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PREFACE

A compilation of experimental and calculated data on the radiative properties of species important in Venusian entry is presented. Molecular band systems, atomic lines, free-bound continua, and free-free continua are considered for the principal radiating species of shock-heated carbon dioxide. A limited amount of data pertinent to the species in the ablation layer is also included. The assumption is made that the Venus atmosphere so closely approximates pure carbon dioxide CO_2 that the inviscid layer radiation is due almost entirely to thermally excited CO_2. The only exception is the inclusion of data on the violet band system of the cyanogen radical CN. For the principal contributors, recommendations are made as to best property values for radiative heating calculations. A review of the basic equations and the relationships of the various emission-absorption gas properties is also included.

INTRODUCTION

Calculations of radiative heat transfer to an entry vehicle require a determination of the concentration of gas species in the shock layer and the radiative contribution of all major species. Such calculations are therefore dependent on inputs of the radiative properties of each species to be considered. These radiative properties, variously presented as cross section, oscillator strength (f-number), transition moment, transition probability, radiative lifetime, absorption coefficient, etc. are based on fundamental atomic structure and, ideally, could be calculated. For some cases, calculations are in fact available, which are sufficiently accurate for radiative heating calculations. For most cases, however, no satisfactory calculations have as yet been undertaken and resort must be made to experimental determinations. A large number of such experimental measurements have been made and reported in the literature in the past decade for many gas species, with emphasis on the gas species which are present in shock heated air; but the gases prevalent in the atmospheres of the other planets have also been treated to a lesser degree.

In the present paper, entry into the atmosphere of the planet Venus is considered. For direct entry, radiative heating is approximately equivalent to convective heating. Thus heating calculations must consider the radiative contribution in some detail, and such calculations require inputs of the radiative properties, not only of the inviscid layer species but also the major species of the ablation layer.

The lower atmosphere of Venus is presently believed to consist almost entirely of carbon dioxide. Reference 1, for instance, concludes that carbon dioxide comprises about 97 percent or more by volume of the lower atmosphere, with nitrogen as the next most abundant gas. The radiation spectrum from the shock layer of a Venus probe would therefore be expected to be dominated by species resulting from shocked CO_2, with contributions from CN, NO, or nitrogen playing a lesser role.

For most of the gas species expected to be present in the shock layer, experimental determinations of the radiative properties are reported in the literature, and for some of these species, the number of experiments reported is rather large. The disagreement of the various reported values is also frequently large and is an indication of the difficulty of such experiments and the differing assumptions which were made in order to reduce the data. Thus, different calculations of shock-layer radiation may vary considerably as a result of using the various reported values for the radiative properties available in the literature.

The present work compiles and compares the radiative-property data that are available in the open literature for Venus entry shock-layer radiation. Recommendations are then made as to best values to use in radiative heating calculations, based on what are believed to be the most accurate data. To some degree the species of the ablation layer have also been considered, but comparatively little data are available. For example, data for several species thought to be emitted from phenolic carbon heat shields could not be found.

No clear-cut criteria were apparent to determine what radiating species ought to be included. Species included herein are normally considered in various radiative computational programs. But other species might well be included if data were available. The primary list of radiators considered is

Molecular band systems:

C_2	Swan
CO	fourth positive
CO^+	comet tail
CN	violet
CH	A – X, B – X, C – X
CF	
C_3	

Atomic lines:
C
O

Free-bound continua:
C
O
C^+
C^-
O^-

Free-free continua:
Electron-ion
Electron-neutral

The band systems of CH, CF, and C_3 are included because, for certain ablator materials, these will play important roles in the ablation layer. The C_2 Swan band system may also be expected to be more important in the ablation layer than in the shock layer. Summaries of the literature found for other band systems, which have been considered of secondary importance, are contained in the appendix. However, there is no conclusive basis to identify each radiation species as being of primary or secondary importance.

SYMBOLS

The International System of Units (SI) is used for all physical quantities in the present study except where specifically noted. Conversion of the equations to cgs units may be accomplished by removing the term $4\pi\epsilon_0$, which has been left intact in the equations.

