kr 1236 Å.

Recent measurements by Inn[2] have indicated that at 1470 Å the photodissociation quantum yield is not unity, but 0.75, and even lower at longer wavelengths. If true, this is a significant result, having a bearing not only on laboratory actinometry, but also on the details of the photochemistry of the CO_2 atmospheres of Mars and Venus. One of the problems associated with the aeronomy of these planets is that the CO_2 is almost undissociated, which is a surprising observation in view of the fact that CO_2 is readily dissociated in the laboratory.

There are two possible explanations for this phenomenon: either the recombination of oxygen atoms and carbon monoxide is unexpectedly rapid under conditions pertinent to the planetary atmospheres, or else CO_2 in fact does not dissociate under these conditions. Both of these possibilities have been investigated. Although the direct three-body recombination of $O(^3P)$ and CO is much too slow[3] to re-form CO_2 except perhaps at low altitudes, there now exist catalyzed recombination schemes that could

proceed fast enough to maintain the observed composition. The one in current favor[4] involves trace amounts of HCl and H_2O.

An alternative to CO_2 dissociation following photon absorption is fluorescence, and Clark and Noxon[5] carried out an experiment to look for fluorescence, with negative results. Felder et al.[6] investigated the possibility of collision-induced dissociation at high CO_2 pressures, but their results indicated, albeit with fairly large error limits, that the yield, at least for 1470 Å excitation, was invariant with pressure.

In the face of these facts stand Inn's measurements.[2] In a preliminary account,[7] we reported that we had measured the CO_2 photodissociation quantum yield at several wavelengths, relative to the value at 1470 Å, and found that it was indeed quite variable, with the maximum yield being obtained at 1470 Å. We considered these experiments worth repeating, and report here the results of a more careful investigation.

EXPERIMENTAL

The experiment consists of measuring by resonance fluorescence the CO produced during CO_2 photodissociation. Measurements are made using various atomic lines of calibrated intensities as photodissociation sources, utilizing an approximately constant fractional light absorption by CO_2 ($\sim$ 1%/cm).

The atomic lamps that were used are listed in Table 1. Since there was no spectral dispersion, in some cases dissociation was performed with multiple lines, so that the final quantum yields are an average for the lines. Table 1 lists the measured relative intensities for the multiple lines as well as the CO_2 absorption cross-section measured for each line. The latter was obtained by measuring the intensity attenuation of the lines as a function of the pressure of CO_2 introduced into a 0.5 meter spectrograph. Table 1 also includes the CO_2 absorption cross-section measured by Nakata et al.,[8] with 0.5 Å resolution. It may be that the increased resolution available with the atomic lines is the cause of the observed differences that appear [e.g., N(1494.7 Å) and Cl(1379.5 Å)].

As shown in the diagram of the apparatus in Figure 1, the atomic line sources are mounted on top. The Xe and Kr lamps are sealed, and the others contain flowing gases with premixed compositions of 1% O_2 in Ar, 10% N_2 in He, 10% H_2 in He, and 0.2% Cl_2 in He.

The attenuating chamber below the source lamp is used to spectrally purify the lamp emissions. Table 2 lists the attenuating gases used in each case. The atomic line of interest was turned off by flowing the blocking gas (in addition to the spectrum purifying gas) through the attenuation chamber. Using this technique to determine the intensity of the atomic line, the attenuation produced by the addition of a known pressure of CO_2 to the cell (34 cm path length) was generally consistent with the measured cross sections (Table 1). Furthermore, the emission

from each lamp was observed with a vacuum monochromator, so that it was clear what gas filter was needed in the upper attenuating chamber.

The relative emission intensities of the dissociating lamps were measured with a Scientific Services Model 203A photodiode, which has a CsI photocathode and is thus insensitive to wavelengths longer than 1900 Å. The photodiode was calibrated after the experiment against an EMR 543P-09-00 photodiode, which has an RbTe photocathode for which an absolute calibration was available. The wavelength dependence of transmission of the cell window above the photodiode, between 1200 Å and 1500 Å, was determined after the experiment.

The CO generated during CO_2 photolysis was measured by CO resonance fluorescence, the exciting lamp being an unfiltered, Kr-filled Pyrex tube, with a sapphire window. As has been shown in earlier work,[9] this is an adequate source of $CO(A\,^1\Pi \rightarrow X\,^1\Sigma^+)$ fourth-positive radiation. Since the only desired emissions from this lamp are the (v'-0) bands, there is considerable undesirable radiation at wavelengths above 1550 Å that both dissociates CO_2 and is a source of scattered light. To decrease this radiation, the 2-cm long attenuation chamber in front of the lamp was flushed with a mixture of 2% H_2O in Ar, which aids considerably in removing the long wavelength radiation.

The detector of the resonance radiation was an EMR 542G-08-18 solar-blind photomultiplier, also with a CsI photocathode. Due to the falloff of sensitivity of the detector, most of the detected radiation was in the

1550 Å to 1700 Å region. A detector attenuation chamber in front of the photomultiplier was swept with dry N_2.

Measurements were made by injecting CO_2 into the closed cell, and observing the increase of fluorescent intensity as CO was generated, with the photomultiplier output passing through a bucking circuit to an HP 425A ammeter, and thence to a strip chart recorder. Since the CO lamp itself was a source of dissociating radiation, it was necessary to use the CO generation rate when the atomic line was removed as a base condition, and obtain the desired generation rate by difference. The atomic line was removed with the blocking gase (see Table 2) as described previously.

The choice was made of performing the experiments at approximately constant optical depth, 30% absorption over the 34 cm length of the cell. Thus, the CO generated by the atomic line lamp was produced in a similar spatial configuration for all cases. However, as there is a factor of 15 variation in the CO_2 absorption cross section for the different lamps, this means that the CO_2 pressure varied by a similar factor. Since both the CO exciting and fluorescent radiations are absorbed by CO_2, and the fluorescent radiation is probably quenched by CO_2, the sensitivity of the system to CO decreased at the higher CO_2 pressures. Thus, after each measurement of the CO generation rate, the same CO_2 pressure was flowed through the cell, and diluted CO was added to determine the system sensitivity.

The various attenuating and lamp gases used were of Matheson C.P. purity, while the CO_2 was Coleman Instrument Grade (99.99%).

RESULTS

Figure 2 shows typical CO generation curves for Xe(1470 Å) and O(1302 -1305 Å) radiation, the lower curve referring to the CO lamp alone, the upper curve to both lamps. Over the same CO range, the CO calibration curves for the different CO_2 pressure conditions are linear.

The data for the six lamps are tabulated in Table 3. In the final columns, all the measurements are put on approximately the same scale by adjusting to complete absorption and an empty cell lamp intensity of 100 na. In Table 4 the final corrections are made for the lower window transmission and the photodiode sensitivity. In the final column, the quantum yields are expressed relative to Inn's value of 0.75 for 1470 Å radiation.

The problems encountered by Felder et al.[6] in their study, with relation to CO ejection from the walls, did not cause any difficulties in this experiment because we worked at generally higher pressures and the CO lamp was filtered to block non-useful radiation. As an example, for the L_α experiment, the CO production rate from the walls with both lamps on but with no CO_2 in the cell was only 7% of that after the CO_2 was

introduced. In any case, any correction for heterogeneous CO production would result in even lower quantum yields than those listed in Table 4.

One observation for which a satisfactory explanation is lacking is the curvature that appears in the CO production plots of Figure 2, which becomes more noticeable after several minutes. This phenomenon is not due to optical thickness of the CO, since the calibration plots are linear over the same concentration region. Since the fractional absorption of the photodissociation radiation is only 30%, the apparently decreasing CO production rate cannot be due to nonhomogeneous absorption in the static CO_2 in the cell. Furthermore, there is no evidence that the cell walls are a sink for CO, as the fluorescent signal from a small amount of CO in the closed cell does not change. Whatever the cause of the effect, we have always obtained the CO production rates from the initial slope of the intensity traces, while the CO buildup is linear with time.

The error limits given in Table 4 reflect only the precision of the data. In terms of accuracy, it is obviously more satisfactory to do the experiments with the strong sources (Xe, N, Cl) than the weak sources (O, H, Kr), as the contribution of the CO lamp to CO_2 photolysis is then relatively less. Using somewhat subjective estimates, we feel that the data with the Xe, N, and Cl lamps is reliable to ±10%, while for the H and Kr lamps, ±20% limits are reasonable. Because of the additional difficulty of the low quantum yield at the oxygen line, ±35% limits are estimated for the triplet of lines at 1302 Å to 1306 Å.

DISCUSSION

Until recently, most measurements of CO_2 photodissociation quantum yields have been carried out at two wavelengths, 1236 Å and 1470 Å. As may be seen in Table 4, these wavelengths give, coincidentally, the highest quantum yields. The workers who obtained a value of unity at 1236 Å would presumably not be prepared to argue that this would exclude a value of 0.85; similarly, our error limits for Kr radiation include a value of unity. Likewise, for Inn's value at 1470 Å of 0.75 ±0.15, there is overlap with the earlier data, and in fact, that is one reason why Inn's results have not been taken as absolute proof of nonunity quantum yields. In any case there is no serious discrepancy between the unity quantum yield determinations of earlier workers and our measurements at 1236 Å and 1470 Å.

However, with the four other lamps used, the situation is quite different, with the most dramatic effect occurring at ~ 1300 Å, where a quantum yield of 0.21 is obtained. An absorption spectrum for CO_2 in the region of interest[8] is presented in Figure 3. Our six points represent photodissociation cross sections, although the line joining them has no physical significance. Comparing the values in Table 4 and the form of the absorption spectrum, there is a correlation that is immediately apparent. The lowest dissociation quantum yield, at ~ 1300 Å, occurs in the most highly structured region [the O(1302 Å) line is practically at the peak of the 1302.5 Å CO_2 band], whereas the highest value, at 1236 Å,

occurs in a region with virtually no structure. This suggests the view that the absorption spectrum consists of a dissociative continuum, with superimposed bands corresponding to one or more bound CO_2 states, from which energy can be lost without dissociation. This would be substantiated if the minima in the absorption spectrum coincided with the points on the dissociative curve. That they do not could be an indication that the spectrum was taken with insufficient resolution. Although our absorption measurements, made with atomic lines, are not substantially different from the data of Nakata et al.[8] taken with an instrumental resolution of $\sim 10\ cm^{-1}$, it is probably not correct to assume that the lines from the atomic lamps have a Doppler width of 0.1 to 0.2 cm^{-1}, and therefore represent absorption cross sections measured at two orders of magnitude higher resolution. We have measured the FWHM for the Xe (1470 Å) line as 23 cm^{-1}, presumably due to emission from Xe_2, and the same characteristic is to be expected from the Kr lamp.[10] Measurements by Poland and Lawrence[11] on oxygen lamps indicate FWHM values of $\sim 1\ cm^{-1}$. Thus, it still remains to be determined whether more structure can be seen in the absorption spectrum with resolution of 0.5 cm^{-1} or better. Because of small rotational constants, the density of rovibronic transitions is much higher in a polyatomic molecule than in a diatomic, and resolution of this sort is required. As an example, in the 3610 Å band of CS_2, the density of transitions[12] is 3 to 10 per cm^{-1}. Therefore, although the lack of fine structure in the CO_2 absorption spectrum has been taken as

an indication of predissociation, it is obvious that such a conclusion cannot yet be drawn.

If nonunity quantum yields are accepted on the basis of our measurements, those of Inn,[2] and those of Sach[13] (who obtained $\phi_{Xe} \sim 0.7$ and $\phi_{Kr} \sim 0.4$, although at much higher CO_2 pressures), then one must determine whether a reasonable explanation exists. The energy above the dissociation limit must be dissipated either in fluorescence or in collisional processes, and as mentioned in the Introduction, both of these possibilities have been investigated. In Clark and Noxon's study,[5] a 1500 Å to 1700 Å continuum source was used to irradiate CO_2, and two types of observations were performed, a search was made for fluorescence, and pressure-dependence for the absorption was determined. No pressure-dependence was detected and indeed, pressure effects in such a system would not be expected at pressures of less than one atmosphere. The conclusions of the fluorescence experiments were based on a value for the radiative lifetime of the excited state of 10^{-7} sec, which is the approximate value that can be calculated from the integrated absorption coefficient over the 1400 Å to 1600 Å range. No fluorescence was seen between 1500 Å and 8000 Å, over a range of CO_2 pressures of 1 mtorr to 10 torr. Low upper limits were thereby set on the fraction of excited CO_2 molecules fluorescing. However, these conclusions are modified if we assume a lifetime of 10^{-5} sec and a cross section for energy transfer of 10^{-9} $cm^3 molec^{-1} sec^{-1}$, instead of 10^{-7} sec and 3×10^{-10} $cm^3 molec^{-1} sec^{-1}$ as used by Clark and Noxon. In

that case, instead of 0.2% being an upper limit for the fraction of CO_2^* molecules that are capable of fluorescing below 8000 Å, the figure becomes 6%, which is getting into the interesting region. The justification for suggesting that the lifetime may be closer to 10^{-5} sec than 10^{-7} sec is based on the situation with other triatomic molecules, in which it is well known that emission lifetimes may be much longer than the lifetime based on the absorption coefficient. For NO_2, CS_2, and SO_2, the discrepancy may be as great as two orders of magnitude.[14] The usual explanation, given initially be Douglas,[14] is that once the molecule has reached the excited electronic state, it interacts with other nearby electronic states which may have densely packed vibrational and/or rotational levels. Through internal conversion processes, the energy may become dispersed throughout the levels in this second state, which does not communicate with the ground state. The unexpectedly long radiative lifetime is then a measure of the internal conversion rate, as the energy returns to the originally excited state. Such observations have only been made on the triatomic molecules below their first dissociation limit, but that does not preclude similar effects appearing in the CO_2 system under consideration. It therefore seems premature to rule out the possibility of CO_2 fluorescence at low pressure.

If a nonpredissociated CO_2^* state is formed, then at pressures high enough that fluorescence does not occur (for the parameters suggested above, quenching predominates over fluorescence at $p > 3$mtorr), the

molecule may either be collisionally stabilized, or possibly collisionally induced dissociation could occur. For the former case, the photodissociation quantum yield would be pressure invariant; for the latter case, it would increase with pressure throughout the pressure region where fluorescence and collisional quenching are competing. Felder et al. attempted to test the possibility of collisionally induced dissociation, and CO production rates were measured from 2 mtorr to 20 torr CO_2, using 1470 Å excitation. Unfortunately, the error limits are too large to reach meaningful conclusions. Relative to $\phi = 1$ at 20 torr, they found $\phi = 2.0 \pm 1.1$ at 10 torr, $\phi = 0.9 \pm 0.52$ at 1 torr, and $\phi = 1.6 \pm 1.1$ at 8 mtorr. At low pressures, the problem with CO photoejection was severe, and difficulties were apparently experienced with the 1470 Å lamp stability (a problem not arising in our experiment, as Table 3 shows). Furthermore, particularly in light of the present work, it would be more definitive to carry out the experiment at 1300 Å rather than 1470 Å, where the photodissociation quantum yield is relatively high. It thus appears to us that on the questions of collisional stabilization or collisionally induced dissociation, the experiments so far performed do not lead to conclusions that are inconsistent with the low quantum yields that we obtain.

Nevertheless, when a triatomic molecule absorbs radiation greater than that required for dissociation, there are many more predissociative pathways available to it than is the case for a diatomic molecule. Even though absorption occurs into bound electronic states, the bent components

of these states can mix with bent components of repulsive states, or bound states having lower dissociation limits, resulting in a higher probability for predissociation. As pointed out in a recent paper by Hall et al.,[15] the presence of vibrational structure in the CO_2 spectrum does not in itself prove that the upper states are stable. Moreover, since diffuse absorption lines are not a prerequisite for a predissociating system, even if it could be demonstrated that the CO_2 spectrum has rotational structure, indicating a lifetime long compared to rotational time constants ($\sim 10^{-12}$ sec), this would not necessarily prove that under the proper conditions fluorescence would be observed (with lifetimes $> 10^{-8}$ sec).

Nevertheless, the recent experiments do indicate that there are stable excited CO_2 states, and further work will be required to obtain a more complete understanding of the phenomenon. Compared to what is known of the electronic states of diatomic molecules, our knowledge of triatomic states is fairly primitive. The most complete calculations to date are in a recent paper by Winter et al.,[16] in which they have determined the energies at the equilibrium distance of ten CO_2 states. However, information on interaction between the various states is almost totally lacking so that one can as yet do little more than speculate about the quantum yield effects.

