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# QUANTITATIVE ABSORPTION AND FLUORESCENCE STUDI.
# OF CO FROM 1060 TO 1550 A

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JUN 1982
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## ABSTRACT

The photoabsorption cross section of CO has been measured in the 1060-1550 A region using synchrotron radiation. The oscillator strengths for the transitions from $CO(X^1\Sigma^+)$ to various excited states are obtained from these data. Fluorescence from excited CO was observed in the 1150-3000 A and 3000-8000 A regions. The quantum yields for the production of fluorescence from the $A^1\Pi$ and $B^1\Sigma^+$ states are unity because their excitation energies are below the dissociation limit. The $C^1\Sigma^+$, v = 0 level has significant fluorescence quantum yields both in the UV and visible region, but the yields for the $E^1\Pi$, v = 0 and $C^1\Sigma^+$, v = 1 levels are very small. The $C^1\Sigma^+$, v = 1 level is presumably predissociated. The cross sections for the production of fluorescence from the $a'^3\Sigma^+$, $d^3\Delta_i$, $e^3\Sigma^- \rightarrow a^3\Pi$, and $B^1\Sigma^+$, $C^1\Sigma^+ \rightarrow A^1\Pi$ transitions upon excitation from the $X^1\Sigma^+$ have also been measured.

(NASA-CR-169292) QUANTITATIVE ABSORPTION AND FLUORESCENCE STUDY OF CO FROM 1060 TO 1550 A (SRI International Corp., Menlo Park, Calif.) 15 p HC A02/MF A01 CSCL 20H

N82-32088

Unclas
G3/72 23740

MP 80-151
02/06/80

## 1. INTRODUCTION

Because carbon monoxide is abundant in interstellar space, the knowledge of its photoexcitation cross sections is important for determining its role in interstellar photochemistry.

Although the photoabsorption cross section of CO in the 1060-1550 Å region has been repeatedly measured (Watanabe, Zelikoff, and Inn 1953, Slanger and Black 1969, Meyer and Samson 1970), the results are not consistent. For example, at 1470 Å, the cross section measured by Slanger and Black (1969) is two orders of magnitude higher than that measured by Watanabe, Zelikoff, and Inn (1953) and Meyer and Samson (1970). This great variation is caused mainly by the different light source bandwidths and gas pressures used for the measurements. Since CO absorption spectra have very narrow rotational lines, the measured cross sections depend on the bandwidth of the excitation sources. The oscillator strength, which is proportional to the integrated absorption cross section and is independent of the light source bandwidth, should be a more meaningful quantity for comparison when the bandwidth of excitation source is limited. However, the oscillator strengths for some CO transitions given by various measurements and theoretical calculations vary over an order of magnitude (Carlson et al, 1978). We attempt here to reconcile previous inconsistencies through the measurement of average absorption cross sections at low pressures, using continuum synchrotron radiation as a background source.

Fluorescence from the triplet systems by photoexcitation of CO from its ground state has been reported (Becker and Welge 1965, Slanger 1968). Direct excitation from the $CO(X^1\Sigma^+)$ ground state to the triplet states is optically forbidden, but some rotational transitions are allowed through the mixture of

the triplet states with the $A^1\Pi$ state (Krupenie 1966, Field 1971). However, the strength for excitation of the $CO(X^1\Sigma)$ into the $d^3\Delta_i$ state at 1470 Å reported by Becker and Welge (1965) is much smaller than that reported by Slanger (1968). Also, the cross sections for the photoexcitation of $CO(X^1\Sigma^+)$ into the triplet states have not been measured previously. We report here the cross sections for CO visible fluorescence at low pressure.

## 2. EXPERIMENTAL

The experimental setup has been described in a previous paper (Lee, 1980). In brief, synchrotron radiation produced by the electron storage ring of the University of Wisconsin was dispersed by a 1-m vacuum monochromator and used as the light source. The absorption cross section was measured by light attenuation when CO was introduced into the 40-cm gas cell. The photon flux of synchrotron radiation was measured by a calibrated photodiode or a combination of sodium salicylate and a photomultiplier. The CO molecular fluorescence was observed 7 cm from the monochromator slit at right angles to the synchrotron radiation by a CsTe solar blind photomultiplier tube (EMI G26H215) in the 1150-3000 Å region and by a visible photomultiplier tube (EMI 9558B) for wavelengths longer than 3000 Å. The measurements were performed at a temperature of 20° C.