A	neutral atom
A^+	singly ionized atom
$A_{J'J''}$	Einstein emission coefficient for a rotational line
A_{UL}	Einstein coefficient for spontaneous emission
$A_{v'}$	summation of $A_{v'v''}$ over all lower vibrational states, $A_{v'} = \sum_{v''} A_{v'v''} = \frac{1}{\tau}$
$A_{v'v''}$	Einstein emission coefficient for a vibrational band
B_ν	Planck intensity function
c	velocity of light
D_0	molecular dissociation energy
d	total degeneracy
E	energy of atomic state
e	electronic charge
e^-	electron
f_{el}	electronic absorption oscillator strength
$f_{J'J''}$	rotational-line absorption oscillator strength

$f_{v'v''}$	vibrational-band absorption oscillator strength
G	Gaunt factor
g	statistical weight
h	Planck constant
I	energy radiated per unit volume per unit solid angle per second in a transition
I_o	ionization energy
$I_{v'v''}$	energy radiated per unit volume per unit solid angle per second in a vibrational-band transition
J	total angular momentum quantum number
j	volume emission coefficient
k	Boltzmann constant
k_ν	spectral absorption coefficient
M	magnetic quantum number
M_e	electric dipole moment of a molecule
m_e	electron rest mass
N	number of particles per unit volume
n	principal quantum number in an atom
p	parity substates due to Λ doubling
Q	internal partition function
$q_{v'v''}$	Franck-Condon factor

$R_e(r)$	electronic transition moment of a band system
R_{rad}	portion of total dipole moment which includes vibration and electronic motion
R_Y	Rydberg constant
r	internuclear separation distance
$\bar{r}$	r-centroid
r_μ	position vector of particle from center of mass
S	electron spin quantum number
$S_{J'J''}$	Hönl-London factor
s	parameter in equation (42)
T	temperature
$\overline{V}$	vector velocity of particle relative to center of mass
X	matrix element of electric dipole moment
Z	nuclear charge
Z_{eff}	effective nuclear charge in electron-neutral interaction
α	parameter in equation (42)
$\delta_{0,\Lambda}$	Kronecker delta where $\delta_{0,\Lambda} = 0$ if $\Lambda \neq 0$ and $\delta_{0,\Lambda} = 1$ if $\Lambda = 0$
ϵ_0	permittivity of free space
Λ	quantum number of angular momentum of electrons about internuclear axis
λ	wavelength
λ_{th}	threshold wavelength for photoionization

ν	frequency
Σ	quantum number of electron spin component in direction of internuclear axis
σ	absorption cross section
σ_n	free-bound absorption cross section for hydrogenic model
σ_{nf}	free-bound absorption cross section from quantum number n-level
σ_ν	spectral absorption cross section
τ	radiative lifetime
τ_e	element of configuration space
ψ	wave function

Subscripts:

A	atom
e^-	electron
f	free (unbound electron) state
J	rotational quantum number
n	bound-state principal quantum number
UL	generalized notation for upper and lower states, respectively, of a transition
v	vibrational quantum number
μ	each fundamental particle in interacting system

Following standard notation, prime denotes upper state and double prime denotes lower state of a molecular transition.

BASIC RELATIONSHIPS

Once the thermodynamic properties (temperature, density, species concentration) are known at each point in the shock layer, the radiative heating can be calculated from the equation of transfer. The solution of this equation requires, in addition, knowledge of the total absorption by the shock-layer gas at each point. This latter quantity in turn is obtained by summing over each radiative absorption process of each species which contributes at the frequency of interest. In other words, the volumetric or linear absorption coefficient, k_ν, of the shock layer gas is given by

$$k_\nu = \sum_i \sum_p k_{\nu,i,p}$$

where the subscript i denotes a particular species and p signifies a radiative absorption process. It is often easier and more convenient to work with the absorption cross section σ_ν rather than k_ν since much of the dependence upon temperature is eliminated. These two quantities are related through the expression

$$k_{\nu,i,p} = N_{i,L}\sigma_{\nu,i,p}$$

where N_L represents the total number of absorbing particles of species i per unit volume. Those radiative processes making a contribution to the absorption in a high-temperature shock layer include discrete transitions in atoms, ion, and molecules (including individual rotational lines, collections of lines comprising a band, and groups of bands forming a band system), photoionization (atomic and molecular), which is also commonly referred to as a bound-free transition, and free-free transitions or bremsstrahlung. For each radiative process, there are a great many species that could be considered. However, in this report, attention has been restricted to those species and radiative processes which are important in the inviscid and ablation layers for Venusian entry. In addition, the radiative processes that contribute between the frequencies of about 2 to 12 eV (wavelength range 100 to 600 nm) are emphasized. These limits, although somewhat arbitrary, were selected because, for temperatures typical of Venusian entry trajectories, most of the energy is contained within this spectral interval.