In the solar flux, 75% of the radiation between 1200 Å and 1500 Å is in the L_α line. Therefore, from the standpoint of overall CO and O

production, the new results suggest a decrease of a factor of about 2 in the photodissociation rates in the Mars and Venus upper atmospheres. However, high in the atmospheres, where the L_α optical density is very low, photodissociation at 1250 Å to 1500 Å will be more important and the average reduction in photodissociation rate may be by a larger factor. It is, of course, still to be ascertained whether these quantum yield values are also valid at submicron CO_2 pressures, representative of the absorbing regions.

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Table 1

ATOMIC LINE LAMP CHARACTERISTICS

Lamp	λ(Å)	Relative Multiple Intensities	CO_2 Absorption Cross Sections (NTP)	
			This Work	Nakata et al.[8]
N	1494.7	0.60	17.1	13.7
	1492.6	1.00	17.1	16.5
Xe	1469.6	-	18.1	17.8
Cl	1396.5	0.35	13.8	12.9
	1389.7	1.00	14.9	13.3
	1379.5	0.13	21.1	16.7
	1363.4	0.17	16.8	16.2
O	1306.0	1.00 (combined)	18.2	22
	1304.9		19.9	22
	1302.2	0.85	32.7	29
Kr	1235.8	-	3.4	3.5
H	1215.7	-	2.2	2.2

Table 2

ATOMIC LINE LAMP ATTENUATORS

Lamp	Filter Gas	Added Blocking Gas
N	2.5% CH_4 in N_2	0.2% O_2 in Ar
Xe	He	Air
Cl	1% H_2O in N_2	2.5% CH_4 in N_2
O	He (CaF_2 window)	10% CH_4 in N_2
Kr	4% CO_2 + 0.5% O_2 in Ar	1.5% N_2O in Ar
H	5% O_2 in Ar	2.5% CH_4 in N_2

Table 3

LAMP INTENSITY AND CO PRODUCTION RATE

		Transmitted Lamp Intensity (na)			CO Production Rate (in mtorr/min)				
Lamp	pCO_2 (torr)	No CO_2	With CO_2	Fraction Absorbed	CO(4+) Lamp	Both Lamps	Difference	Normalized*	Average
N	0.58	29.0	19.5	0.328	0.009	0.026	0.017	0.179	
		29.0	19.5	0.328	0.010	0.030	0.020	0.213	
		31.0	21.0	0.323	0.011	0.029	0.018	0.184	0.192 ±0.014
Xe	0.55	138	96	0.304	0.004	0.104	0.100	0.238	
		138	96	0.304	0.006	0.111	0.105	0.250	
		139.5	96	0.312	0.007	0.118	0.111	0.255	0.248 ±0.008
Cl	0.72	46.0	27.5	0.402	0.013	0.046	0.033	0.178	
		46.0	26.5	0.424	0.013	0.043	0.030	0.154	
		45.0	27.0	0.400	0.013	0.044	0.031	0.173	0.168 ±0.010
O	0.38	6.20	4.30	0.306	0.0049	0.0065	0.0016	0.085	
		6.25	4.20	0.328	0.0038	0.0067	0.0029	0.140	
		6.50	4.10	0.370	0.00525	0.0068	0.00155	0.065	0.097 ±0.029
H	4.0	5.35	3.85	0.280	0.036	0.043	0.0071	0.467	
		5.50	3.80	0.310	0.034	0.040	0.0061	0.363	0.415 ±0.052
† Xe	0.50	122	85	0.305	0.0014	0.0786	0.0772	0.207	†
† Kr	2.4	7.20	5.16	0.281	0.0099	0.0180	0.0081	0.400	†

*Normalized to total absorption and 100 na lamp intensity.

†The initially taken Kr data was found to be invalid due to incorrect manipulation of the filter gases. At a later time, single runs were made to obtain a comparison between Xe and Kr.

Table 4

QUANTUM YIELD DETERMINATION

Lamp	Normalized CO Production Rate (Table 3)	Lower Window Fractional Transmission	Photodiode Quantum Efficiency	Final Quantum Yield*
N	0.192 ±0.014 mtorr/min	0.390	14.5%	0.58 ±0.05
Xe	0.248 ±0.008	0.375	15.0	0.75
Cl	0.168 ±0.010	0.315(1390 Å)	16.2	0.46 ±0.04
O	0.097 ±0.029	0.250	16.2	0.21 ±0.07
H	0.415 ±0.052	0.175	14.5	0.57 ±0.09
Xe	0.207	0.375	15.0	0.75
Kr	0.400	0.220	15.0	0.85

†

*Relative to Ø(Xe) = 0.75

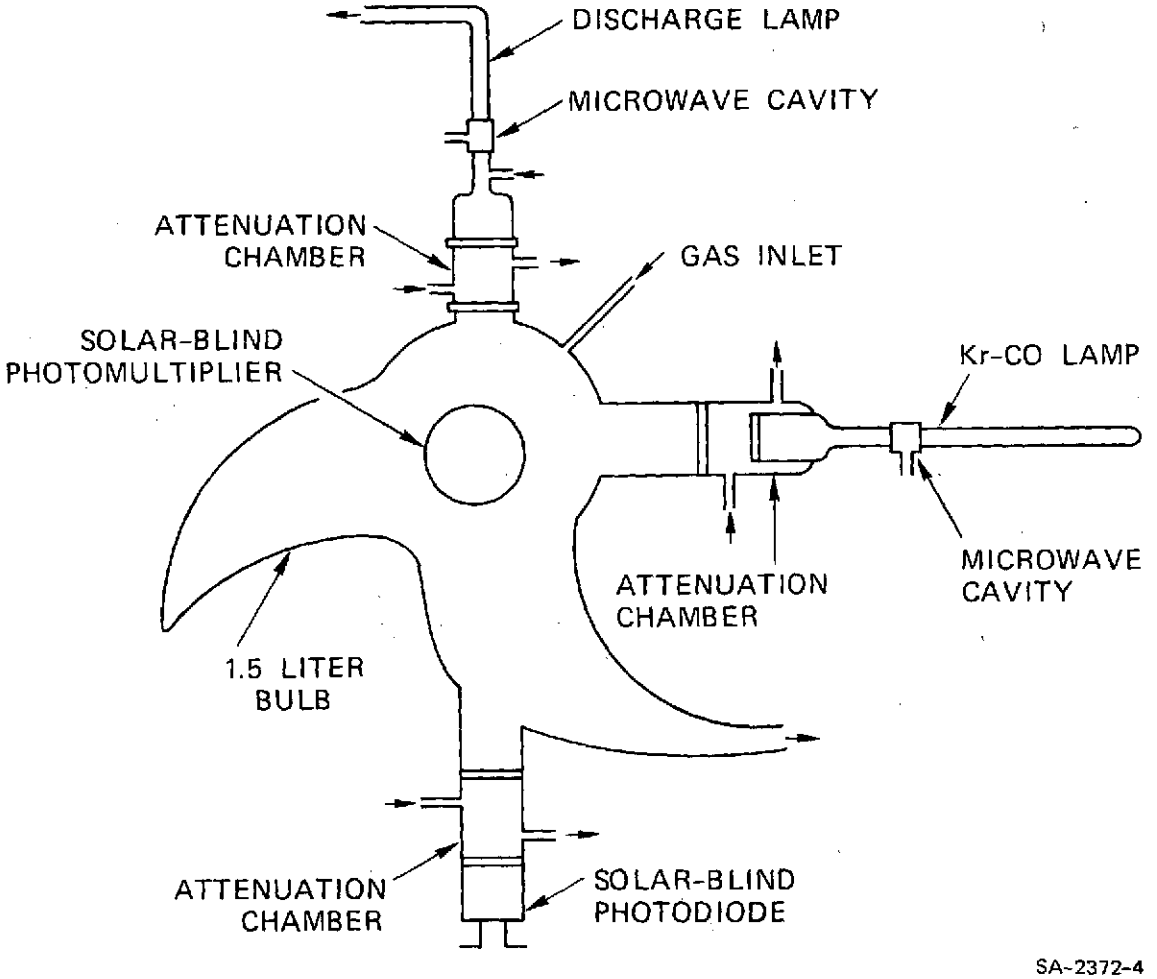
†See note on Table 3.

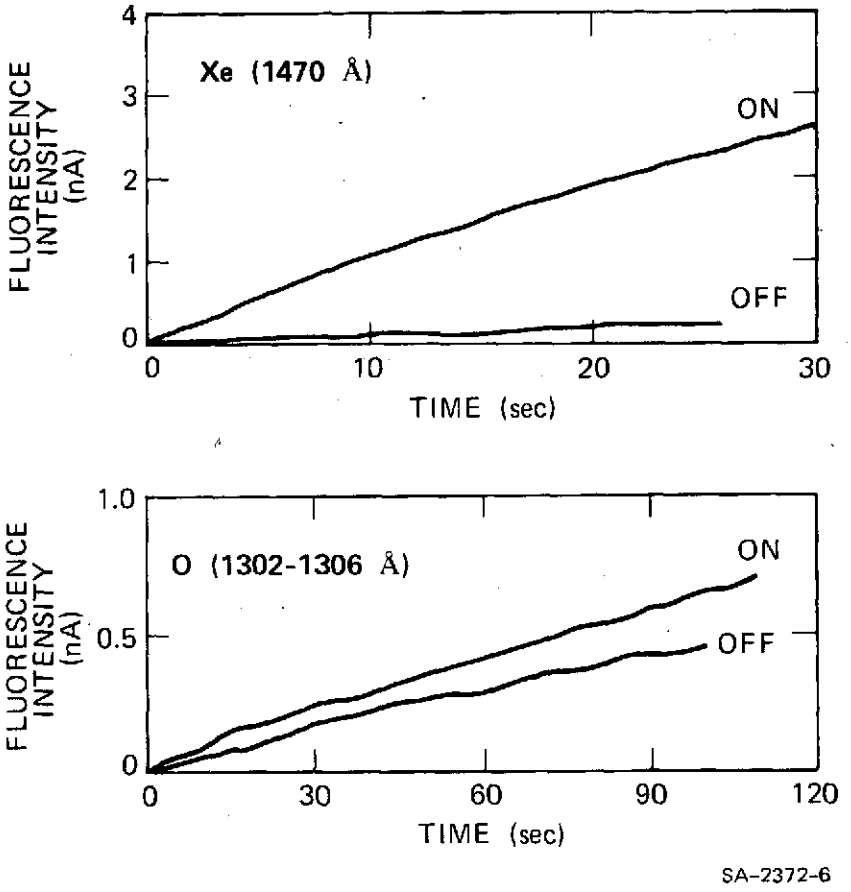
FIGURES

1. Apparatus for Photodissociation Measurements

2. CO fluorescence signal buildup for two lamps: intensity (nanoamperes) vs time (seconds). Lower line--CO lamp only, upper line--both lamps. CO_2 pressures--Xe, 0.55 torr; O, 0,38 torr.

3. CO_2 photoabsorption and photodissociation coefficients; CO_2 pressure range, 0.38-4.0 torr. Open circles--measured absorption coefficients. Photoabsorption data from reference 8.


DISCHARGE LAMP
MICROWAVE CAVITY
ATTENUATION CHAMBER
GAS INLET
SOLAR-BLIND PHOTOMULTIPLIER
Kr-CO LAMP
MICROWAVE CAVITY
ATTENUATION CHAMBER
1.5 LITER BULB
ATTENUATION CHAMBER
SOLAR-BLIND PHOTODIODE
SA-2372-4


Xe (1470 Å)
ON
OFF
FLUORESCENCE INTENSITY (nA)
TIME (sec)
0
1
2
3
4
0
10
20
30
O (1302-1306 Å)
ON
OFF
FLUORESCENCE INTENSITY (nA)
TIME (sec)
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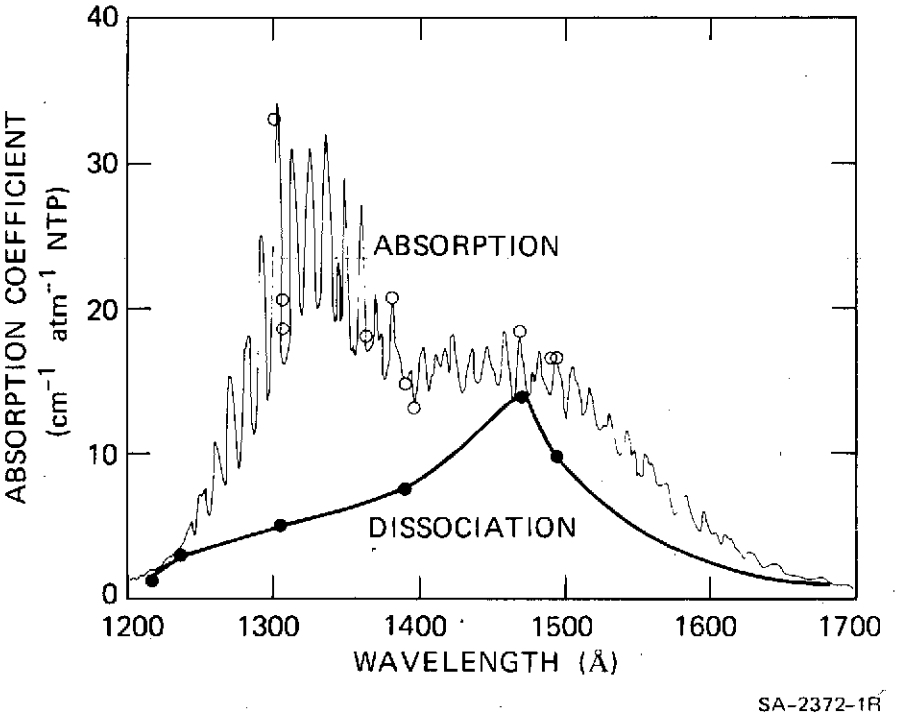
0.5
1.0
0
30
60
90
120
SA-2372-6


40
30
20
10
0
ABSORPTION COEFFICIENT
(cm^{-1} atm^{-1} NTP)
ABSORPTION
DISSOCIATION
1200
1300
1400
1500
1600
1700
WAVELENGTH (Å)
SA-2372-1R

APPENDIX B

ELECTRONIC-TO-VIBRATIONAL ENERGY TRANSFER EFFICIENCY IN THE $O(^1D)$-N_2 AND $O(^1D)$-CO SYSTEMS

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Electronic-to-vibrational energy transfer efficiency in the $O(^1D)$–N_2 and $O(^1D)$–CO systems*

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(Received 27 August 1973)

With the aid of a molecular resonance fluorescence technique, which utilizes optical pumping from the $v=1$ level of the ground state of CO by $A^1\Pi - X^1\Sigma^+$ radiation, we have investigated the efficiency of E-V transfer from $O(^1D)$ to CO. $O(^1D)$ is generated at a known rate by O_3 photodissociation at 1470 Å in an intermittent mode, and the small modulation of the fluorescent signal associated with $CO(v=1)$ above the normal thermal background is interpreted in terms of the $E-V$ transfer efficiency. The $CO(v=1)$ lifetime in this system is determined mainly by resonance trapping of the ir fundamental band, and is found to be up to ten times longer than the natural radiative lifetime. For CO, $(40 \pm 8)\%$ of the $O(^1D)$ energy is converted into vibrational energy. By observing the effect of N_2 on the $CO(v=1)$ fluorescent intensity and lifetime, it is possible to obtain the $E-V$ transfer efficiency for the system $O(^1D)$–N_2 relative to that for $O(^1D)$–CO. The results indicate that the efficiency for N_2 is $(83 \pm 10)\%$ of that for CO. In both cases the initial vibrational distribution remains unspecified. The relatively high efficiency of the $O(^1D)$–N_2 reaction implies that it is the sole source of the N_2 vibrational temperature in the earth's upper atmosphere.

INTRODUCTION

Electronic-to-vibrational ($E-V$) energy transfer has been studied in only a few systems, and most involve transfer of energy from an electronically excited atom to a molecule, or the reverse process, electronic excitation of an atom by a vibrationally excited molecule. Studies to date have included the systems $Na(3^2P)$–N_2,[1] $Na(3^2P)$–CO,[2] $Hg(^3P_{0,1})$–CO,[3] $Hg(^3P_{0,1})$–NO,[4] and $O(^1D)$–O_2.[5] It is clearly desirable to investigate more instances of such processes, to aid in the development of an adequate theoretical understanding of this energy transfer mechanism.

In this paper we present measurements of the $E-V$ transfer efficiency for $O(^1D)$ interactions with CO and N_2. In neither case is the initial vibrational distribution obtained, only the total fraction of electronic energy converted into vibrational energy. The system $O(^1D)$–N_2 is of particular aeronomic interest, because practically all solar radiation between 1000 and 3000 Å produces $O(^1D)$ at some altitude in the earth's atmosphere, by photodissociation of either O_2 or O_3, and at all altitudes below 200 km at least 75% of the $O(^1D)$ is deactivated by N_2. Thus, the reaction

$$O(^1D) + N_2 - O(^3P) + N_2^\ddagger, \tag{1}$$

if efficient, can determine the N_2 vibrational temperature of the upper atmosphere, which in turn is related to the electron temperature and to the radiation from infrared emitting species such as CO_2 and H_2O.