CO gas obtained from Liquid Carbonic with a minimum purity of 99.5% was used without further purification. The cell was continuously pumped by a sorption pump and a constant pressure maintained by a slow flow of fresh CO gas. This flow system conveniently prevented the accumulation of impurities in the cell. Since the flow rate was very slow, the cross sections measured in this system are found to be no different from those for a static system.

## 3. RESULTS AND DISCUSSION

### 3.1 Photoabsorption cross section

The photon flux, $I(\lambda_o)$, through the gas at a wavelength $\lambda_o$ is given by

$$I(\lambda_o) = \int I_o g(\lambda) e^{-n\sigma(\lambda)\ell} d\lambda$$

where the integration is over the monochromator bandwidth, $I_o$ is the photon flux without gas in the cell, $g(\lambda)$ is the monochromator slit function ($\int g(\lambda)d\lambda = 1$ when it is integrated over the monochromator bandwidth $\Delta\lambda$), n is the gas concentration, $\ell$ is the length of the gas cell, and $\sigma(\lambda)$ is the photoabsorption cross section.

If the molecular absorption band is much broader than $\Delta\lambda$, then $I(\lambda_o)$ will depend on the gas concentration by Beer's law, and the photoabsorption cross section is proportional to $\ell n(I_o/I)$. However, as noted earlier, CO has very sharp structure in the region studied. Several rotational lines are covered in a minimum monochromator bandwidth of 0.3 Å. Therefore, $\ell n(I_o/I)$ is not linearly dependent on the gas pressure, as shown in Figure 1. Since the cross sections for the rotational lines are very large, the portion of photon fluxes resonant with the rotational lines will be totally absorbed at low gas pressure. Thus $I(\lambda_o)$ represents only the nonresonant photon flux when the gas pressure becomes high. As shown in Figure 1, $\ell n(Io/I)$ is quickly saturated at pressures higher than 2 mtorr. This pressure dependence is consistent with the earlier measurements of Slanger and Black (1969), where they used the $CO(A^1\Pi \rightarrow X^1\Sigma^+)$ emission from a rare-gas resonance lamp as an excitation source.

For low gas pressure, we have $e^{-n\sigma(\lambda)\ell} \sim 1 - n\sigma(\lambda)\ell$, and

$$\ell n(I_o/I) = n\ell \int g(\lambda)\sigma(\lambda)d\lambda$$

The cross section averaged over the monochromator bandwidth defined as

$$\bar{\sigma}(\lambda_o) = \int g(\lambda)\ \sigma(\lambda)\ d\lambda$$

can be obtained from $\ell n(I_o/I)$. The result for the average cross section in the 1060-1550 Å region is shown in Figure 2, where the monochromator bandwidth is 0.3 Å. The uncertainties for the data are estimated to be within 10% of the given values. The positions for the various electronic states and their vibrational levels (Krupenie 1966, Tilford and Simmons 1972) are indicated in Figure 2.

Our measured average cross sections are about two orders of magnitude higher than the cross sections reported by Watanabe et al (1953) and Myer and Samson (1970). The pressures of 0.05-30 torr used in the measurements of Myer and Samson (1970) are well beyond the linear absorption region (see Figure 1), so their measured cross sections will be considerably lower than the true average cross section measured in the linear region. The cross section at 1470 Å measured at low gas pressure by Slanger and Black (1969) is about a factor of 4 higher than the present value. Since Slanger and Black (1969) used the $CO(A^1\Pi \rightarrow X^1\Sigma^+)$ emission band as light source, their measured cross section will be close to the rotational line cross section, which is of course larger than the average cross section reported here.

It is more meaningful to compare the vibrational oscillator strength, which is proportional to $\int\sigma(\nu)d\nu = \int\bar{\sigma}(\nu)d\nu$ integrated over the molecular