The spectral absorption coefficient k_ν or the more fundamental quantity, the absorption cross section σ_ν can be obtained experimentally or can be calculated by recourse to the theory of quantum mechanics. Both procedures are extensively employed and, in many instances, are used together, with experiment providing values for those parameters that are not possible or practical to calculate with present technology. In the following paragraphs, a brief outline is given of the quantum theory for calculating absorption coefficients, and of how these theoretical relations are employed to interpret the experimental measurements.

Line Radiation

The radiation emitted when electronically excited atoms undergo transitions to lower levels gives rise to line radiation of frequency ν_{UL} in which the photon energy of such a transition is

$$h\nu_{UL} = E_U - E_L \tag{1}$$

The intensity of the line is given by

$$I_{UL} = \frac{1}{4\pi} N_U A_{UL} h\nu_{UL} \tag{2}$$

Since

$$\frac{N_U}{N_L} = \frac{g_U}{g_L} \exp\left(-\frac{h\nu_{UL}}{kT}\right) \tag{3}$$

equation (2) becomes

$$I_{UL} = \frac{N_L}{4\pi} \frac{g_U}{g_L} A_{UL} h\nu_{UL} \exp\left(-\frac{h\nu_{UL}}{kT}\right) \tag{4}$$

The relationship between the spontaneous transition probability and the absorption oscillator strength, or f-number, is (ref. 2)

$$A_{UL} = \frac{g_L}{g_U} \frac{8\pi^2}{4\pi\epsilon_0} \frac{e^2}{m_e} \frac{\nu_{UL}^2}{c^3} f_{LU} \tag{5}$$

Also, since

$$N_L = \frac{N}{Q} g_L \exp\left(-\frac{E_L}{kT}\right)$$

the integrated absorption coefficient for an individual atomic line may be written as

$$\int k_\nu \, d\nu = \frac{N}{Q} \exp\left(-\frac{E_L}{kT}\right) \frac{g_L f_{LU}}{4\pi\epsilon_0} \frac{\pi e^2}{m_e c \nu_{UL}^3} \left[1 - \exp\left(-\frac{h\nu_{UL}}{kT}\right)\right] \tag{6}$$

where equations (4) and (5) have been combined and used in Kirchoff's law:

$$I_{UL} = \int k_\nu B_\nu \, d\nu \approx B\nu_{LU} \int k_\nu \, d\nu$$

Equation (6) gives no information about the spectral profile of the line.

Spectral line profiles are dependent on the state of the gas in which the line is emitted (pressure, temperature, electron density, etc.). The inclusion of the important line broadening mechanisms into a prediction of half-widths for polyelectronic atoms is very complicated and usually has a significant degree of uncertainty. However, in high-temperature plasmas, the energy contained in the wings of the lines is of importance and broadening must be accounted for. Due to the wide ranges of the various parameters that affect line shapes, and the complexity of the pertinent theories, no description of this aspect of line radiation will be included here. State-of-the-art discussions of this problem may be found, for example, in the texts by Penner, Griem, and Armstrong and Nicholls (refs. 2 to 4).

Diatomic Molecular Systems

The absorption strength of a diatomic molecular band system is generally stated in terms of an overall electronic absorption oscillator strength f_{el} which is frequently treated as a constant for the band system. This concept for molecular systems derives directly by analogy to its use in the integrated absorption intensity of a single line transition. This extension has been criticized by several investigators (Schadee, ref. 5, Wentink, Isaacson, and Spindler, ref. 6, Wentink, Marram, Isaacson, and Spindler, ref. 7, and Tatum, ref. 8) since it introduces ambiguities. These investigators also indicate that use of a single f_{el}-value for an entire band system has little real meaning. To appreciate these comments fully, it is first necessary to understand how the band-system oscillator strength is obtained. This derivation is briefly outlined below, employing the notation adopted by Schadee (ref. 5).