The atmospheric N_2 vibrational temperature has been modeled by various investigators,[6–7] but the lack of knowledge of the $E-V$ transfer efficiency for the $O(^1D)$–N_2 interaction has always introduced a large uncertainty into the calculations. A recent paper by Fisher and Bauer[8] dealt with this system, using a model of curve crossing involving covalent N_2O states. They concluded that no more than 5% of the 1.97 eV electronic energy of $O(^1D)$ goes into N_2 vibrational energy.

On the basis of our previous work with resonance fluorescence techniques in CO,[9] we have been able to extend this type of measurement to the study of molecules in the $v''=1$ level of the $X^1\Sigma^+$ ground state. By utilizing the (0-1) band of the $A^1\Pi - X^1\Sigma^+$ system, we find that it is very easy to monitor the ambient $v''=1$ concentration in CO, and by modulating the $O(^1D)$ source, we can ascertain the contribution of the reaction

$$O(^1D) + CO - O(^3P) + CO^\ddagger \tag{2}$$

to the CO ($v''=1$) concentration. The effect of added N_2 on the CO ($v''=1$) concentration can then be analyzed to obtain the efficiency of Reaction (1).

EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. The essence of the technique is that CO molecules in the $v''=1$ level are continually monitored by scattering of the $A-X$ (0-1) radiation from the lamp mounted at the bottom of the cell. The lamp is fueled with a mixture of 1% CO_2 in argon, an excellent source of CO Fourth-Positive radiation. The ratio of population between the $v''=1$ and $v''=0$ levels, $[v''=1]/[v''=0]$, is 3.1×10^{-5} at 297 °K, and since the lamp is also a source of all the $(v'-0)$ bands, some method must be used to prevent detection of the $v''=0$ levels.

The longest wavelength $(v'-0)$ band is the $(0-0)$ band at 1544 Å, whereas the longest wavelength $(v'-1)$ band is the $(0-1)$ band at 1597 Å. Thus we need a means of discriminating against the $(0-0)$ band relative to the $(0-1)$ band by approximately five orders of magnitude, i.e., the observed fluorescent signal must relate only to the $v''=1$ population, although the $v''=0$ population is 3×10^4 times greater. Since we did not wish to diminish the fluorescent signal by passing the lamp radiation through a monochromator, the same effect was achieved by blocking the CO lamp radiation with ethane, passed through attenuation chamber No. 1. This chamber was 6 cm in length, and the C_2H_6 absorption cross sections at 1544 and 1597 Å are 2.0 and 0.1 $cm^{-1}\cdot atm^{-1}$, respectively.[10] Thus, with undiluted ethane, it is possible to

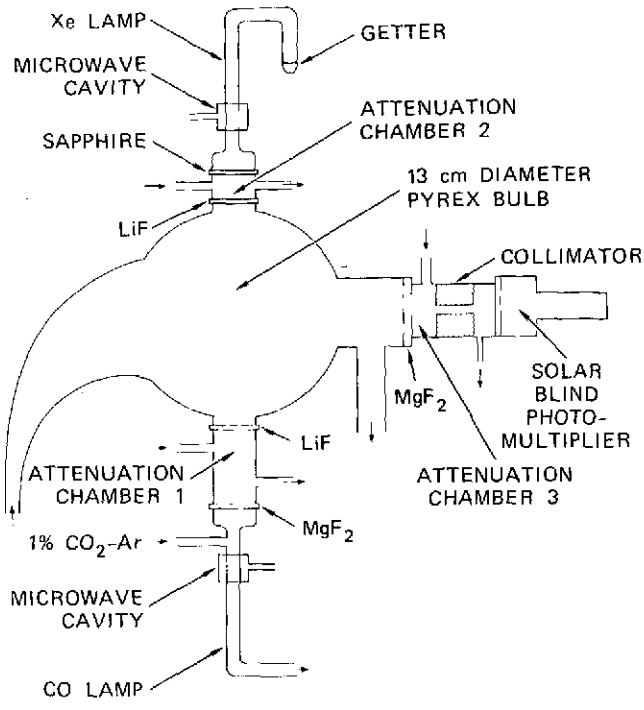

FIG. 1. Reaction cell and lamps.

attenuate the 1544 Å radiation by a factor of 1.6×10^5. However, such a large discrimination factor is not necessary, since at the pressures of CO used in the cell (generally greater than 1 torr), the CO acts as an internal filter. In an earlier paper[11] we measured the cross section for absorption of $A-X$ $(v'-0)$ radiation as 3×10^4 $cm^{-1}\cdot atm^{-1}$ (defining the cross section as the natural log of the attenuation factor divided by the product of path length times CO pressure), so that at 1 torr CO, the $(v'-0)$ radiation penetrates into the cell to a depth of only 0.25 mm (for an optical density of unity). Most of the $(v'-0)$ radiation is therefore trapped very close to the entrance window, out of sight of the detector. Radiation in the wings of the $(v'-0)$ rotational lines will penetrate to a greater extent, as will radiation from high rotational levels, but the undiluted ethane is no longer needed to achieve the necessary discrimination. A 20% mixture in helium at atmospheric pressure was found to be adequate. Figure 2 shows the lamp output spectrum with and without ethane filtering.

The source of $O(^1D)$ is the photodissociation of O_2 by the 1470 Å radiation from the Xe resonance lamp. It is naturally a requirement that the 1470 Å radiation not be a source of $CO^\dagger$. However, we have demonstrated in the past[12] that CO does absorb 1470 Å radiation weakly, to produce $CO(d^3\Delta)_{v=7}$. At the pressures used in the present experiment, it is clear that the unattenuated 1470 Å radiation is a source of $CO^\dagger$, the pathway being

$$CO \xrightarrow{1470\ \text{Å}} CO(d^3\Delta)_{v=7} \xrightarrow{M} CO(A^1\Pi)_{v=2} \rightarrow CO(X^1\Sigma^+)_{v\geq1} + h\nu \quad (3)$$
$$\downarrow V\text{-}V \text{ transfer}$$
$$CO(X^1\Sigma^+)_{v=1}$$

The cross-relaxation between the $d^3\Delta$ and $A^1\Pi$ states, discussed in an earlier series of papers,[11,12] is easily shown by measuring the intensity of the $A-X$ radiation as a function of inert gas, M.

We eliminate this source of $CO(v''=1)$ and prevent $CO(v''=1)$ production in the absence of O_2 by passing a 20% mixture of CO in Ar at atmospheric pressure through the 2 cm long attenuation chamber No. 2, in front of the Xe lamp. This reduces the total 1470 Å flux by ~ 20%, but decreases by a factor of 5 that component within the 1470 Å line profile that excites the $d^3\Delta_{v=7}$ level. Ultrahigh purity CO (> 99.8%) is required for this attenuation task, as lesser grades absorb too much of the 1470 Å line. It should be emphasized that the Xe lamp does *not* emit CO Fourth-Positive radiation.

The experiment is carried out by observing the transient signal with an EMR 542G-08-18 solar blind photomultiplier (LiF window, CsI photocathode) as the Xe lamp is pulsed. The lamp itself is turned off in ~ 30 μsec, while the decaying signal associated with $CO(v''=1)$ decays with a lifetime of 30–400 msec. Apart from the desired signal, light seen by the phototube consists of radiation scattered by the walls of the vessel and fluorescent scattering from the thermal population of $v''=1$ at 297 °K, the concentration of which is 9.8×10^{11} molecules/cm^3 torr. Both of these sources could be greatly diminished, the one by directing the lamps into Woods' horns rather than at each other, and the other by cooling the gas in the cell. However, as transient measurements were carried out, the high background light level did not create a significant problem. The 1470 Å radiation scattered from the walls is, of course, modulated, but the lamp turn-off time of 30 μsec does not interfere with the much longer decays of $CO(v''=1)$. Nevertheless, a mixture of 0.2% N_2O in Ar was passed in front of the photomultiplier, through attenuation chamber No. 3,

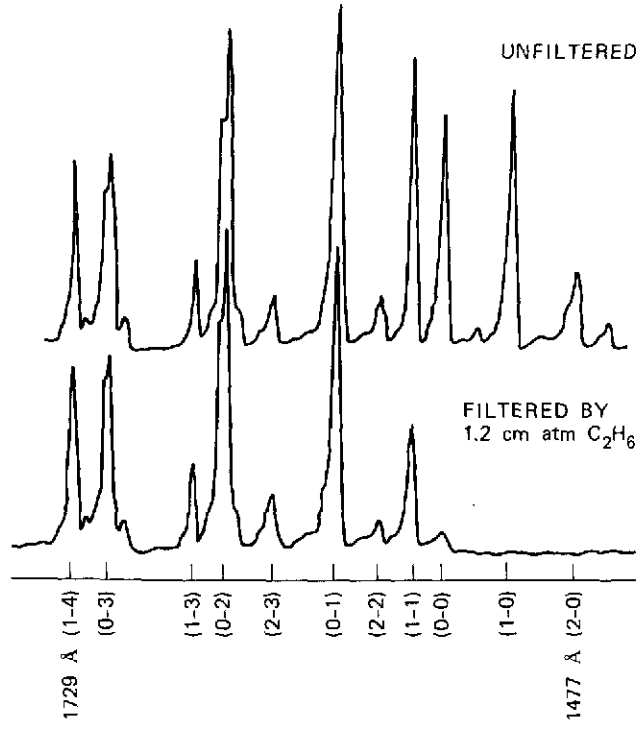

FIG. 2. CO lamp output, showing effect of ethane filtering.

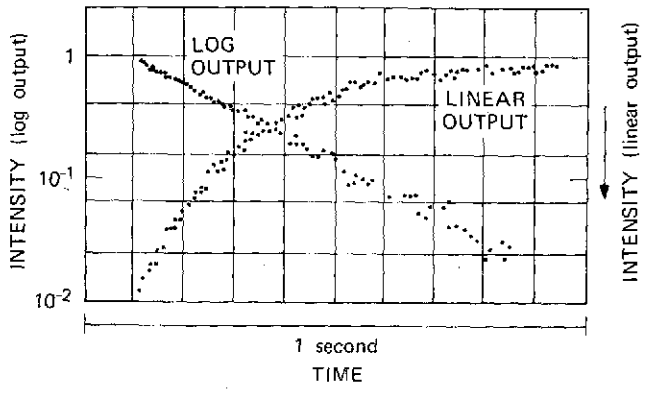

FIG. 3. Typical $CO(v''=1)$ decay curve, [CO] = 10 torr, [Ar] = 15 torr, $[O_2]$ = 0.1 torr (t = 0 level off scale).

in order to decrease the light from the Xe lamp, mainly to avoid overloading the signal averaging system while the lamp was on.

Most of the dc signal from the phototube was bucked out, and an operational amplifier was used to increase the residual signal by a factor of 10^3. The signal was then fed into a 100-channel PAR waveform eductor, which was operated with a time constant of 50 sec and an additional gain of a factor of 10. A standard integration time of 4 min was used to obtain each transient decay curve, which was photographed from an oscilloscope trace. A typical $CO(v''=1)$ decay curve is shown in Fig. 3; the steady state signal obtained with the Xe lamp on is off scale at the bottom of the trace. The straight line is a trace from a logarithmic amplifier, showing the exponential behavior of the decay (the log output is inverted with respect to the linear output). A pulse generator was used to trigger the eductor sweep and the cycling of the lamp. The lamp was operated with equal on and off times, with a frequency between 0.25 and 2.5 Hz, depending on the lifetime of the $CO(v''=1)$ transient, which was a function of both CO and total pressure. The frequency was always low enough that steady state conditions were reached while the lamp was on.

In dealing with long-lived vibrationally excited species, it is essential that pure gases be used because traces of polyatomic impurities, in the parts per million range, can be very effective in removing the vibrational energy. This is particularly true in the case of CO, and is attested to in the work of Millikan,[13] in which a system of two cooled and packed traps was used to remove the impurity that was destroying the $CO(v''=1)$ being studied. We have subsequently found such a purification system essential in our study[14] of CO_2 recombination, $O + CO + M \rightarrow CO_2 + M$; the technique is described in that paper. The other gases that were used in the system were UHP O_2(99.99% min), UHP N_2(99.999% min), and prepurified Ar(99.998% min). These gases were used without trapping, after it was shown that liquid oxygen trapping had no effect on the $CO(v''=1)$ lifetimes. In addition, lamp calibrations were made using Coleman grade CO_2(99.99% min). The ethane used in the CO lamp attenuation chamber was research grade purity (99.99% min). It was essential to use this grade, because ethylene contamination in the C.P. grade destroys the discrimination between 1544 and 1597 Å absorption.

To determine the $E-V$ transfer efficiency, it was necessary to calibrate the Xe lamp intensity. This was done by CO_2 actinometry. Careful measurements carried out by Inn[15] have demonstrated that the quantum yield for CO production from CO_2 at 1470 Å is 0.75; our own recent measurements[16] of relative quantum yields in the 1200–1500 Å region show values significantly less than unity. Therefore, the lamp was calibrated by adding a standard pressure of CO_2(1.7 torr) to the closed cell and observing the buildup of CO in the cell from the fluorescent scattering of the CO lamp radiation. As the CO lamp also dissociates CO_2, the effect of the Xe lamp alone is obtained by the difference in CO production rates with both lamps on and with the CO lamp alone on. The signal from the CO fluorescence is itself calibrated by adding diluted CO to the flowing system in the presence of the standard pressure of CO_2. A typical calibration run is shown in Fig. 4. There is some curvature of the CO buildup plots, so the slopes are taken from the initial phase, between the start of the run (CO_2 injection) and the 10 sec mark.

RESULTS AND DISCUSSION

$O(^1D)$-CO interaction

The principal loss process of $CO(v''=1)$ in the present system is expected to be radiation at the 4.7 μ fundamental frequency, which has an associated radiative lifetime of 33 msec. However, we observe much longer lifetimes, the explanation for which is that the radiation is imprisoned at the CO pressures used. Measurements by Nill *et al.*[17] on the $P(9)$ line of the 4.7 μ band show a line center absorption coefficient of 2.1 $cm^{-1} \cdot torr^{-1}$ at 300 °K, so that a photon at this frequency travels an average of only 0.5 cm/torr CO before reabsorption. As we used CO pressures generally greater than 1 torr, radiative lifetimes several times larger than 33 msec are expected. Figure 5 is a plot of observed $CO(v''=1)$

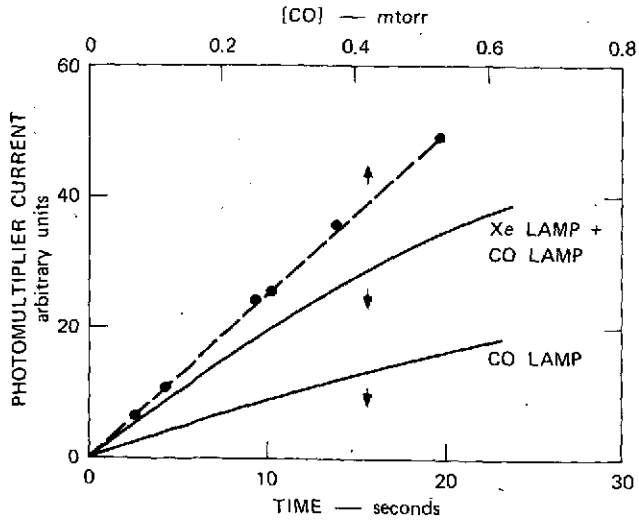

FIG. 4. CO production rate and CO calibration, $[CO_2]$ = 1.7 torr.

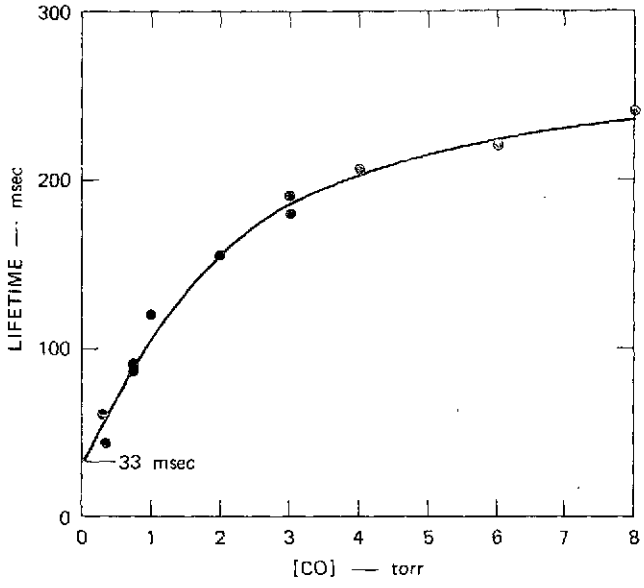

FIG. 5. $CO(v''=1)$ lifetime vs [CO], [Ar] = 50 torr, $[O_2] = 0.1$ torr.

decay times versus [CO]; the extrapolated value at zero CO is indeed close to 33 msec.

