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Photodissociation quantum yields of CO₂ between 1200 and 1500 Å*

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Measurements of the photodissociation quantum yields of CO₂ have been carried out using various atomic line sources between 1200 and 1500 Å. The production of CO was monitored by resonance fluorescence, and the results indicate that where the CO₂ 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 (a) 1216 Å, 0.57 ± 0.11 , (b) 1302–1306 Å, 0.21 ± 0.07 , (c) ~1390 Å, 0.46 ± 0.05 , (d) 1492–1495 Å, 0.58 ± 0.06 . The CO₂ 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 CO₂ has often been used as an actinometer in the vacuum-uv spectral region, since it has been generally believed that dissociation between 1200 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 measurements¹ 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 Inn² 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 CO₂ atmospheres of Mars and Venus. One of the problems associated with the aeronomy of these planets is that the CO₂ is almost undissociated, which is a surprising observation in view of the fact that CO₂ 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 CO₂ 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 slow³ to re-form CO₂ 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 favor⁴ involves trace amounts of HCl and H₂O.

An alternative to CO₂ dissociation following photon absorption is fluorescence, and Clark and Noxon⁵ carried out an experiment to look for fluorescence, with negative results. Felder *et al.*⁶ investigated the possibility of collision-induced dissociation at high CO₂ 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 CO₂ 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 CO₂ photodissociation. Measurements are made using various atomic lines of calibrated intensities as photodissociation sources, utilizing an approximately constant fractional light absorption by CO₂ (~1%/cm).

The atomic lamps that were used are listed in Table I. 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 I lists the measured relative intensities for the multiple lines as well as the CO₂ absorption

TABLE I. Atomic line lamp characteristics.

Lamp	λ(Å)	Relative multiplet intensities	CO ₂ absorption cross sections (NTP)	
			This work (cm ⁻¹ atm ⁻¹)	Nakata <i>et al.</i>
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

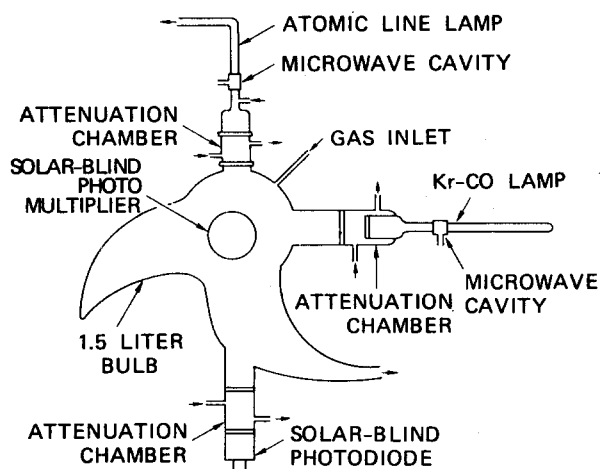


FIG. 1. Apparatus for photodissociation measurements.

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 CO₂ introduced into a 0.5 m spectrograph. Table I also includes the CO₂ absorption cross sections 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 Fig. 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% O₂ in Ar, 10% N₂ in He, 10% H₂ in He, and 0.2% Cl₂ in He.

The attenuating chamber below the source lamp is used to spectrally purify the lamp emissions. Table II 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 CO₂ to the cell (34 cm path length) was generally consistent with the measured cross sections (Table I). 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 203 A 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 CO₂ 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(A¹Π - X¹Σ⁺) 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 CO₂ 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% H₂O 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 1550-1700 Å region. A detector attenuation chamber in front of the photomultiplier was swept with dry N₂.

Measurements were made by injecting CO₂ 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 425 A 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 gas (see Table II) 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 CO₂ absorption cross section for the different lamps, this means that the CO₂ pressure varied by a similar factor. Since both the CO exciting and fluorescent radiations are absorbed by CO₂, and the fluorescent radiation is probably quenched by CO₂, the sensitivity of the system to CO decreased at the higher CO₂ pressures. Thus, after each measurement of the CO generation rate, the same CO₂ 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 CO₂ was Coleman Instrument Grade (99.99%).