To define an electronic oscillator strength for a band system, one begins with the oscillator strength for an individual rotational line and then sums this expression over all rotational lines in a given band and over all bands comprising a band system. The f-number for absorption from lower rotational state J'' to upper state J' is given by (e.g., refs. 5 and 9)

$$f_{J'J''} = 4\pi\epsilon_0 \frac{m_e c \lambda^2_{J'J''}}{8\pi^2 e^2} \frac{d_{J'}}{d_{J''}} A_{J'J''} \tag{7}$$

where $\lambda_{J'J''}$ is the wavelength of the transition, $d_{J'}$ and $d_{J''}$ are the upper- and lower-state degeneracies, respectively, and $A_{J'J''}$ is Einstein's coefficient for spontaneous emission. According to quantum theory and the Born-Oppenheimer approximation (ref. 9), the Einstein spontaneous emission coefficient for a diatomic molecule is written as

$$A_{J'J''} = \frac{1}{4\pi\epsilon_0} \frac{64\pi^4}{3h\lambda^3_{J'J''}} \frac{R_{rad} S_{J'J''}}{d_{J'}} \tag{8}$$

where $S_{J'J''}$ is the Hönl-London factor (i.e., rotational line intensity factor) and R_{rad} is the portion of the dipole moment that involves the vibrational and electronic motions. In more explicit terms, this quantity becomes

$$R_{rad} = \sum \left| \int \psi_{v'} R_e(r) \psi_{v''} dr \right|^2 \tag{9}$$

with

$$R_e(r) = \int \psi_{v'} M_e \psi_{v''} d\tau_e \tag{10}$$

and the summation being over all degenerate levels of the upper and lower states of the transition. Commonly referred to as the electronic transition moment, $R_e(r)$, as implied by the functional notation, generally varies with internuclear separation distance r. The dipole moment is M_e.

Several types of degeneracy occur in a diatomic molecule. The first is the rotational degeneracy associated with the magnetic quantum number M ($M = -J, -J + 1, \ldots, J$). In the absence of a magnetic field, these $2J + 1$ levels coincide. A second degeneracy is the Λ doubling of each rotational line in molecules whose electronic angular momentum $\Lambda \neq 0$. This splitting is due to a finer interaction between the rotational and electronic motions. The two Λ components are rarely resolved and thus lead to a degeneracy of $2 - \delta_{0,\Lambda}$. The $2S + 1$ electronic-spin multiplicity of an electronic state is usually treated as a $2S + 1$ fold degeneracy since the energy differences of the resulting substates are small in most cases. Schadee (ref. 5) uses the symbolism M, p, and Σ to distinguish these three degeneracies and the same notation is employed here.

The Hönl-London factors obey a sum rule; but, because different normalizations have been employed, many tabulations of Hönl-London factors differ to within a constant factor. (See refs. 5, 8, and 9). Each normalization implies a slightly different treatment of rotational statistical weights. The normalization used in this report is (ref. 5)

$$\sum_{\Sigma'\Sigma''} \sum_{J''} S_{J'J''} = (2S + 1)(2J' + 1) \tag{11}$$

or in other words, the sum of the Hönl-London factors for all transitions from the levels with equal J' is equal to the number of initial sublevels. The factor $2 - \delta_{0,\Lambda}$ does not appear in equation (11) because $S_{J'J''}$ as defined in equation (8) represents the average angular factor for the two Λ components. (Schadee (ref. 5) gives a bibliography of Hönl-London factors for various molecular transitions.) It is important to emphasize that with this normalization, the Hönl-London factors, transition probabilities, and oscillator strengths, of the two Λ components are always equal. Intensities, and such phenomena as intensity alterations in homonuclear molecules, are governed by the populations of the component levels. Tatum, in reference 8, provides an excellent discussion, with several examples, of how to incorporate properly the electronic and rotational degeneracies when calculating level populations.

When equations (8), (9), and (10) are combined with equation (7), the result becomes

$$f_{J'J''} = \frac{8\pi^2 m_e c}{3he^2 \lambda_{J'J''}} \frac{\sum_{p'p''} \sum_{\Sigma'\Sigma''} \left|R_{e,v'v''}\right|^2}{\left(2 - \delta_{0,\Lambda''}\right)(2S'' + 1)} \frac{S_{J'J''}}{2J'' + 1} \tag{12}$$

The quantity $\sum\sum\left|R_{e,v'v''}\right|^2$ is another way of representing equation (9). If the interaction between the rotation and electronic-vibrational motions is negligible, and in most cases this interaction can be safely neglected, $\sum\sum\left|R_{e,v'v''}\right|^2$ is the same for each rotational line of the (v'v'') band. Equation (12) may then be summed over all rotational transitions and averaged over the Σ substates to yield a band oscillator strength as follows:

$$f_{v'v''} = \frac{8\pi^2 m_e c}{3he^2\lambda_{v'v''}} \frac{\sum\sum |R_{e,v'v''}|^2}{\left(2 - \delta_{0,\Lambda''}\right)(2S'' + 1)} = \frac{m_e c\lambda^2_{v'v''}}{8\pi^2 e^2} \frac{\left(2 - \delta_{0,\Lambda'}\right)(2S' + 1)}{\left(2 - \delta_{0,\Lambda''}\right)(2S'' + 1)} A_{v'v''} \tag{13}$$

In performing this summation, the ratio $\frac{\lambda_{v'v''}}{\lambda_{J'J''}}$ was taken as unity. This ratio deviates from unity only slightly in nearly all cases and thus introduces little error.