Figures 3 and 5 thus demonstrate not only that there is an easily detectable signal resulting from the $O(^1D)$–CO interaction, but that the signal is associated with a species that fits the expected behavior of $CO(v''=1)$. We accept this as proof that the observed undispersed vacuum-uv fluorescent signal is caused by absorption of 1597 Å radiation by $CO(v''=1)$ and its fluorescence at longer wavelengths. Figure 6 demonstrates that in the absence of O_2 there is no transient signal. A limiting value of the lifetime is expected at high CO pressures, because the absorption lines become pressure-broadened as the CO pressure increases. Thus, the absorption cross section decreases linearly with pressure, with the result that the mean free path of an ir photon is always precisely the same, and the radiative loss rate is constant. Margottin-Maclou *et al.*[18] have quantitatively determined modes of vibrational energy loss in CO by considering wall deactivation, radiative trapping, and collisional processes. Although their results and ours are not directly comparable because of different system geometries and CO pressure regimes, the observed radiative lifetimes are in general agreement. Their extrapolated data would indicate a limiting lifetime of ≤500 msec for the type of data presented in Fig. 5. Our value of 250 msec may indicate trace impurities in the system. For instance, a reactant in the Ar that removes $CO(v''=1)$ with 1% collision efficiency would need to be present at a level of only 450 parts per billion to account for the difference in lifetimes.

To calculate the $E-V$ transfer efficiency for Reaction (2), we must relate the signal associated with $CO(v''=1)$ to the $O(^1D)$ production rate. The latter is easily obtained, as demonstrated in Fig. 4 and discussed previously. The measurements of the $CO^\dagger$ production rate are of course made with O_2 as the $O(^1D)$ source, and the same optical depth of C_2 is used as was used for CO_2 in the calibration. At 1470 Å the absorption cross section ratio[19] between O_2 and CO_2 is 23, so that the O_2 pressure equivalent to 1.7 torr CO_2 is 75 mtorr. Inn[15] has shown that only 75% of the 1470 Å photons absorbed by CO_2 lead to dissociation; therefore, to obtain the $O(^1D)$ production rate in O_2 from the CO_2 calibration, we must divide P_{CO} by 0.75 (assuming unity for the quantum yield of $O(^1D)$ from O_2 at 1470 Å). The subsequent data show that the average $O(^1D)$ production rate was 6.5×10^{11} atoms/sec cm^3; from the diameter of the cell and the O_2 pressure, we can calculate that approximately 40% of the radiation is absorbed. Since the cell volume is about 1.5 liters, the photon flux into the cell is $\sim 2.4\times10^{15}$ photons/sec, a figure that is quite reasonable for this type of lamp.[20]

The determination of the concentration of $CO(v''=1)$ produced by $O(^1D)$ interaction is very simple, as the thermal $CO(v''=1)$ concentration is a built in calibration standard. The additional concentration, in torr, is

$$[CO(v''=1)]_{O(^1D)} = [I_0(\text{transient})/I(\text{thermal})] \times 9.8\times10^{11}\times[CO]_{\text{torr}}\,, \quad (4)$$

where I_0(transient) is the intensity at $t=0$ of the transient signal, as shown in Figs. 3 and 6, and I(thermal) is the difference between the unmodulated background signal (processed through the signal averager) when the CO flow to the system is on and when the CO flow is off. For this measurement, it is essential that the CO lamp be adequately blocked with C_2H_6 because although the transient signal can be associated only with $CO(v''=1)$, the background thermal signal will contain fluorescence excited by any $A\rightarrow X(v''=0)$ that penetrates the CO and C_2H_6 filters. The ratio I_0(transient)/I(thermal) is typically 3%, i.e., the $CO(v''=1)$ concentration is being modulated by 3% in this experiment. This naturally means that the CO lamp radiation, the principal source of the background light both from fluorescence and from wall reflection, must be much more stable than this. As can be seen from the base line in Fig. 3, instability in

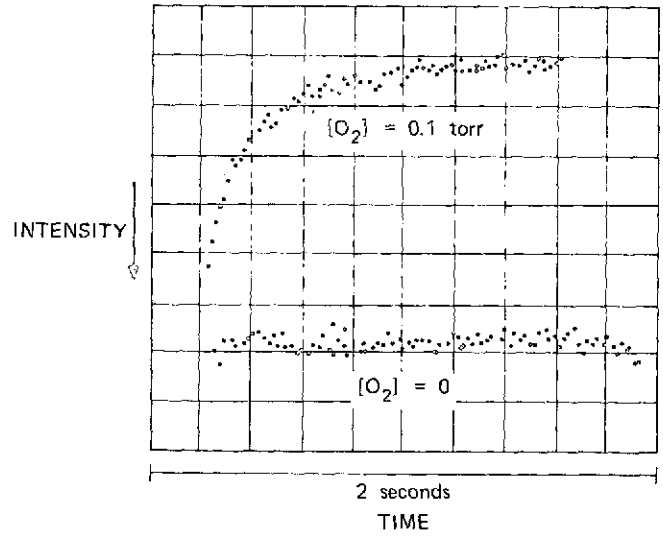

FIG. 6. $CO(v''=1)$ decay curve, showing effect of O_2 addition [CO] = 1.5 torr, [Ar] = 50 torr ($t=0$ level off scale).

the lamp is not a problem.

The electronic energy of $O(^1D)$ is 1.97 eV, whereas the vibrational energies of the two most resonant levels of $CO(X^1\Sigma^+)$, $v''=7$ and $v''=8$, are 1.79 and 2.03 eV, respectively. There is therefore a small chance that the $v''=8$ level can be reached from $O(^1D)$ transfer, particularly when the $O(^1D)$ has not been thermalized, since at formation, $O(^1D)$ produced by 1470 Å O_2 photolysis has a translational energy of 0.7 eV. However, addition of argon produces no effect that can be attributed to thermalization of "hot" $O(^1D)$.

Since CO is presumably formed in a distribution of vibrational levels, it must be determined whether $V-V$ transfer processes are rapid enough that all vibrational energy cascades down to $v''=1$, and also whether $V-T$ processes are slow enough that no $CO(v''=1)$ is lost by that route. Hancock and Smith[21] measured rates for $V-V$ transfer in $CO(v''=4-13)$; in all cases it requires less than 1000 collisions for the process

$$CO(v''=n\leq 7)+CO(v''=0)\rightarrow CO(v''=n-1)+CO(v''=1) \quad (5)$$

which means that at 1 torr, the transfer requires only 10^{-4} sec. Thus, for the time scales under consideration, certainly all the vibrational energy has cascaded down to $v''=1$. The $V-T$ relaxation time for the reaction

$$CO(v''=1)+CO(v''=0)\rightarrow 2CO(v''=0) \quad (6)$$

is given by $p\tau=8\times10^3$ torr · sec,[22] so that at 1 torr CO the loss of $CO(v''=1)$ by this means is completely negligible.

One of the system characteristics that it is necessary to establish is a linear response to the $CO(v''=1)$ concentration. Figure 7 shows a plot of the thermal $CO(v''=1)$ signal (measured with high C_2H_6 blocking of the lamp radiation to eliminate any $v''=0$ as an excitation source), and at first glance it would appear that the response is markedly nonlinear. If this were caused by the optical thickness of $CO(v''=1)$ in the space between the CO lamp and the viewing region, it would be a serious problem that would hamper any attempt to determine the $CO(v''=1)$ concentration at high [CO]. However, the cause is the quenching of the emitting state, $CO(A^1\Pi)_{v'=0}$, by CO, and thus both I_0(transient) and I(thermal) are similarly affected.

To satisfy ourselves on this point, we must measure the rate of the reaction

$$CO(A^1\Pi)_{v=0}+CO\rightarrow \text{Products}. \quad (7)$$

This is best carried out by measuring competitive quenching of $A^1\Pi(v'=0)$ by CO and N_2, using relatively high pressures of CO and N_2, such that quenching is an important loss process compared with radiation. Quenching of $A^1\Pi(v'=0)$ by N_2 can then be measured separately, at low [CO], such that N_2 quenching competes with radiation but CO quenching does not. The results, as yet unpublished, indicate a value for $A^1\Pi(v'=0)$ quenching by CO of $5.2\pm0.4\times10^{-10}$ cm^3 molecule^{-1} · sec^{-1} and by N_2 of $2.8\pm0.2\times10^{-10}$ cm^3 molecule^{-1} · sec^{-1}. This latter value compares with an earlier value of 3×10^{-10} of ours,[9] subsequently duplicated by Comes and Fink.[23]

Referring to Figure 7 we may calculate the quenching effect of the added CO, competing against the radiative rate of 1.0×10^8 sec^{-1}. When the data are corrected by this quenching factor, the dotted curve results, which is much closer to linearity in [CO]. The remaining curvature is presumably due to the optical thickness of the system to $A-X$ $(0-1)$ radiation; from earlier mentioned cross section measurements,[11] we would expect the corrected plot to reach a peak (corresponding to unity optical depth) at ~40 torr CO. This appears reasonable, and we conclude that over the [CO] range of interest (0–3 torr), the $CO(v''=1)$ signal is proportional to $[CO(v''=1)]$.

Another important consideration is the question of the uniformity of the distribution of the $CO(v''=1)$ associated with the $O(^1D)$–CO interaction. Since the thermal $CO(v''=1)$ is of course uniformly distributed within the closed cell, it is necessary that the $CO(v''=1)$ produced by the Xe lamp be uniformly distributed by the time it is lost by radiation, otherwise the $CO(v''=1)$ production rate will appear to be too high. As it happens, more than 80% of the spherical cell (not including the Woods' horns) is illuminated by the Xe lamp, although not uniformly. One must depend on mass transport and diffusion of radiation to make the distribution uniform. The average distance that a particle in the cell will travel as a function of time is given by[24]

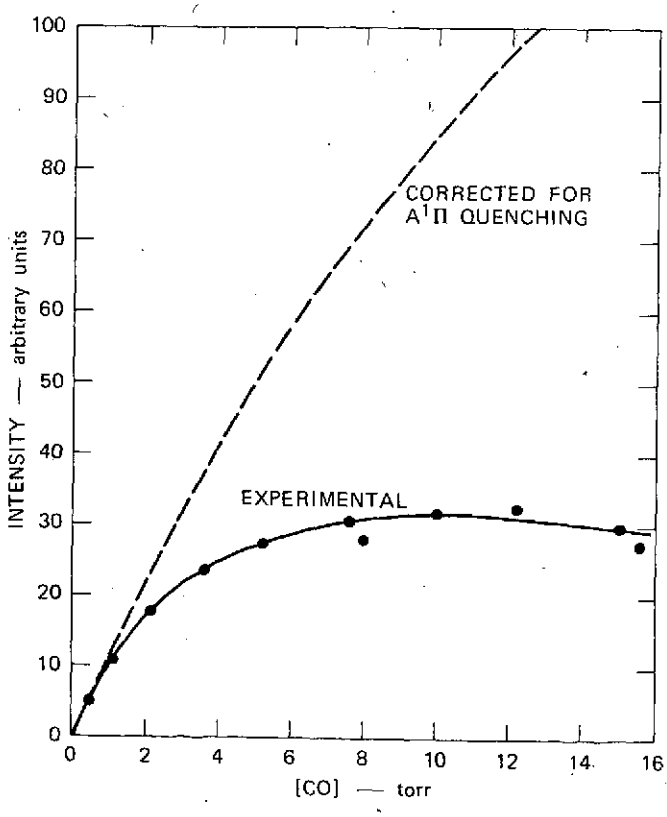

FIG. 7. CO fluorescence intensity vs [CO], for excitation by $A-X$ $(0-1)$ bands.

TABLE I. $CO(v''=1)$ production data. $[O_2]=75$ mtorr.

Set	[CO] (torr)	[Ar] (torr)	I_0(transient)[a]	I(thermal)[a]	τ (msec)	$P[CO(v''=1)]$ ($cm^{-3}\cdot sec^{-1}$)
1	3	3	0.50	11.05	57	2.33×10^{12}
2	3	4	0.34	7.92	77	1.64×10^{12}
	3	4	0.23	4.95	70	1.94×10^{12}
3	2	0	0.185	5.12	38	1.87×10^{12}
	3	0	0.195	6.93	42	2.06×10^{12}
	4	0	0.225	8.25	65	1.60×10^{12}
	4	0	0.235	8.25	62	1.78×10^{12}
4	2	0	0.225	5.12	39	2.16×10^{12}
	2	0	0.19	5.12	38	1.94×10^{12}
	2	0	0.17	5.12	38	1.68×10^{12}

[a]Units of voltage on oscilloscope display.

$$\langle X\rangle=\sqrt{2Dt/p}\,, \tag{8}$$

where D is the diffusion coefficient at 1 torr, 150 cm^2 torr/sec, and p is the pressure in torr. For almost half the measurement conditions, $P_{CO}=P_{total}=2$ torr, with a lifetime of ~40 msec, so that the average distance traversed is 2.5 cm, which will aid considerably in distributing the newly formed $CO(v''=1)$. As Fig. 5 shows, in the presence of 50 torr Ar, the $CO(v''=1)$ lifetime at 2 torr is 160 msec, indicating that in the absence of Ar, the wall loss of $CO(v''=1)$ is the major loss process, which requires that the $CO(v''=1)$ be rapidly moving out of the viewing region and filling the cell.

Two possible sources of $CO^\dagger$ other than $O(^1D)$ should be mentioned. For 1470 Å radiation, the energy going into translation following O_2 photodissociation is 1.4 eV, shared equally by the $O(^1D)$ and $O(^3P)$ fragments. Thus, although 0.7 eV will be quickly removed by thermalization, it is important to determine whether in the first two or three collisions there is a significant probability of exciting $CO^\ddagger$.

A recent paper[25] on the relaxation of vibrationally excited CO by $O(^3P)$ has shown that the process is quite rapid, but even so, the probability for transfer of CO vibrational energy to $O(^3P)$ at the temperature equivalent to 0.7 eV (8100 °K) is about 5%. The reverse rate is then calculated to be about 30% smaller, so the effect of this $CO^\dagger$ source on the present measurements is small. The same argument holds for the transfer from hot oxygen atoms to N_2, where the probability will be even smaller.[26]

The other possible source of $CO^\ddagger$ is from the reactions

$$O(^1D)+O_2\rightarrow O_2(b^1\Sigma_g^+)+O(^3P) \tag{9}$$

$$O_2(b^1\Sigma_g^+)+CO\xrightarrow{k_q}O_2+CO^\dagger \tag{10}$$

where the rate coefficient[27] for k_q is 4.3×10^{-15} cm^3 $molecule^{-1}\cdot sec^{-1}$. However, for the data of Table I, the ratio of CO to O_2 was 20, and as CO deactivates $O(^1D)$ about 30% faster than does O_2,[28] only 4% of the $O(^1D)$ can be deactivated by O_2, and of this amount, only about half-forms $O_2(b^1\Sigma^+)$.[5] Thus, this should also be an unimportant $CO^\dagger$ source.

The data obtained for the evaluation of the $O(^1D)$–CO $E-V$ transfer efficiency are presented in Tables I and II. Table I contains the figures for calculation of the $CO(v''=1)$ production rate, and each set is associated with a Xe lamp calibration, shown in Table II. Set 4 had a lamp calibration made both before and after the transient data were taken. $P[CO(v''=1)]$ is obtained from the concentration defined in Eq. (4), divided by the observed lifetime, while $P[O(^1D)]$ is defined by

$$P[O(^1D)]=\frac{P_{CO}(\text{Xe lamp})}{0.75\times\text{CO sens}}\,. \tag{11}$$

The values for the transfer efficiencies are obtained from the expression.

$$E-V\text{ transfer efficiency}=\{P[CO(v''=1)]/P[O(^1D)]\}\times\{E(v''=1)/E[O(^1D)]\}\,, \tag{12}$$

where $E(v''=1)$ is the fundamental CO vibrational quantum, 0.266 eV, and $E[O(^1D)]$ is 1.97 eV. The mean of the values obtained from Tables I and II is 41.6%, and the standard deviation is 5.3%. We estimate that the relative systematic errors contribute an additional uncertainty of ±7%, and applying a small correction for the production of $CO^\dagger$ by hot oxygen atoms, we recommend a value of (40±8)% for the $O(^1D)$–CO $E-V$ transfer efficiency.