band and is independent of monochromator bandwidth. The oscillator strengths for the $v' = 0 \leftarrow v'' = 0$ vibrational bands of the A, B, C, and E ← X transitions are listed in Table 1. The oscillator strength is calculated from the measured peak absorption cross section, $\sigma$ ($10^{-18}$ cm), the wavelength, $\lambda$ (Å), and the molecular vibrational half-bandwidth, $\Delta\lambda$ (Å), by the equation $f = 113\ \sigma\Delta\lambda/\lambda^2$, which is derived from $f = \mu hc^2\nu B/\pi e^2 = (\mu c^2/\pi e^2)\int\sigma d\nu$ (Herzberg 1967). The oscillator strengths obtained from the lifetime measurements by Carlson et al (1978) are also listed in Table 1 for comparison. The agreement for the A ← X and C ← X transitions is surprisingly good. However, the present value for the B ← X transition is only about one-third of the value of Carlson et al. The reason for this disagreement is not clear. The oscillator strengths for the A ← X transition obtained from various experimental measurements and theoretical calculations are generally consistenc within a factor of 2, but the values for the B ← X and C ← X transitions show great discrepancies, varying from $0.29 \times 10^{-2}$ to $5.3 \times 10^{-2}$ and from $0.15 \times 10^{-2}$ to $1.63 \times 10^{-2}$, respectively.

In the wavelength region from 1060 to 1550 Å, absorption continua under the discrete states are very small. We estimate that the absorption cross section for a dissociative continuum is smaller than $8 \times 10^{-20}$ $cm^2$. At higher gas pressures additional absorption bands show up at the positions of $^{13}CO$ isotope absorption. The doublet features for some of the absorption bands shown in the absorption spectrum given by Myer and Samson (1970) result from such an isotopic effect.

## 3.2 Fluorescence cross section

For photon wavelengths longer than the dissociation threshold of 1116.1 Å (Krupenie 1966), the excited CO decays only through emission, so the fluorescence quantum yields for the $A^1\Pi$ and $B^1\Sigma^+$ states must be equal to unity. However, for energies above the dissociation limit, the excited molecules may decay through either emission or dissociation. Since the $C^1\Sigma^+$ and $E^1\Pi$ states absorb light at energies above the first dissociation limit of CO, the quantum yield for fluorescence from these states may be less than unity because of possible dissociation channels.

We find that the $C^1\Sigma^+$, $v = 0$ state has significant fluorescence intensity in the 1150-3000 Å region, but the emissions from the $C^1\Sigma^+$, $v = 1$ and $E^1\Pi$, $v = 0$ states are very weak. Similarly, only the $C^1\Sigma^+$, $v = 0$ state fluoresces at $\lambda > 3000$ Å. It is apparent that the $C^1\Sigma^+$, $v = 1$ state is predissociated. Although emission from the E, $v' = 0 \rightarrow X$, $v'' = 0$ transition has been observed (Hopfield and Birge 1927, Simmons and Tilford 1974), this fluorescence cross section may be small. Simmons and Tilford (1974) have observed that accidental predissociation occurs at the R(30) and P(32) lines of the E, $v' = 0 \rightarrow X$, $v'' = 0$ band, but the intermediate state that predissociates the E state has not been identified.

The cross sections for the production of fluorescence from the $a'^3\Sigma^+$, $d^3\Delta_i$, $e^3\Sigma^- \rightarrow a^3\Pi$ transitions in the $\lambda > 3000$ Å region are shown in Figure 3 as a function of excitation wavelength. The fluorescence cross section is obtained from the fluorescence radiation rate and put into absolute scale by normalization to the $OH(A^2\Sigma^+ \rightarrow X^2\Pi)$ fluorescence rate from $H_2O$ photodissociation, for which the cross section is known (Lee, 1980). However, in this normalization the photomultiplier response was assumed as constant. Since the CO triplet emission systems have wavelengths spread widely in the

visible and infrared region (Krupenie 1966), it is difficult to include the photomultiplier response in the absolute normalization. Actually, the photomultiplier response for the $OH(A^2\Sigma^+ \rightarrow X^2\Pi)$ band at 3100 Å is higher than that for the CO triplet systems, so the fluorescence cross sections shown in Figure 3 present only the values of low limit.

In general, the cross sections for the production of the triplet systems are smaller than $6 \times 10^{-20}$ $cm^2$. The triplet systems have significant absorption cross sections only when they are perturbed by the $A^1\Pi$ state. For example, the $d^3\Delta_i$ $v = 4$ and $e^3\Sigma^-$ $v = 1$ levels have significant absorption cross sections because they are perturbed by the $A^1\Pi$ $v = 0$ level. Because of the small cross section, the fluorescence radiation rate for every excitation band is linearly dependent on the gas pressure up to 100 mtorr. This linear pressure dependence has also been reported by Slanger (1968) for 1470 Å excitation.