TABLE II. 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 ₂ O 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 ₂ O in Ar
H	5% O ₂ in Ar	2.5% CH ₄ in N ₂

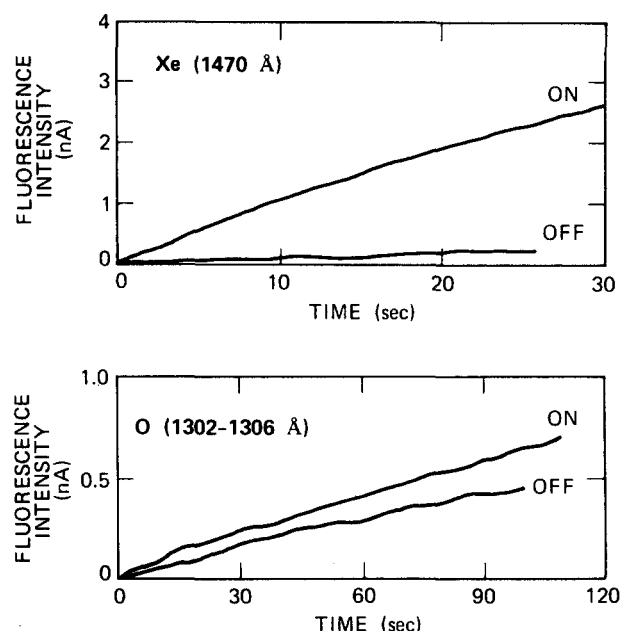


FIG. 2. CO fluorescence signal buildup for two lamps: intensity (nA) vs time (sec). Lower line—CO lamp only, upper line—both lamps. CO₂ pressures—Xe, 0.55 Torr; O, 0.38 Torr.

RESULTS

Figure 2 shows typical CO generation curves for Xe (1470 Å) and O(1302–1306 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 CO₂ pressure conditions are linear.

The data for the six lamps are tabulated in Table III.

TABLE III. Lamp intensity and CO production rate.

Lamp	p_{CO_2} (Torr)	Transmitted lamp intensity (nA)			CO production rate (mTorr/min)				Average
		No CO ₂	With CO ₂	Fraction absorbed	CO(4+) lamp	Both lamps	Difference	Normalized ^a	
N	0.58	29.0	19.5	0.328	0.009	0.026	0.017	0.179	0.192 ± 0.014
		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	
Xe	0.55	138	96	0.304	0.004	0.104	0.100	0.238	0.248 ± 0.008
		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	
Cl	0.72	46.0	27.5	0.402	0.013	0.046	0.033	0.178	0.168 ± 0.010
		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	
O	0.38	6.20	4.30	0.306	0.0049	0.0065	0.0016	0.085	0.097 ± 0.029
		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	
H	4.0	5.35	3.85	0.280	0.036	0.043	0.0071	0.467	0.415 ± 0.052
		5.50	3.80	0.310	0.034	0.040	0.0061	0.363	
Xe ^b	0.50	122	85	0.305	0.0014	0.0786	0.0772	0.207	...
Kr ^b	2.4	7.20	5.16	0.281	0.0099	0.0180	0.0081	0.400	...

^aNormalized to total absorption and 100 nA lamp intensity.

^bThe Kr data taken initially were 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.

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 IV 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 CO₂ in the cell was only 7% of that after the CO₂ was introduced. In any case, any correction for heterogeneous CO production would result in even lower quantum yields than those listed in Table IV.

One observation for which a satisfactory explanation is lacking is the curvature that appears in the CO production plots of Fig. 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 CO₂ 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.

TABLE IV. Quantum yield determination.

Lamp	Normalized CO production rate (Table III) (mTorr/min)	Lower window fractional transmission	Photodiode quantum efficiency (%)	Final quantum yield ^a
N	0.192 ± 0.014	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 ^b	0.207	0.375	15.0	0.75
Kr ^b	0.400	0.220	15.0	0.85

^aRelative to $\phi(\text{Xe}) = 0.75$.^bSee note on Table III.