In a very recent paper by Collins and Husain,[29] dealing with vibrationally excited $O_2(^1\Delta_g)$, they observed that when O_3 was flash photolyzed in the Hartley band, in the presence of CO, vibrationally excited CO was detected in absorption. This was interpreted as an indication of the $E-V$ transfer between $O(^1D)$ and CO, and they evaluated the efficiency by calibrating the $CO(v''=1)$ absorption at 1597 Å against the thermal background, and determining the $O(^1D)$ production on the basis of the expectation that in the Hartley continuum, O_3 dissociation gives $O(^1D)$ and $O_2(^1\Delta_g)$, each with a quantum yield of unity. Absorption measurements of the $O_2(^1\Delta_g)$ produced were thus taken as a measure of $O(^1D)$. The reported $E-V$ transfer efficiencies were 6.0% when the experiment was done in the presence of 50 torr Ar, and 9.4% when it was done in 100 torr He, figures much lower than the one we obtained.

Referring only to their Ar value, it is clear from their experimental description that they have ignored the quenching of $O(^1D)$ by the gases in the reaction mixture. The initial mixture was 50 torr Ar, 0.5 torr CO, and

TABLE II. Xe lamp calibration. $[CO_2] = 1.7$ torr.

Set	P_{CO}[a] Xe Lamp + CO Lamp	CO Lamp	Difference	CO Sensitivity[a]	$P[O(^1D)]$ ($cm^{-3} \cdot sec^{-1}$)
1	3.80	2.03	1.77	86	8.8×10^{11}
2	2.23	0.92	1.31	103	5.5×10^{11}
3	2.40	0.75	1.65	114	6.2×10^{11}
4	2.15	0.82	1.33	101	5.6×10^{11}
4′	2.27	0.78	1.49	97	6.6×10^{11}

[a] P_{CO} is in units of nanoamperes of photomultiplier current per second, whereas the CO sensitivity is in units of nanoamperes per millitorr.

0.05 torr O_3, and before the photolysis was carried out, 90%–95% of the O_3 had already been destroyed, due to the presence of CO and associated impurities. On the assumption that the O_3 is destroyed in a catalyzed reaction in which O_2 is the principal product, the reaction mixture at photolysis is 50 torr Ar, 0.5 torr CO, 0.075 torr O_2, and 0.003–0.005 torr O_3, the latter being 90% destroyed by the flash.

Using the recent NBS evaluations for the relevant $O(^1D)$ rate coefficients[28] and the recent value of Heidner and Husain[30] for Ar quenching of $O(^1D)$, 7.1×10^{-13} cm^3 $molecule^{-1} \cdot sec^{-1}$, one may calculate that only 47% of the $O(^1D)$ is quenched by CO. Thus, the reported efficiency of 6.0% must be divided by 0.47, giving a value of 12.7%.

There are other factors that will tend to increase the number even further. Absorption by $v'' = 2$ and 3 levels was observed at minimum delay times,[31] and should probably be included in the efficiency calculation. At wavelengths longer than 3100 Å, the $O(^1D)$ quantum yield is no longer unity, and a small correction for this effect should probably be considered. The decomposition of O_3 in the presence of CO is not well understood, and CO_2 has been observed as a product.[32] If the O_3 loss is attributed to catalyzed CO oxidation, this will also lead to a higher transfer efficiency, as CO_2 is an efficient $O(^1D)$ deactivator.

It seems to us that based on Husain's data, a figure of 15% should be accepted as a lower limit for the $E-V$ transfer efficiency. It must also be remembered in evaluating the experiment that it was not actually designed to investigate the $O(^1D)$–CO reaction.

$O(^1D)$–N_2 interaction

The effect of N_2 addition to the $O(^1D)$–CO system can be interpreted in terms of the efficiency of Reaction (1). This is because $N_2^\dagger$ and $CO^\dagger$ are linked by the reaction

$$N_2(v''=1) + CO(v''=0) \rightleftarrows N_2(v''=0) + CO(v''=1) + 188 \text{ cm}^{-1}, \quad (13)$$

where the forward rate constant is 1.44×10^{-14} cm^3 $molecule^{-1} \cdot sec^{-1}$ at 300 °K,[33] and the reverse rate constant, by the principle of detailed balancing, is lower by a factor of 2.46. Since vibrationally excited N_2 does not radiate, its principal loss process is by energy transfer to CO. The forward rate of Reaction (13) is 460 sec^{-1}/torr CO, much faster than the observed $CO(v''=1)$ loss rate, so that equilibrium is achieved rapidly compared with the rate at which $CO(v''=1)$ radiates. Assuming for the moment that $O(^1D)$ does not interact with N_2, the $CO(v''=1)$ concentration can not be affected by addition of N_2, since the loss rate (ir radiation) will remain constant. However, the vibrational energy is partitioned between N_2 and CO, there being an equal partitioning when $[N_2]/[CO] = 2.46$. Thus, the effect of adding N_2 will be to store vibrational energy in the system, and since the ir flux from $CO(v''=1)$ must remain constant, it will take longer, in a transient experiment, for the vibrational energy of the system to disappear. An increase in the $CO(v''=1)$ decay time is therefore expected as N_2 is added, regardless of the details of the $O(^1D)$–N_2 interaction.

Another consequence of the addition of N_2 will be to quench the emitting $CO(A^1\Pi)_{v'=0}$ level. As we have evaluated the N_2 and CO quenching coefficients for this level, we can calculate the effect.

Yet another effect of N_2 addition is related to the fact that the N_2 experiments are carried out with a 50 torr Ar background. Quenching of $O(^1D)$ by Ar is not negligible, so that as N_2 is added, an increasing fraction of the $O(^1D)$ is quenched by N_2 and CO, which will lead to false conclusions unless a correction is made.

The concept of the experiment is to add N_2 to the system such that $O(^1D)$ is predominantly deactivated by N_2 instead of by CO. If $O(^1D)$ deactivation by N_2 does *not* produce $N_2^\dagger$ (essentially the conclusion reached in the theoretical study of Fisher and Bauer[8]), then the fluorescent intensity associated with $CO^\dagger$ will drop abruptly (after all corrections have been made), and there will be an intensity decrease proportional to k''_{N_2}/k''_{CO}, the ratio for N_2 and CO quenching of $O(^1D)$. The rate coefficients recommended by NBS[28] are

$$k''_{CO} = 0.75 \pm 0.15 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$$

and

$$k''_{N_2} = 0.55 \pm 0.15 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}.$$

The new value of Heidner and Husain[30] is used for the Ar rate coefficient.

On the other hand, if 100% of the $O(^1D)$–N_2 interaction leads to $N_2^\dagger$, then, since the $O(^1D)$–CO interaction gives $CO^\dagger$ with only 40% efficiency, one expects an *increase* in the $CO^\dagger$ signal, once corrections have been made. For the case where the $O(^1D)$–CO and $O(^1D)$–N_2 $E-V$ transfer

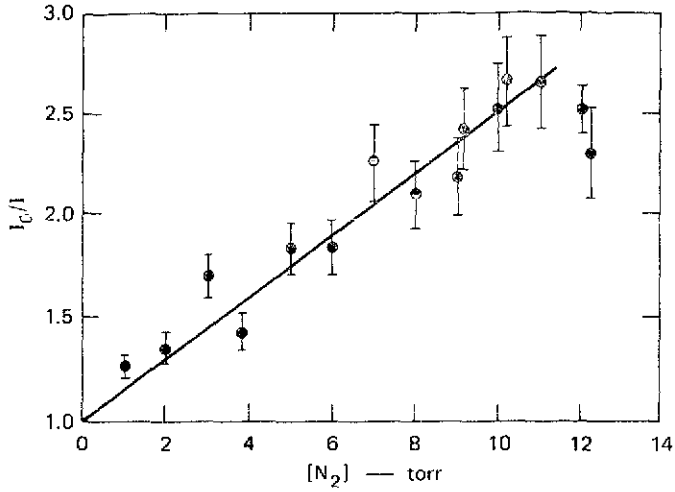

FIG. 8. I_0/I vs $[N_2]$, $[CO]=1.5$ torr, $[Ar]+[N_2]=50$ torr, $[O_2]=0.1$ torr.

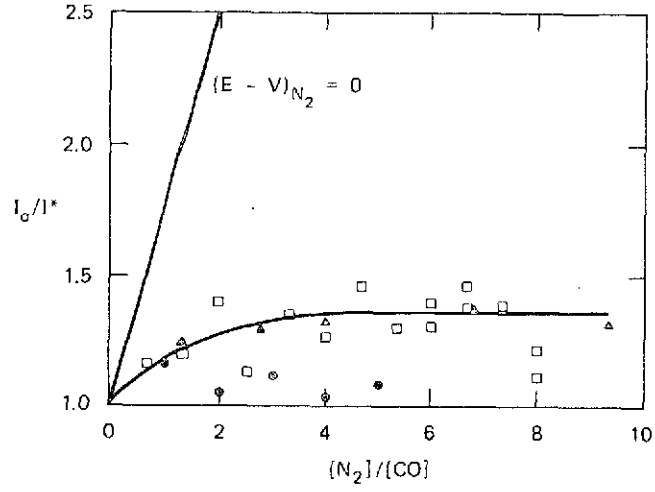

FIG. 10. I_0/I^* vs $[N_2]$, $[O_2]=0.1$ torr; ▲ $[CO]=0.75$ torr, $[Ar]=50$ torr; □ $[CO]=1.5$ torr, $[Ar]+[N_2]=50$ torr, ◉ $[CO]=3.0$ torr, $[Ar]+[N_2]=50$ torr.

efficiencies are equal, addition of N_2, after the necessary corrections, should not affect the $CO^\dagger$ concentration.

The data for N_2 are plotted in Figs. 8 to 10 for experiments carried out at three different pressures of CO. The data in Figs. 8 and 9, at 1.5 torr CO, are the most extensive. Figure 8 shows a Stern–Volmer plot of the intensity attenuation as a function of $[N_2]$, and from the same decay curves, Figure 9 shows the observed lifetimes. In Figure 9, the line marked "expected" is the predicted behavior of the lifetimes as N_2 is added and vibrational energy is stored, and has a slope such that the lifetime is doubled for $[N_2]=2.46$ [CO]. The data tend to follow this line initially but deviate as the predicted lifetime becomes so long that additional loss processes of $N_2^\dagger$ cannot be ignored. These include impurity quenching, system pump-out (~ 0.5 sec^{-1}), and the expected pressure-broadening effect of N_2, which will decrease the resonance trapping in CO and thus decrease the $CO^\dagger$ concentration produced from $O(^1D)$. Therefore, to the extent that the lifetimes deviate from the predicted curve, one expects a decrease in intensity, which then requires a correction factor.

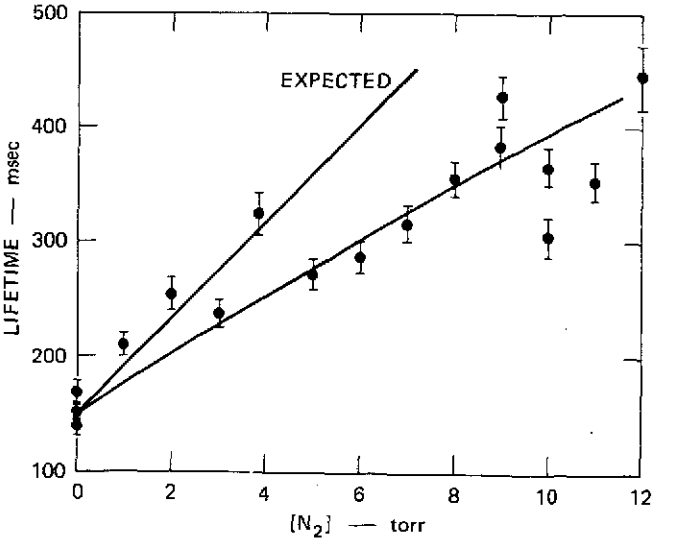

FIG. 9. Lifetime vs $[N_2]$, $[CO]=1.5$ torr, $[Ar]+[N_2]=50$ torr $[O_2]=0.1$ torr.

The overall factor that must be applied to the raw data in Fig. 8, to convert the observed I_0/I to a corrected I_0/I^*, is given by

$$I^*(N_2)-I\left(1+\frac{k'_{N_2}[N_2]}{\tau^{-1}(A^1\Pi)+k'_{CO}[CO]+k'_{Ar}[Ar]}\right)\times\left(\frac{1+(k''_{Ar}[Ar]/\{k''_{CO}[CO]+k''_{N_2}[N_2]\})}{1+\{k''_{Ar}[Ar]/k''_{CO}[CO]\}}\right)\frac{(\tau_{expected})}{(\tau_{observed})}\,, \tag{14}$$

where the k' values refer to $A^1\Pi$ quenching, the k'' values refer to $O(^1D)$ quenching, and the lifetime factor comes from the two lines in Fig. 9 (quenching by the small amount of O_2 is ignored). Values for $\tau(A^1\Pi)$ as well as k'_{N_2} and k'_{CO} for $A^1\Pi(v=0)$ quenching have been given earlier, and k'_{Ar} is 2.4×10^{-11} cm^3 molecule^{-1} · sec^{-1}, from the work of Comes and Fink.[23]

Multiplying each data point on Fig. 8 by the appropriate value of I/I^* then gives the data presented in Fig. 10, in which the abscissa is $[N_2]/[CO]$; thus the values for the two other pressures of CO investigated, 0.75 and 3.0 torr, can also be included. The raw data for these pressures are given in Table III, the $O(^1D)$ and $A^1\Pi$ corrections being the terms given in Eq. (14).

The expected behavior of the corrected data is that when enough N_2 has been added that essentially all the $O(^1D)$ is deactivated by N_2, a plateau will be reached that will express the $E-V$ transfer efficiency of N_2 relative to CO. For instance, a plateau at $I_0/I^*=2$ indicates that the N_2 efficiency is one-half of the CO efficiency. The line marked $(E-V)_{N_2}=0$ on Fig. 10 is that expected if the N_2 transfer efficiency is zero, whereas for the Fisher and Bauer predicted value of $\leq 5\%$, a plateau at $I_0/I^*\geq 8$ would be expected. Using the value $k''_{CO}/k''_{N_2}=1.35$, for $[N_2]/[CO]=10$, 88% of the $O(^1D)$ is deactivated by N_2;

TABLE III. Data for determination of I_0/I^*.

[CO][a]	$[O_2]$[a]	[Ar][a]	$[N_2]$[a]	I_0/I	τ(msec)	$O(^1D)$ corr	$A^1\Pi$ corr	$\frac{\tau \text{ expected}}{\tau \text{ observed}}$[b]	I_0/I^*
0.75	0.1	50	0	...	87	...	...	...	...
			1.0	1.15	99	0.81	1.06	1.08	1.24
			2.1	1.25	154	0.74	1.12	1.16	1.30
			3.0	1.37	207	0.71	1.18	1.23	1.33
			5.0	1.64	230	0.68	1.30	1.36	1.37
			7.0	1.85	273	0.66	1.42	1.49	1.32
			0	...	90	...	...	...	...
3.0	0.1	50	0	...	190	...	...	...	...
		50	3	1.45	252	0.94	1.14	1.17	1.16
		44	6	1.68	244	0.93	1.29	1.32	1.06
		41	9	2.15	328	0.92	1.43	1.46	1.12
		38	12	2.35	347	0.92	1.58	1.57	1.04
		35	15	2.87	331	0.92	1.72	1.66	1.09
		50	0	...	180	...	...	...	...

[a]Pressures in torr.
[b]Obtained from plot of τ vs $[N_2]$, rather than from the individual data points.

thus the plateau is almost reached for the span of the data in Fig. 10.

The corrected data in Fig. 10 appear to fit expectations, although the values obtained for 3 torr CO fall somewhat below the data taken at the lower pressures. The plateau for the 0.75 and 1.5 torr CO data is at $I_0/I^* \sim 1.35$, whereas for 3 torr CO a value of 1.1 seems reasonable. This leads to values of the N_2 $E-V$ transfer efficiency relative to CO of 75% and 90%, respectively. We will thus express the N_2 efficiency relative to CO as $(83 \pm 10)\%$ or, as an absolute figure, $(33 \pm 10)\%$.

The $O(^1D)$–N_2 system has been previously studied in our group by a Raman scattering technique.[34] Lack of signal intensity resulted in wide error limits, and the value obtained ultimately (See Citation 10 in Ref. 35) was $(42 \pm 33)\%$. This result, of course, did not settle the issue, since it almost encompasses the calculations of Fisher and Bauer[8] within the error limits. It now appears that the Fisher and Bauer model must be at least refined, if not discarded. Not only are our results in disagreement with their prediction, but they have used the same model to investigate the rate of quenching of $N_2(v''=1)$ by $O(^3P)$ for which recent measurements indicate a 300 °K rate constant several orders of magnitude higher than their extrapolated value.[26]

For a proper understanding of the $E-V$ process, it is naturally important to know the actual vibrational distribution. Because of rapid cascading from high vibrational levels and because radiation from these levels is both untrapped and has a shortened radiative lifetime, the problem of monitoring $v'' \geq 2$ levels is an order of magnitude more difficult than the experiment we have carried out. Information on the initial distribution in CO will presumably require ir measurements.