The yields for fluorescence from the $C \rightarrow A$ and $B \rightarrow A$ transitions decrease with increasing excitation energy. The yield is more than 20% for the $B^1\Sigma^+$, $v = 0$ level and 10% for the $v = 1$ level, but for the $C^1\Sigma^+$, $v = 0$ level it decreases to less than 2%. The $E^1\Pi$, $v = 0$ and $C^1\Sigma^+$, $v = 1$ levels exhibit insignificant fluorescence both in the UV and visible region. These results imply that the states at energies higher than the $C^1\Sigma^+$, $v = 1$ state ($\lambda < 1060$ Å) are probably predissociated.

## 4. CONCLUDING REMARKS

The average absorption cross sections reported here are much larger than the published data. However, the oscillator strengths derived from these absorption cross sections agree with those from lifetime measurements (Carlson et al 1978). The validity of our results is further strengthened by the fact that the oscillator strengths for the NO molecule, which were measured in the same experiment (Guest and Lee, 1980), also agree well with other experiments.

Except for the $C^1\Sigma^+$, $v = 1$ and $E^1\Pi$, $v = 0$ states, the CO excited states are not dissociated by the photon energies in the region considered here. This result indicates that CO is not significantly dissociated by interstellar UV radiation, which is most intense in the wavelength region we studied. In contrast, the NO molecule has very high photodissociation yields (Guest and Lee 1980) which leads to a high dissociation rate by interstellar UV radiation. These results may be useful for explaining the observation that CO is very abundant in the interstellar medium, whereas NO is found only in dark clouds that do not expose NO to UV radiation.

ACKNOWLEDGMENTS

The authors are grateful to the staff of the Synchrotron Radiation Center (SRC) of the University of Wisconsin, particularly E. M. Rowe and R. Otte. We thank Dr. C. G. Olson for the use of the MacPherson Vacuum Monochromator. We also thank Dr. T. G. Slanger, Dr. G. Black, Dr. D. L. Huestis and Dr. J. R. Peterson for helpful discussions. J. A. Guest thanks Prof. R. N. Zare for financial support under NSF Grant PHY 79-08694. The SRC is supported by the National Science Foundation under Grant No. DMR-77-21888.

This work is supported by the National Aeronautics and Space Administration/Astrophysics Division under Contract No. NASW-3270.

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## FIGURE CAPTIONS

Fig. 1 The logarithm of the ratio of the incident photon flux, $I_o$, to the attenuated photon flux, I, at gas pressures up to 100 mtorr for photon wavelengths of 1076, 1368, 1393, and 1479 Å.

Fig. 2 The photoabsorption cross section of CO in the 1060-1550 Å region. The wavelength positions of various states (Krupenie 1966) are indicated.

Fig. 3 The cross sections for fluorescence in the $\lambda > 3000$ Å region upon excitation of the $CO(X^1\Sigma^+)$ ground state molecule in the 1060-1550 Å region. The wavelength positions of various states (Krupenie 1966) are indicated. The fluorescence cross sections for the triplet states of $\lambda > 1240$ Å are small, and their magnitudes are indicated by the right-hand scale.

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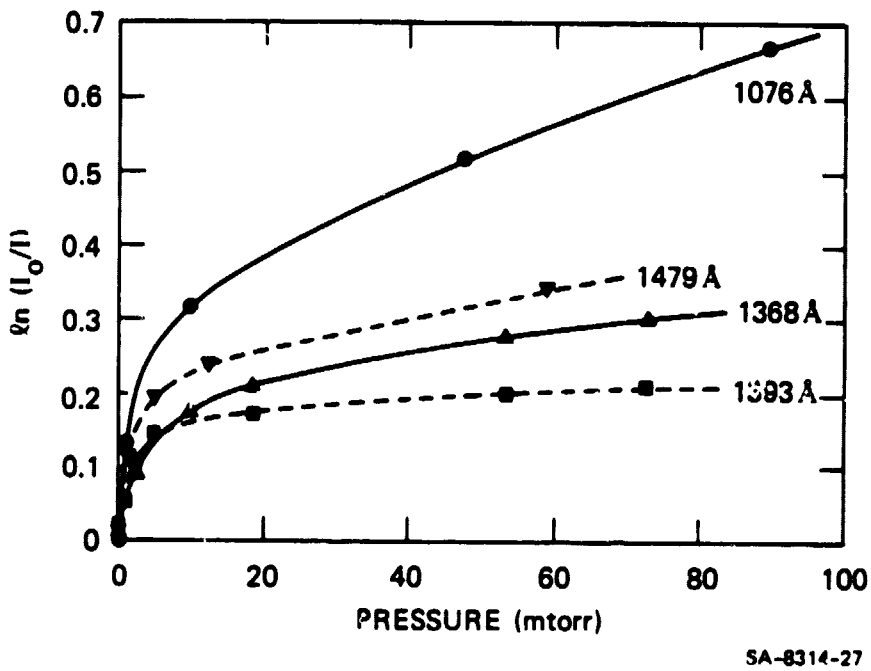