The error limits given in Table IV 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 CO₂ photolysis is then relatively less. Using somewhat subjective estimates, we feel that the data with the Xe, N, and Cl lamps is reliable to $\pm 10\%$, while for the H and Kr lamps, $\pm 20\%$ limits are reasonable. Because of the additional difficulty of the low quantum yield at the oxygen line, $\pm 35\%$ limits are estimated for the triplet of lines at 1302–1306 Å.

DISCUSSION

Until recently, most measurements of CO₂ photodissociation quantum yields have been carried out at two wavelengths, 1236 and 1470 Å. As may be seen in Table IV, 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 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 CO₂ in the region of interest⁸ is presented in Fig. 3. Our six points represent photodissociation cross sections, although the line joining them has no physical significance. Comparing the values in Table IV 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 CO₂ 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 CO₂ 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 ~ 10 cm⁻¹, it is probably not correct to assume that the lines from the atomic lamps have a Doppler width of 0.1–0.2 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 Xe₂, and the same characteristic is to be expected from the Kr lamp.¹⁰ Measurements by Poland and Lawrence¹¹ on oxygen lamps indicate FWHM values of ~ 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 states 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 CS₂, the density of transitions¹² is 3–10 per cm⁻¹. Therefore, although the lack of fine structure in the CO₂ absorption spectrum has been taken as an indication of

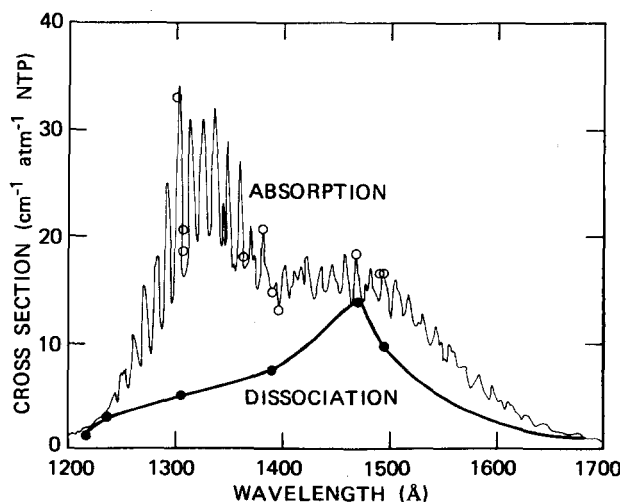


FIG. 3. CO₂ photoabsorption and photodissociation coefficients; CO₂ pressure range, 0.38–4.0 Torr. Open circles—measured absorption coefficients in this work. Photoabsorption data from Ref. 8.

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 Sach¹³ (who obtained $\phi_{\text{xs}} \sim 0.7$ and $\phi_{\text{Kr}} \sim 0.4$, although at much higher CO₂ 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 1500–1700 Å continuum source was used to irradiate CO₂, 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 less than 1 atm. 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 1400–1600 Å range. No fluorescence was seen between 1500 and 8000 Å, over a range of CO₂ pressures of 1 mTorr to 10 Torr. Low upper limits were thereby set on the fraction of excited CO₂ molecules fluorescing. However, these conclusions are modified if we assume a lifetime of 10⁻⁵ sec and a rate constant for energy transfer of 10⁻⁹ cm³ molecule⁻¹.sec⁻¹, instead of 10⁻⁷ sec and 3 × 10⁻¹⁰ cm³ molecule⁻¹.sec⁻¹ as used by Clark and Noxon. In that case, instead of 0.2% being an upper limit for the fraction of CO₂^{*} 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 NO₂, CS₂, and SO₂, the discrepancy may be as great as two orders of magnitude.¹⁴ The usual explanation, given initially by 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 CO₂ system under consideration. It therefore seems premature to rule out the possibility of CO₂ fluorescence at low pressure.

If a nonpredissociated CO₂^{*} 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 CO₂, 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 III 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 and 1500 Å is in the L_α line. Therefore, from the standpoint of over-all CO and O production, the new results suggest a decrease of a factor of ~ 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 1250–1500 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 CO₂ pressures, representative of the absorbing regions.

ACKNOWLEDGMENTS

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