If the collision complexes in the two cases, N_2O^* and CO_2^*, decompose with a statistical distribution of energy among the N_2 and CO vibrational levels, then we can use the average energy transferred into vibration, which we have obtained, to calculate a Poisson distribution. Recent results of Fushiki and Tsuchiya[36] on the $Hg(^3P_0)$ + CO system show that a Poisson distribution is a reasonable approximation to the observed $CO(v'')$ distribution, where the average energy transferred is 4.8 vibrational quanta, or 27% of the available electronic energy. Levine and Bernstein[37] have developed an "impulsive transfer" model for the same system and indicate that results similar to a Poisson distribution are expected. However, they compare their calculation to the experimental results of Polanyi's group,[3] although Fushiki and Tsuchiya[36] have shown that these results are skewed towards low v, that is, cascading had taken place.

If the same type of distribution is valid in the present case, then we expect that for CO, where the average vibrational level excited is $v''=3$, 50% of the molecules are in the $v''=2$ and $v''=3$ levels, and 85% are in levels $v''=1$–4. For N_2, essentially all the energy would appear in levels $v''=1$–3.

AERONOMIC IMPLICATIONS

Apart from minor relaxation processes involving $N_2(A^3\Sigma_u^+)$, the principal potential sources of $N_2^\ddagger$ in the upper atmosphere are the two reactions

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2^\ddagger + 1.97 \text{ eV}, \quad (15)$$

$$N(^4S) + NO \rightarrow N_2^\ddagger + O(^3P) + 3.27 \text{ eV}. \quad (16)$$

We have recently published a paper[35] showing that 25% of the exothermicity of Reaction (16) goes into N_2 vibration, and we have now established that 33% of the exothermicity in Reaction (15), or 0.64 eV, does the same. The only parameters then needed to calculate the $N_2(v''=1)$ production rate in the upper atmosphere are the rates of Reactions (15) and (16). The rate of Reaction (15) is essentially equal to the production rate of $O(^1D)$, at all altitudes below 200 km, and this rate is principally due to photodissociation. The rate for Reaction (16) depends on the concentration of $N(^4S)$ and NO, and these values are not very well known.

In a recent paper by Jamshidi *et al.*,[38] average source functions for both reactions are calculated, assuming that for Reaction (15) the typical $O(^1D)$–N_2 deactivation leads to $N_2^\dagger$ excitation of $v=\frac{1}{3}$ (0.097 eV). As we find that the transfer efficiency is 6.6 times greater, we can scale-up their calculations for reaction (15) by this factor, leading to the conclusion that at latitudes below 300 km, Reaction (16) can essentially be ignored as an $N_2^\dagger$ source, and the extent to which the N_2 vibrational temperature is out of local thermodynamic equilibrium is determined by Reaction (15). The $N_2(v''=1)$ production rate from $O(^1D)$ deactivation at altitudes of 100, 125, 150, 200, 250, and 300 km is then, respectively, 5×10^6, 5×10^5, 1.7×10^5, 4×10^4, 1.5×10^4, and 9×10^3 $cm^{-3}sec^{-1}$.

CONCLUSIONS

We have measured the $E-V$ energy transfer efficiency from $O(^1D)$ to CO and to N_2 by monitoring the $CO(v''=1)$ level, excited by $O(^1D)$ produced by O_2 photodissociation. The fraction of the 1.97 eV $O(^1D)$ electronic energy appearing in vibrations is $(40\pm8)\%$ for CO. For N_2, the efficiency is $(83\pm10)\%$ relative to CO. The experiment is facilitated by resonance trapping of the 4.7 μ CO ir fundamental band, which causes the $CO(v''=1)$ lifetime to be much longer than the natural 33 msec lifetime and thus increases the concentration of $CO(v''=1)$. The transfer efficiency to N_2 is considerably higher than recent theoretical estimates, and makes the reaction the dominant one in determining the N_2 vibrational temperature in the earth's upper atmosphere.

ACKNOWLEDGMENT

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APPENDIX C

INFRARED MEASUREMENTS ON $O(^1D)$-QUENCHING SYSTEMS

In this section we describe the apparatus and the experimental data for the attempted ir measurements.

The flash lamp used in the experiment was described in Quarterly Report No. 4. It consists of a 3-inch I. D. teflon cell, having two tungsten electrodes on opposite sides spaced about 10 mm apart, and a brass end plate with a 3/4-inch MgF_2 window in the center. The lamp is operated with an atmosphere of argon flowing through it. Power is supplied through copper straps from a 600-joule electric driver unit manufactured by the Candela Corporation; the driver unit is charged by a 25 kV, 5 mA D. C. power supply.

The lamp is triggered by a spark gap in the driver unit, which in turn is triggered by an auxiliary circuit. When it was established that the lamp intensity was sufficient for our purposes, no attempt was made to minimize the flash duration, which might have been done in a variety of ways, since the expected decay times in both CO and CO_2 were long compared with the flash duration. Figure 1 shows a trace of the lamp output in the visible spectral region, measured with a photodiode.

The reaction cell, also described in Quarterly Report No. 4, consisted of a solid rod of copper, four-inches in diameter, of which the top three inches were hollowed out and supplied with four window ports at 90° to each other, with a fifth port in the top flange through which the ir detector was to look. This type of construction was used for the CO_2 work because it was believed necessary to limit the quenching of vibrationally excited CO_2 by CO_2 and by Ar, and thus a system capable of operating at low temperatures (-150°C) was needed. In fact, with the lamp intensity we obtained, a sufficient signal from $CO_2^{\ddagger}$ should have been observed even without cooling of the cell. A schematic diagram of the apparatus is shown in Figure 2.

The first consideration was to assure ourselves that the lamp intensity was adequate for our experiment. This was done by measuring

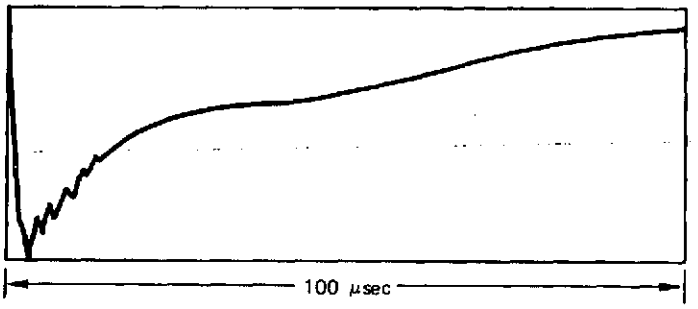

FIGURE 1 PROFILE OF VISIBLE LIGHT FROM FLASH LAMP, 20 kV, 1 atm Ar

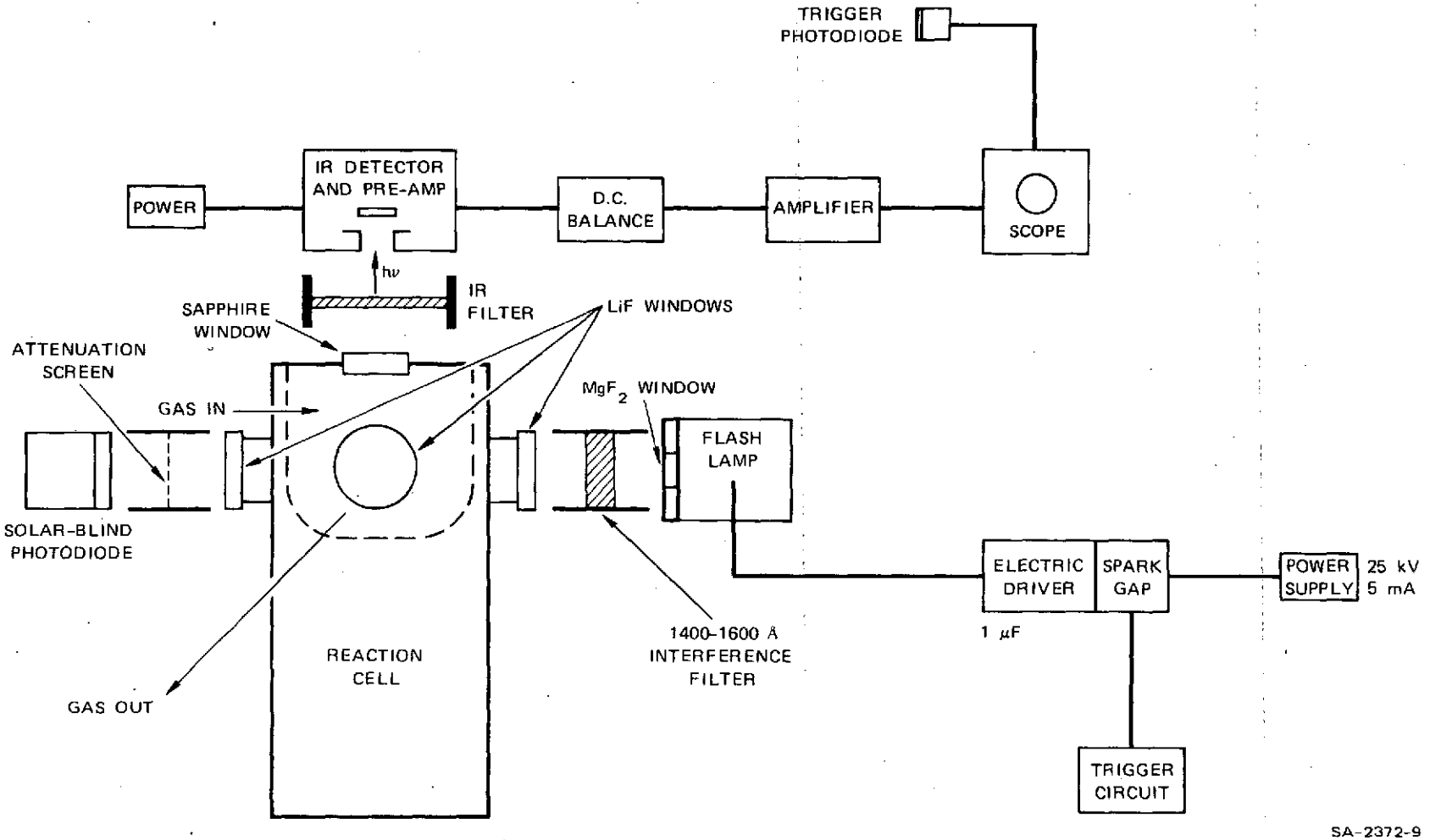

FIGURE 2 APPARATUS SCHEMATIC

the CO produced in a flash by CO_2 photodissociation. A second cell was set up downstream from the first, equipped with a CO resonance lamp and a solar-blind photomultiplier. With CO_2 in an argon buffer flowing through the system, the flash lamp was fired, and about 1 sec later the CO produced in the flash was detected as it passed through the second cell. To obtain an absolute yield, we added a calibrated amount of CO (0.3 cm^3, 0.04% CO in N_2, 1 atm, or 3 x 10^{15} CO molecules) upstream from the reaction cell at the same CO_2 pressure, and it gave the same shape of signal. Calibration of the CO detector against added CO showed that the observed signal pulses were far from saturation (i.e. high optical density). Under the best conditions, the lamp pulse (at 1 torr CO_2) was 25% of the calibration pulse. When it decreased to less than 10% of the calibration pulse, the lamp window was removed and cleaned. The usual lamp pulse produced 5 x 10^{14} molecules of CO from 1 torr CO_2. We demonstrated that the pulse was indeed due to CO by attenuating the CO resonance lamp with 1 x 10^{-3} cm atm. of CO. This amount of CO should completely block the pumping CO radiation [the (0-0) and (1-0) Fourth Positive Bands] and affect little else, and the fact that no signal pulse then appeared upon flashing the lamp, clearly showed that the signal was from the CO produced. Figure 3 shows the appearance of the CO signal pulses, and also a pulse from the cell containing only Ar, to show the relatively small amount of CO generated from the cell walls.

Although it was not convenient or necessary to obtain a spectrum of the flash lamp, it was possible to measure the output of vacuum-uv radiation in such a manner that conclusions could be drawn about the distribution of radiation.

A solar-blind photodiode (CsI photocathode) was set up facing the flash lamp, viewing it through the evacuated cell. Between the cell and the flash lamp was a chamber purged with flowing N_2, containing an interference filter having 18% transmission at 1400 Å, 6.5% at 1600 Å, and

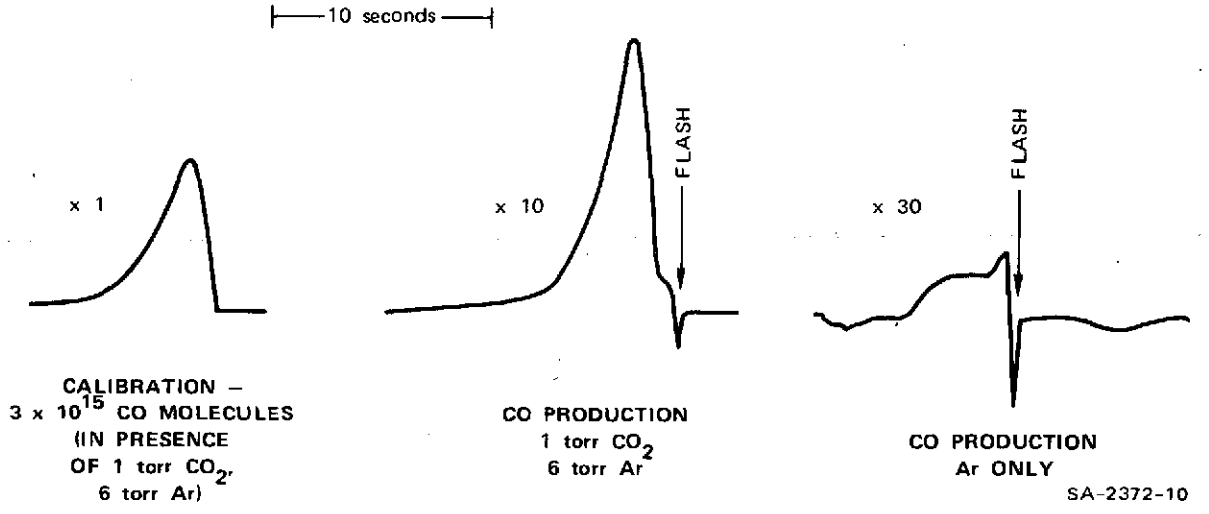

FIGURE 3 LAMP INTENSITY CALIBRATION

1% at 2000 Å (Seavom, Engins Matra, Paris). Between the cell and the photodiode was another purge chamber, 2 cm in length, through which Ar and CO_2 could be flowed. The light intensity to the photodiode was measured as a function of the fraction of CO_2 in the purge chamber, the data being taken at a fixed time after the flash initiation (60 μ sec), since before this time electrical oscillations picked up by the diode were severe. A screen transmitting 0.1% of the incident radiation was used to attenuate the light before it reached the photodiode. In Figure 4 the attenuation by CO_2 is shown as a function of CO_2 pressure, along with a series of lines indicating the attenuation slope expected for various wavelengths. Clearly the largest fraction of the light below ~ 1800 Å is at wavelengths < 1550 Å.

Auxiliary experiments had been carried out in which various gases had been flowed through the purge chamber between the lamp and the cell and their effect on the amount of CO generated had been measured. The curve of Fig. 4 shows a single point so obtained with CO_2. It lies above the other data since the total light seen by the diode will extend to longer wavelengths and thus give a lower apparent CO_2 cross section than will a measurement obtained from CO production data, which will be insensitive to light at $\lambda > 1700$ Å. The cross section obtained from the single point is $\sigma(NTP) = 14.6\ cm^{-1}\ atm^{-1}$, which is an average CO_2 value[1] for 1400 Å < λ < 1500 Å.