Figure 1

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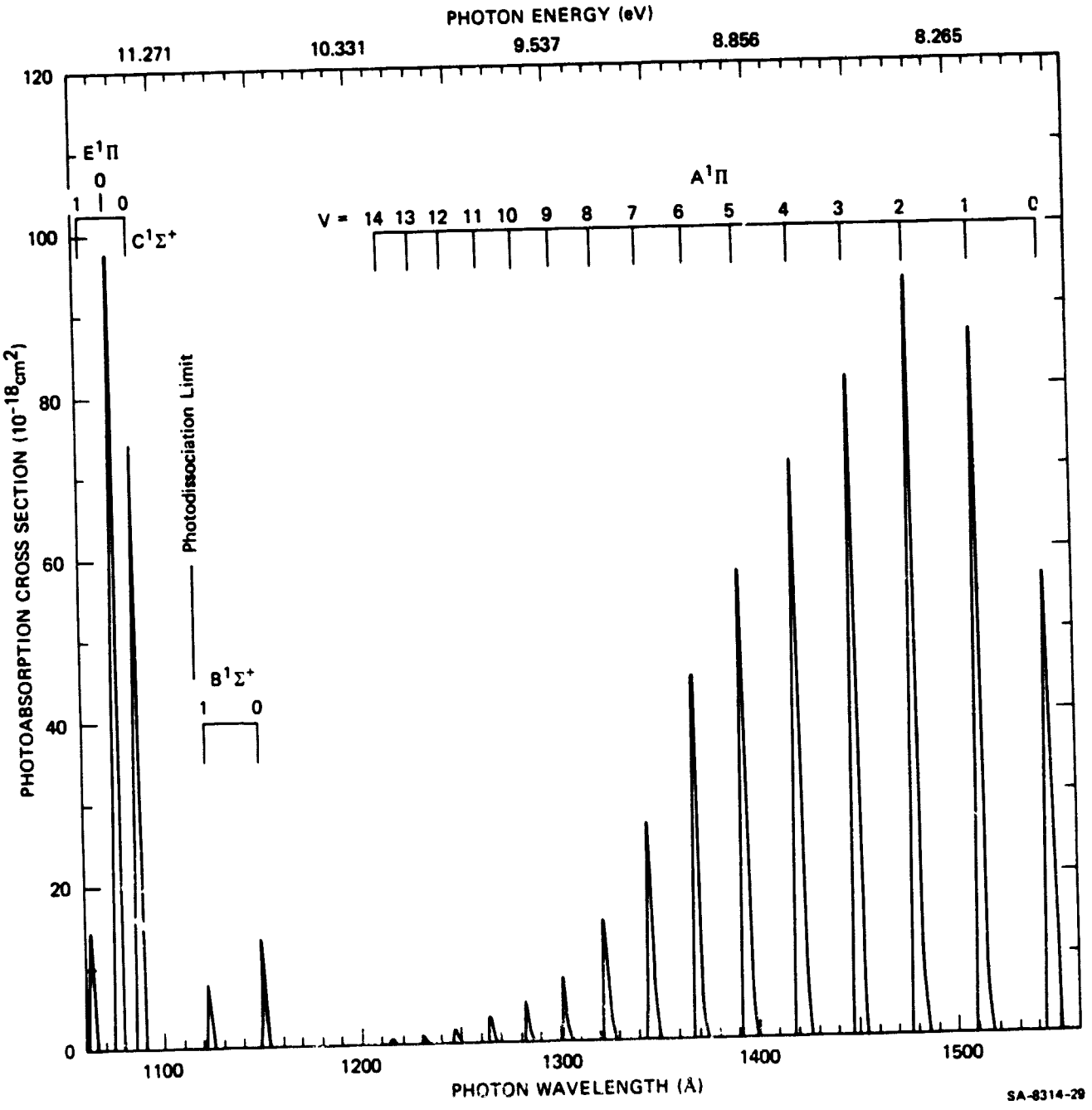