Equation (13) cannot, in general, be simplified further. However, if the electronic and vibrational motions are strictly independent, which is equivalent to stating that R_e is not a function of r, the electronic transition moment can be removed from the integral in equation (9). Substitution of this approximation into equation (13) gives

$$f_{v'v''} = \frac{8\pi^2 m_e c}{3he^2\lambda_{v'v''}} \frac{q_{v'v''}\sum R_e^2}{\left(2 - \delta_{0,\Lambda''}\right)(2S'' + 1)} \tag{14}$$

where $q_{v'v''}$ is the square of the vibrational overlap integral or, as it is more commonly referred to, the Franck-Condon factor. This parameter specifies the vibrational contribution to the total transition probability. To obtain an oscillator strength characteristic of a band system, equation (14) is summed over all vibrational bands. In performing this manipulation, the $\lambda_{v'v''}$ are replaced by a reference wavelength (usually that of the 0 – 0 transition $\lambda_{0,0}$) and factored from the summation. When the sum rule

$$\sum_{v'} q_{v'v''} = \sum_{v''} q_{v'v''} = 1$$

is applied, there results

$$f_{el} = \frac{8\pi^2 m_e c}{3he^2\lambda_{0,0}} \frac{\sum R_e^2}{\left(2 - \delta_{0,\Lambda''}\right)(2S'' + 1)} \tag{15}$$

and upon combining with equation (14)

$$f_{el} = f_{v'v''} \frac{\lambda_{v'v''}}{\lambda_{0,0} q_{v'v''}} \tag{16}$$

a form that is frequently seen in the literature.

There are two obvious shortcomings associated with equation (16). In band systems which encompass a wide frequency interval, replacement of $\lambda_{v'v''}$ by the reference wavelength $\lambda_{0,0}$ can lead to errors. A second error arises from use of a constant R_e^2 value for the entire band system. It has now been established for many band systems that the interaction between the vibrations and electronic motions is appreciable, thus making the electronic transition moment dependent on the vibrational transition. This variation, as well as that of the wavelength, makes it difficult to define a meaningful overall electronic oscillator strength. Despite these limitations, equation (16) continues to be employed since it provides a convenient and simple means for estimating the absorption strength of band systems.

When the electronic-vibrational interaction is nonnegligible, the factorization shown in equation (14) can still be achieved by means of the r-centroid approximation, a concept based on the Franck-Condon principle and first introduced by Jarmain and Fraser (ref. 10). In this approximation, the electronic transition moment is evaluated at the r-centroid, $\bar{r}_{v'v''}$, defined as the internuclear separation of atomic nuclei at which the electronic-vibrational transition occurs. This quantity, along with $q_{v'v''}$, may be calculated from the vibrational wave functions, but it is not yet feasible for many-electron molecules to establish theoretically the relationship between $\sum R_e^2$ and $\bar{r}_{v'v''}$. For several transitions, this relation has been determined experimentally from measured vibrational band intensities (see, for example, the survey by Schadee). When this dependence is known and is employed in conjunction with equation (14), it is preferable to use equation (16).

Nicholls (ref. 11) has shown that on the basis of a Morse approximation to the potential function $\bar{r}_{v'v''}$ is a unique and monotonic function of $\lambda_{v'v''}$. As a consequence, one may also expect $\sum R_e^2$ to be a unique function of $\lambda_{v'v''}$. The computations made by Schadee (ref. 5) tend to confirm this expectation. Because of this relationship between $\sum R_e^2$ and $\lambda_{v'v''}$, Schadee concludes that it is meaningful to define

$$f_{el}(\lambda) \equiv \frac{8\pi^2 m_e c}{3he^2\lambda} \frac{\sum R_e^2(r)}{\left(2 - \delta_{0,\Lambda''}\right)(2S'' + 1)} \tag{17}$$