Using CH_4 to attenuate the CO production we obtained a value of $\sigma_{CH_4}(NTP)$ of $0.17\ cm^{-1}\ atm^{-1}$. Our own values[2] for the CH_4 absorption cross section in the 1400-1500 Å region, which are a factor of 2-8 lower than those of Watanabe et al,[6] lead to an average wavelength of 1450 Å. We thus conclude that the light causing CO_2 photodissociation is basically in the 1400-1500 Å region. There are, in fact, a series of strong Ar II lines between 1450 Å and 1475 Å.[3]

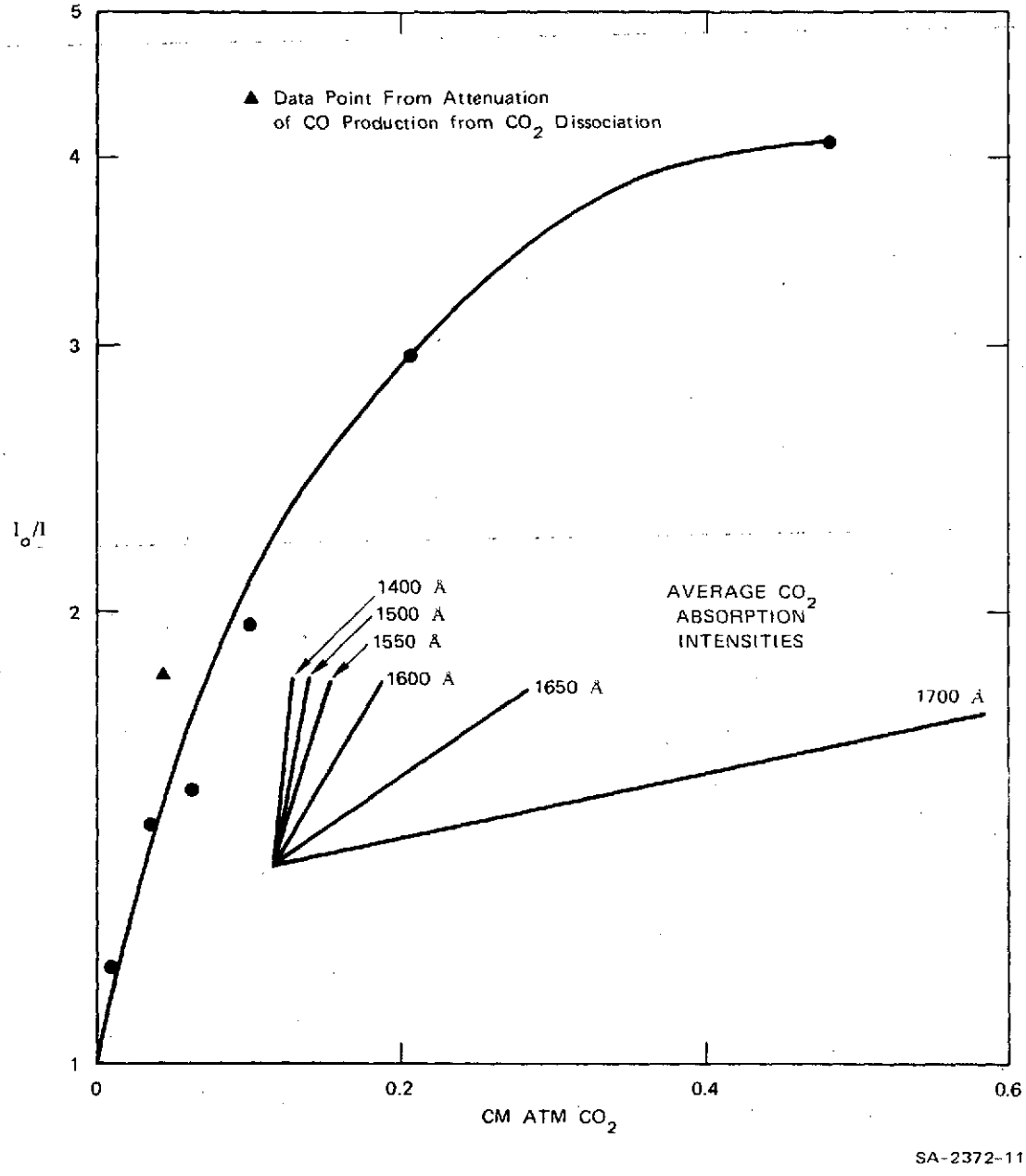

FIGURE 4 CO_2 ATTENUATION OF PHOTODIODE SIGNAL INTENSITY

The only practical reason for knowing the radiation distribution is to ascertain the fraction of light absorbed by 1 torr CO_2. Measurements cannot be made at CO_2 pressures high enough to absorb the incident flash radiation totally, since the CO resonance radiation then becomes too strongly attenuated. From this information about the radiation distribution, it may be concluded that $\sim$ 15% of the absorbable light is absorbed by 1 torr CO_2. Thus, using a value of 5×10^{14} CO molecules produced per flash, and assuming a photodissociation quantum yield of 0.75 in this wavelength region, it may be concluded that $\sim 4 \times 10^{15}$ CO_2-absorbable quanta enter the cell per flash. If we use the light to dissociate O_2 instead of CO_2, we then expect $\geq 4 \times 10^{15}$ $O(^1D)$ atoms to be produced per flash.

As the work on the $O(^1D)$-CO system firmly established an efficiency of 40% for the E $\rightarrow$ V transfer, we conclude that 3×10^{15} eV/flash can be transferred to CO vibrational excitation, or that 1.2×10^{16} CO(v=1) can be produced per flash. If half of this energy is lost by infrared radiation (a conservative estimate as the V-T processes are very slow), then at a distance of 10 cm from the cell center (the distance to the detector) the infrared flux will be 5×10^{12} photons/cm^2 flash.

The detector was a Philco-Ford InSb chip, 0.1 cm^2 in area, operated in the photovoltaic mode and mounted on the bottom of a small Dewar flask, which was filled with liquid N_2. The space between the detector and the cell was purged with dry N_2 to avoid condensation of water. The ir signal was amplified by a Burr-Brown operational amplifier built into the detector box and then passed through a second stage of amplification. It was then processed through a TMC Computer of Average Transients Model 1000 (CAT) or fed directly to a scope, the CAT or the scope being triggered by the output of a visible-response photodiode, which detected the light reflected from the walls of the room.

The detector was calibrated for sensitivity by making observations of the chopped emission from a stainless steel strip heated to 1000°C, using the 4.7 μ filter that was to be used to observe the $CO^{\ddagger}$ radiation. This filter had a half-width of 0.077 μ and a peak transmittance of 72%. From standard black-body curves and the geometry of the apparatus, we calculated that the power reaching the detector was 0.3 μwatts, which gave a 3-volt deflection on the oscilloscope, and thus an overall sensitivity of 1×10^{7} volts/watt. Since the two amplifiers had a combined gain of 420, the detector itself had a response of 2.5×10^{4} volts/watt, in good agreement with the manufacturer's typical value of 4×10^{4} volts/watt.

The expected number of 4.7 μ photons from the $E \rightarrow V$ transfer experiment is $5 \times 10^{12}/cm^{2}$ flash at the detector, or 5×10^{11} photons/flash for the 0.1 cm^{2} detector area, which is equivalent to 2.5×10^{-8} watt sec. Assuming an exponential decay of the radiation, at the CO(v=1) radiative lifetime of 30 msec, one then expects a peak power (immediately after the flash) of 0.75 μwatts, equivalent to 7.5 volts on the oscilloscope, and a scope signal of 3 volts after 30 msec. These large signals would indicate that a signal averager is not needed for the experiment.

Figure 5 shows traces of the ir signal taken with 10 torr Ar, 1 torr CO, and 0.2 torr O_2 in the cell. At this O_2 pressure, approximately half the absorbable vacuum uv radiation is absorbed. Thus, a peak signal of $\sim$ 4 volts is expected. The three traces, for which the noise level is 0.05 volts, show no indication at all of a $CO^{\ddagger}$ signal decay. The first trace shows the recovery of the detector from saturation, which is complete in 1 msec. The decay is coming from the negative light direction and is thus electrical pickup; the appearance is the same with an empty cell.

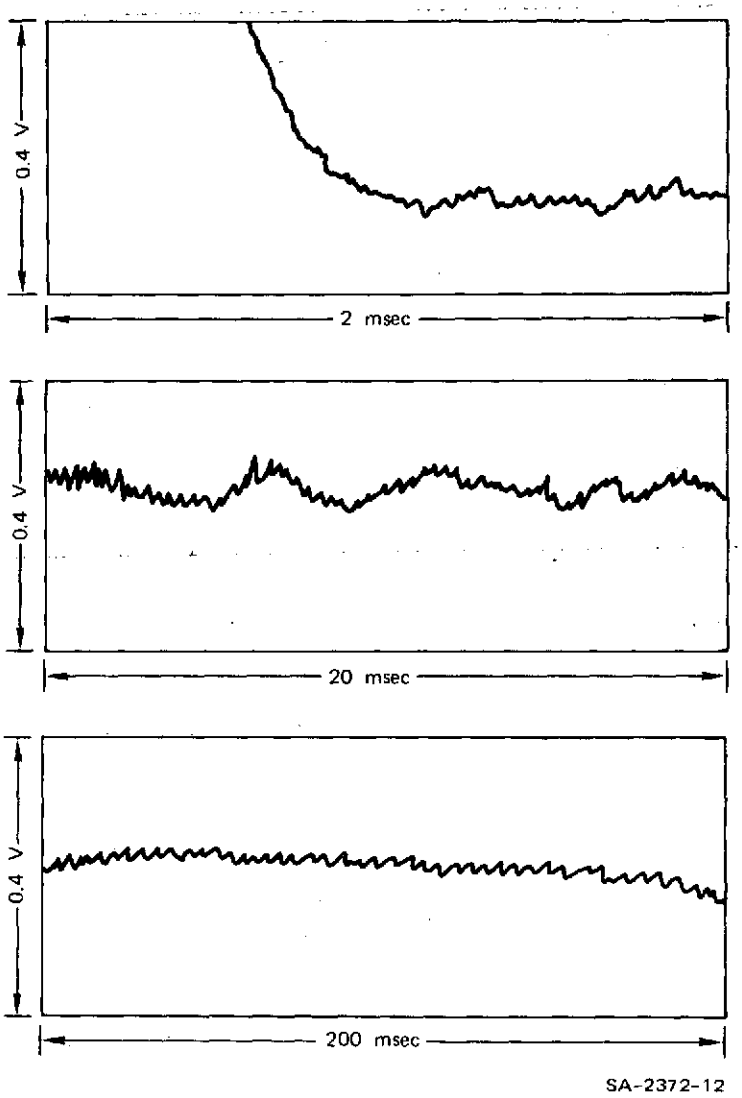

FIGURE 5 INFRARED DETECTOR RESPONSE TO FLASHED MIXTURE, 20 kV, 1 atm Ar

10 torr Ar
1 torr CO
0.2 torr O_2

To make certain that the detector had not temporarily become insensitive even after the saturating pulse had passed, we directed an ir light signal at 5 kHz toward the detector while the lamp was flashed. Figure 6 shows the resultant trace, indicating that as soon as the saturating pulse has terminated, the detector is again operating at full sensitivity.

At this point the conclusion was that either $CO^{\ddagger}$ was not made or it was made but not seen. To satisfy ourselves that $CO^{\ddagger}$ and $CO_2^{\ddagger}$ were detectable we generated them by adding CO and CO_2 to a nitrogen discharge afterflow, which can be expected to give $CO^{\ddagger}$ and $CO_2^{\ddagger}$ by the reaction

$$N_2^{\ddagger} + CO(CO_2) \rightleftharpoons N_2 + CO^{\ddagger}(CO_2^{\ddagger}) \qquad (1)$$

The data are presented in Figure 7, showing voltage on the scope as a function of added gas. The signals were taken without ir filters after it was clear that the only signal in the two cases came from the fundamental bands. By assuming that, apart from reaction (1) the $CO^{\ddagger}$ lifetime equals the radiative lifetime of 30 msec (at pressures of < 0.1 torr, radiation trapping is not significant), and assuming that the $N_2^{\ddagger}$ loss rate is $\sim 5\ sec^{-1}$ and the $N_2^{\ddagger}$ concentration is $\sim 1\%$ of the N_2 pressure, one may calculate that the expected power to the detector is ~ 1 μwatt at 40 μ CO. Using a sensitivity value of 1×10^7 volts/watt, the data of Fig. 7 show that the observed power was 0.8 μwatts. Thus, it would seem that the assumptions made are not unreasonable, and particularly that the $CO^{\ddagger}$ lifetime is not far from 30 msec. The plateau behavior of the CO_2 data shows that the CO_2 quickly extracts the vibrational energy from N_2 and then radiates it, in accord with the fast forward rate of reaction (1) and the 2-msec radiative lifetime of $CO_2(001)$. From the CO measurements, the conclusion to be drawn would seem to be that of the two choices mentioned above, the correct one is that $CO^{\ddagger}$ is not made.

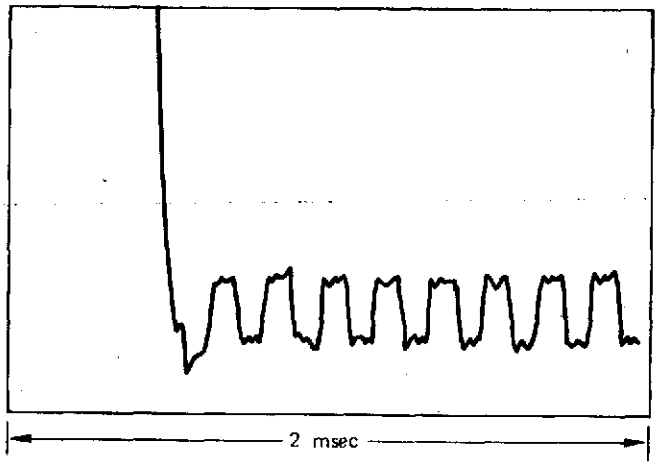

FIGURE 6 INFRARED DETECTOR RESPONSE TO FLASH LAMP PULSE WITH SUPERIMPOSED 5 kHz INFRARED SIGNAL

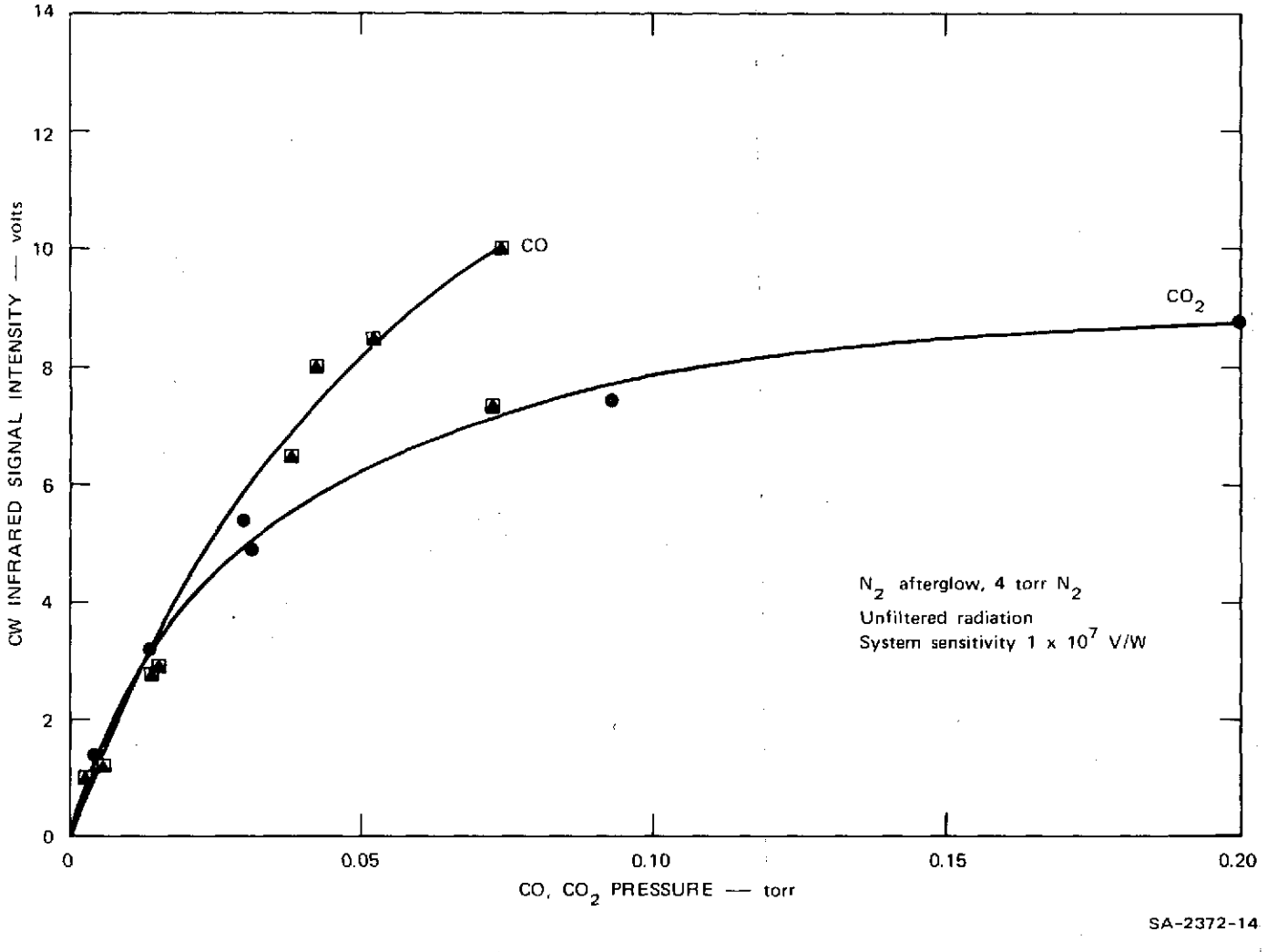

FIGURE 7 SCOPE VOLTAGE VERSUS CO, CO_2 PRESSURE

The absence of $CO^{\ddagger}$ production would be most unexpected and would conflict with our uv measurements of the $O(^1D)$-CO system, the results of Collins and Husain (12% E → V transfer efficiency),[4] and the calculations of Tully.[8] To check this conclusion further, we replaced the ir detector with a solar-blind photomultiplier tube and directed the CO resonance lamp into the primary cell. Flashing the lamp produced no signal associated with an enhanced CO(v=1) population, although the saturation problem is worse in this case than with the ir detector. Figure 8 shows a trace with a noise level of 0.01 V, and saturation recovery in 10 msec. The expected voltage at t=0 is $\sim$ 0.1 V, and thus $\sim$ 0.04 V at 30 msec. This signal-to-noise ratio is smaller than that for the ir measurements but does tend to confirm the lack of $CO^{\ddagger}$ production.