Figure 2

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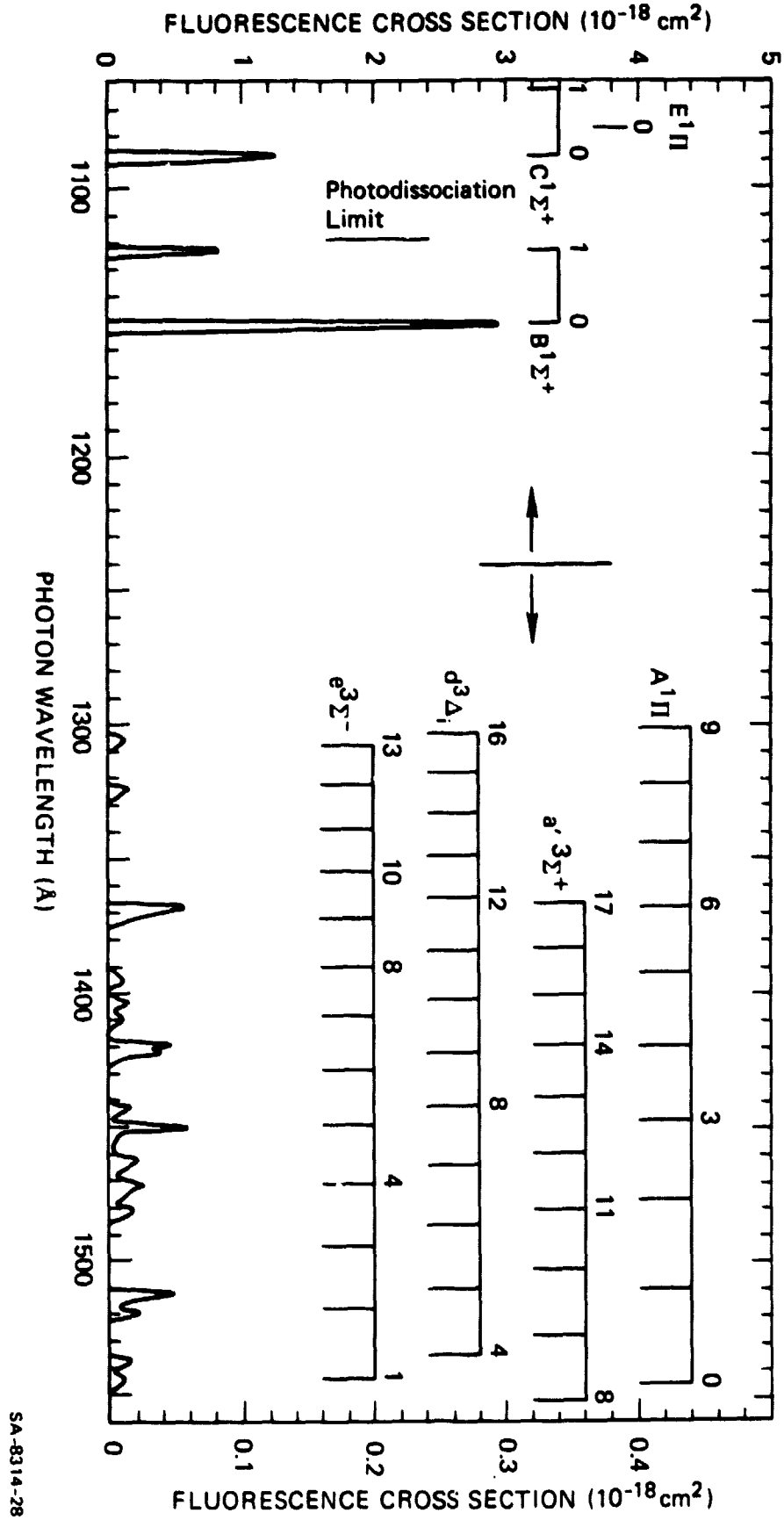


Figure 3

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