As it does not seem possible to doubt that the reaction $O(^1D) + CO \rightarrow O(^3P) + CO^{\ddagger}$ takes place, we felt it necessary to prove the assumption that $O(^1D)$ was formed.

Using a technique we have used previously,[5] we determined the amount of $O(^3P)$ produced by using as the monitor the chemiluminescence from the reaction

$$O(^3P) + NO + Ar \rightarrow \underset{\downarrow}{NO_2^*} + Ar \qquad (2)$$
$$NO_2 + h\nu$$

A decay plot for this emission is shown in Figure 9, and the exponential behavior can be followed down to 2 msec after the flash. At shorter times, the recovery from saturation obscures the signal. From the intensity at t=0, the detector parameters, and knowledge of the fraction of NO_2^* that radiates,[5] one may calculate the amount of O_2 photodissociation. This figure should of course be comparable to the CO production from CO_2 but slightly higher, due to additional absorption between 1650 Å and 1750 Å. The value obtained was 7×10^{15} O_2 dissociated per flash for total absorption. The lower trace in Fig. 9 represents the decay

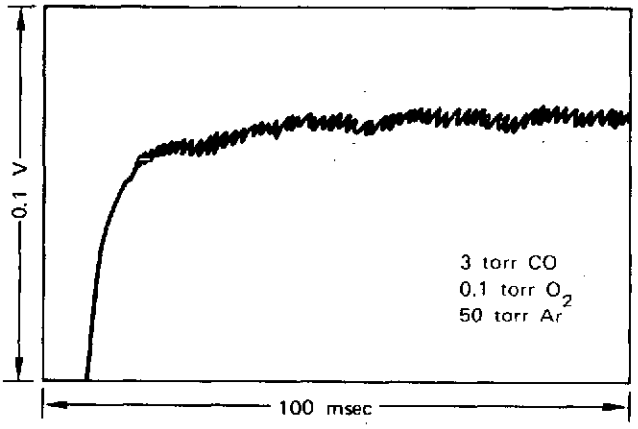

FIGURE 8 RESPONSE OF SOLAR-BLIND PHOTOMULTIPLIER TO FLASH (RESONANCE FLUORESCENCE EXPERIMENT)

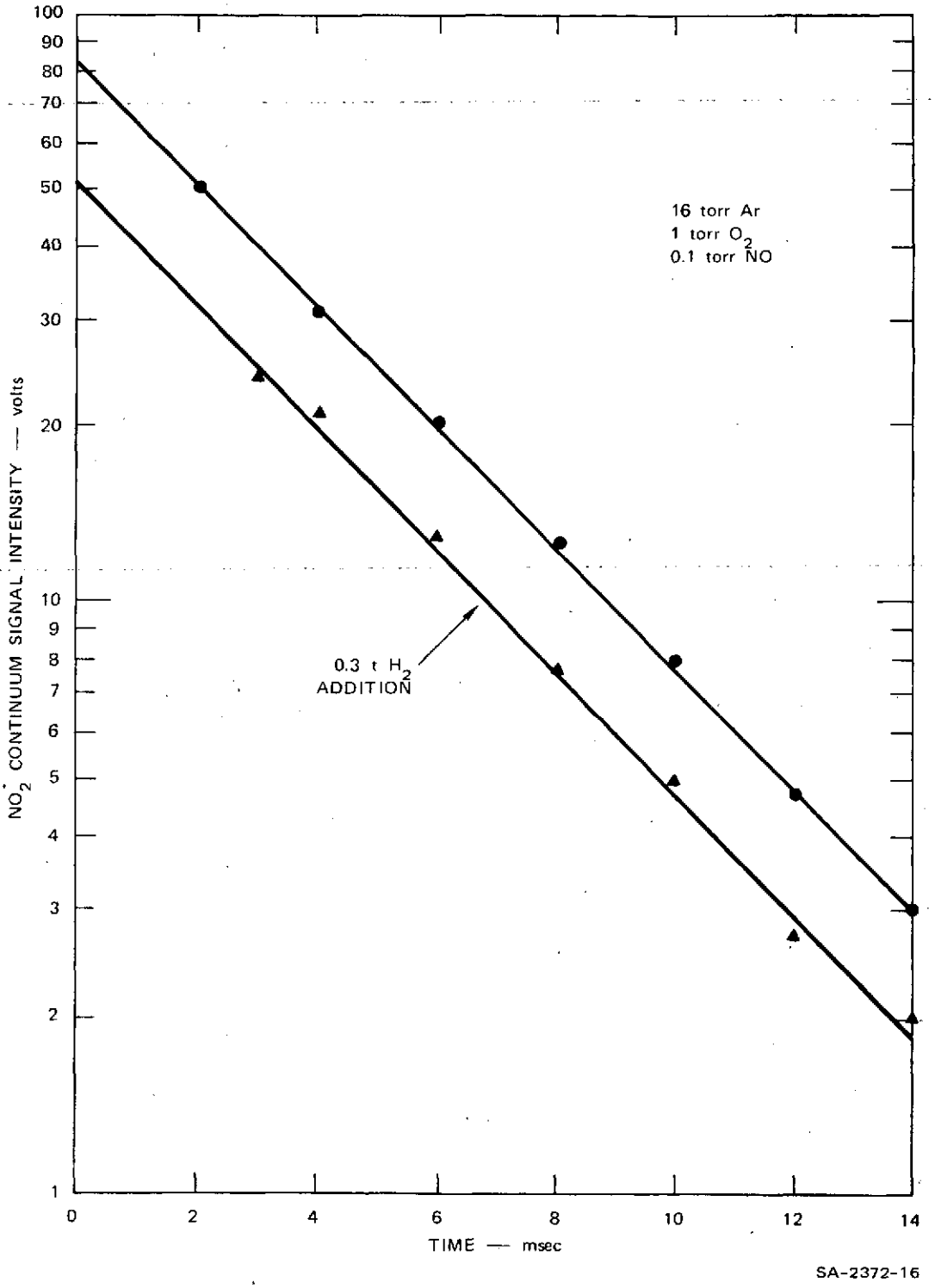

FIGURE 9 DECAY OF NO_2^* CONTINUUM SIGNAL

when 0.3 torr H_2 is added to the reaction mixture. The lifetime is the same, but the intensity is less because H_2 removes $O(^1D)$ before it can be deactivated to $O(^3P)$. From the known values for the relevant $O(^1D)$ quenching rates,[6] the reduction in intensity can be shown to demonstrate that $O(^1D)$ and $O(^3P)$ are produced in equal amounts, which is of course to be expected for dissociation in the Schumann-Runge continuum.

We also used the photodiode results discussed earlier in which the solar-blind diode looks directly at the flash. From the area under a trace of scope voltage *vs* time, the instrumental sensitivity parameters, and the knowledge that CH_4 removes half of the CO_2-absorbable light, we were able to conclude that the intensity of light entering the cell that is absorbable by CO_2 is at least 2×10^{15} quanta/flash, in reasonable agreement with the value of 4×10^{15} quanta/flash obtained from CO_2 photolysis and 7×10^{15} quanta/flash from O_2 photolysis. Therefore, the absorbable light intensity is clearly several times 10^{15} quanta/flash, and we are faced with the problem that less than 1% of the expected $CO^{\ddagger}$ is seen.

We know that $CO^{\ddagger}$ is susceptible to quenching by materials present in CO cylinders (possibly $Fe(CO)_5$), as is also the case with $O(^3P)$ atoms, but the usual dry-ice cooled alumina and copper wool traps that proved successful in the past[7,8] were used on the CO line, as well as liquid oxygen trapping of the incoming gas mixture. It is probable that the $CO^{\ddagger}$ wall loss rate is higher on the copper surface of the cell than on the Pyrex that we have usually used, but introduction of a Pyrex liner into the cell did not lead to any improvement.

Attempts were also made to look at emission from $CO_2^{\ddagger}$, using both O_2 and CO_2 as $O(^1D)$ sources. These measurements were made both at room temperature and with the cell cooled to -150°C. From data of Margottin-Maclou *et al*,[9] one may calculate that the fraction of $CO_2(001)$ radiating should be 20-40%, whereas for $CO_2(00Y)$ where $Y > 1$, the fraction should

be at least 80%. In any case, no radiation was seen at 4.3 μ.

It is difficult to arrive at an obvious explanation for the lack of observation of $CO^{\ddagger}$ and $CO_2^{\ddagger}$. A flowing gas volume emitting 10^{16} ir photons only 10 cm away from the detector should not be hard to observe. Although the majority of $CO^{\ddagger}$ molecules are probably made with $v'' > 1$, the V-V processes are rapid,[10] and at 1 torr CO it should require only 220 μsec for CO molecules formed at the maximum value of $v'' = 7$ to cascade down to $v'' = 1$. In any case, radiation from the higher levels would be detected with somewhat more efficiency than from $v'' = 1$, as the higher level radiation is not trapped and also exhibits a faster radiative lifetime.

Since ir radiation from $CO^{\ddagger}$ and $CO_2^{\ddagger}$ was observed when expected in the afterglow experiments, it appears that the problem is somehow associated with the flash. The principal new species made in the flash is $O(^3P)$, and its quenching of $CO^{\ddagger}$ has recently been determined between 2000°K and 4000°K by Center.[11] If the data are extrapolated to 300°K, a quenching coefficient of 4×10^{-14} cm^3 $molec^{-1}$ sec^{-1} is obtained which, for a possible maximum instantaneous $O(^3P)$ concentration of 2×10^{14} cm^{-3}, would give a $CO^{\ddagger}$ loss rate of 8 sec^{-1}, a figure that would not explain the lack of observation of $CO^{\ddagger}$.

The data of Eckstrom[12] over the same temperature range, however, indicates that the $p\tau$ product is insensitive to temperature; thus the extrapolation to 300°K gives a quenching coefficient of 1×10^{-12} cm^3 $molec^{-1}$ sec^{-1}, or for $[O(^3P)] = 2 \times 10^{14}$ cm^{-3}, a decay time constant of 5 msec. This is still not fast enough to eliminate any signal from $CO^{\ddagger}$; in Figure 5(a) one sees that there is no signal at 1-2 msec, and with a 5-msec decay time, the signal at 1-msec should be almost the same as in the case where the decay time is 30-100 msec. Nevertheless information on $CO^{\ddagger}$ quenching by $O(^3P)$ at 300°K should be obtained.

A further hypothesis is that the important quencher is not $O(^3P)$ but $O_2(b\,^1\Sigma_g^+)$, which in our system would have a concentration at $\sim$ t=0 of

about 1×10^{13} cm^{-3}. Although quenching of $O_2(b^1\Sigma_g^+)$ by CO is slow[13] ($k = 4 \times 10^{-15}$ $cm^3 molec^{-1} sec^{-1}$), it is possible that interaction between $CO^{\ddagger}$ and $O_2(b^1\Sigma_g^+)$ is considerably faster. To suppress the $CO^{\ddagger}$ ir signal, a rate coefficient of 1×10^{-10} $cm^3 molec^{-1} sec^{-1}$ would be needed. It is unlikely but not impossible that the rate is that fast.

The $CO_2^{\ddagger}$ experiment is in principle more difficult than the $CO^{\ddagger}$ experiment, since the saturation pulse is terminated only after 0.7 - 1.0 msec, while the expected decay time constant will be 1-2 msec. If there is an additional factor of 2 increase in the decay rate, this might explain the apparent lack of signal. Quenching by $O(^3P)$ has been measured by Center,[14] but again down to only 2000°K, so extrapolation to 300°K is questionable. Quenching of $O_2(b^1\Sigma_g^+)$ by CO_2 is 100 times faster than by CO,[13] so that in this case it is more reasonable that the quenching of $CO_2^{\ddagger}$ by $O_2(b^1\Sigma_g^+)$ might account for the apparent high $CO_2^{\ddagger}$ loss rate.

It seems to us that the search for an explanation for our negative results is best directed along the lines of looking for a rapid homogeneous chemical interaction. Two possibilities have been discussed, and it may be possible to visualize others. The problem is not a simple one. To our knowledge, there are two other groups working on making ir measurements on the $O(^1D)$-CO, N2, CO_2 systems--C. von Rosenberg at Avco and Smith and Rosenwaks at Cambridge, England. We are not aware that either group has yet been successful.

In conclusion we should mention that we are currently measuring transfer efficiencies in various $E \rightarrow V$ reactions, and so far all have been found to be high. When this project began, the only relevant results were the calculations of Fisher and Bauer[15] and of Delos,[16] indicating $\leq$ 5% efficiency for the $O(^1D)$-N_2 system, and the early measurements of Donovan and Husain[17] on the $CO(a^3\Pi)$-CO system, showing 20% transfer efficiency. We now have results on the five systems shown

in Table 1, as yet unpublished, and if one may generalize, it appears that as the systems increase in complexity, from triatomic to tetratomic, the fraction of electronic energy transferred to vibrations increases. The $O(^1D)$-CO_2 system is tetratomic, although only one particle is vibrationally excitable. We would be surprised if the $O(^1D)$-CO_2 efficiency is not at least as high as that for the $O(^1D)$-CO system, and it could be as high as some of the other systems in the table. For the purposes of atmospheric modeling, we feel that there is justification for assuming a transfer efficiency of 50% for the $O(^1D)$-CO_2 case. Since such a value precludes the energy starting out in the lowest vibrational levels, the atmosphere will not be optically thick for radiation from the initially excited levels, and one may assume that the largest fraction of the ir emission will either reach the ground or be lost to space.

TABLE 1

SOME E → V TRANSFER EFFICIENCIES

System	Efficiency
$O(^1D) + N_2 \rightarrow O(^3P) + N_2^{\ddagger}$	33%
$O(^1D) + CO \rightarrow O(^3P) + CO^{\ddagger}$	40%
$CO(d^3\Delta) + CO \rightarrow 2CO^{\ddagger}$	65%
$CO(d^3\Delta) + N_2 \rightarrow CO^{\ddagger} + N_2^{\ddagger}$	80%
$CO(a^3\Pi) + CO \rightarrow 2CO^{\ddagger}$	87%

For subsequent work on the $O(^1D)$-CO_2 problem, it is probably necessary to make other kinetic measurements. We have suggested that interactions of $O(^3P)$ and $O_2(b^1\Sigma_g^+)$ with $CO^‡$ and $CO_2^‡$ may be of critical importance, and such studies should be carried out. It would not be difficult to produce CO(v=1) and CO_2(001) by ir resonance fluorescence and to observe the effect of $O(^3P)$ and $O_2(b^1\Sigma_g^+)$ addition.

Since the apparent high loss rate of $CO^‡$ was not contemplated, based on the uv resonance fluorescence measurements, no effort was made to eliminate the electronic disruption taking place at $t < 1$ msec. If indeed the signal is to be found during the first millisecond, it will be necessary to provide adequate shielding between the lamp and the detector. As the scattered light signal is terminated within 100 μsec, one can certainly decrease the ir detector dead time to this range.

One further possibility is to use O_3 instead of O_2 as the $O(^1D)$ source, utilizing the lamp radiation at 2300 - 2800 Å, which is presumably much more intense than the vacuum-uv radiation. We have avoided this approach, which is being used by von Rosenberg, because we feared the quenching effect of O_3 on $CO^‡$. However, it might be possible to work at O_3 pressures sufficiently low to avoid the problem. In subsequent work this idea should be considered.

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