as a wavelength dependent electronic f-number, rather than try to establish a constant overall oscillator strength. With better potential approximations, such as Rydberg-Klein-Rees, the $f_{el}(\lambda)$ values may deviate slightly from the mean value defined by equation (17). However, for transitions where calculations based on both the Morse and Rydberg-Klein-Rees potentials are available, the difference between $f_{el}(\lambda)$ results is generally less than 10 percent. Such a discrepancy falls within the limits of observational accuracy, and equation (17) is still a meaningful definition. In this report, electronic oscillator strengths according to equation (17) are presented since this form directly accounts for the explicit wavelength variation of f_{el} as well as the wavelength dependence implicit in $\sum R_e^2$. Whenever sufficient experimental data were available, empirical formulas which express f_{el} as a function of wavelength have been constructed. This form should be particularly useful in radiative transport calculations, or other applications, since knowledge of the r-centroids is not required.

A comparison of equation (17) with equation (14) shows that the electronic oscillator strength f_{el} can be obtained from measured vibrational band oscillator strengths $f_{v'v''}$ by division by the appropriate Franck-Condon factor; that is

$$f_{el}(\lambda) = \frac{f_{v'v''}}{q_{v'v''}} \tag{18}$$

For bands where $f_{v'v''}$ is unavailable, the known variation of the electronic transition moment with $\bar{r}_{v'v''}$ can be used directly in equation (14) to calculate f_{el}. As pointed out previously, a priori calculations of $\sum R_e^2$ have not yet proven feasible in a multi-electron molecule. Consequently, $\sum R_e^2$ must be determined through suitable experimentation. The techniques frequently employed involve measurements of radiative lifetimes τ of excited vibrational levels, measurements of the total power emitted per unit volume $I_{v'v''}$ by a vibrational band, and the integrated absorption $\int k_\nu \, d\nu$ of selected rotational lines within a vibrational band. These quantities are related to the electronic transition moment through Einstein's coefficient for spontaneous emission $A_{v'v''}$ as follows:

$$I_{v'v''} = \frac{1}{4\pi} N_{v'} A_{v'v''} h\nu_{v'v''} \tag{19}$$

$$\frac{1}{\tau} = \sum_{v''} A_{v'v''} \equiv A_{v'} \tag{20}$$

$$\int k_\nu \, d\nu = \frac{1}{4\pi\epsilon_0} \frac{\pi e^2}{m_e c} N_{J''} f_{J'J''} \left[1 - \exp\left(- \frac{h\nu_{J'J''}}{kT}\right)\right] \tag{21}$$

where the induced emission term has been incorporated. Although the equations (19) to (21) are written in terms of frequency, hereafter, following common practice, wavelength is used. Thus, the relations for $A_{v'v''}$ and $f_{J'J''}$ are

$$A_{v'v''} = \frac{1}{4\pi\epsilon_0} \frac{64\pi^4}{3h\lambda^3_{v'v''}} \frac{q_{v'v''} \sum R_e^2(r)}{\left(2 - \delta_{0,\Lambda'}\right)(2S' + 1)} \tag{22}$$

and

$$f_{J'J''} = f_{el}\left(\lambda_{v'v''}\right) q_{v'v''} \frac{\lambda_{v'v''}}{\lambda_{J'J''}} \frac{S_{J'J''}}{2J'' + 1} \tag{23}$$

which follows from equations (12), (13), (17), and (18).

Although the parameters defined by equations (19) to (21) are directly related to $\sum R_e^2$ (or equivalently $f_{el}(\lambda)$), their determination is not without difficulty. Approximations needed to obtain $\sum R_e^2$ can strongly influence the accuracy of the final result. In emission and absorption measurements, perhaps the biggest difficulty is accurate specification of the number of absorbing or emitting particles per unit volume (i.e., $N_{v'}$ or $N_{J''}$). This requires determination of state properties and the assumption that local thermodynamic equilibrium conditions prevail so that the fraction of molecules in a given energy may be calculated according to the Boltzman distribution. Furthermore, the total number of molecules of a particular type must also be known. This quantity can be obtained from energy conservation principles, provided the molecule's dissociation energy is known. Uncertainties in this latter parameter can strongly influence the value deduced for the electronic transition moment.

The value of $\sum R_e^2$ inferred from radiative lifetime measurements is independent of the dissociation energy because in this method, only the relative change, with time, of the excited-state population is monitored. The time constant for this decay is the inverse of the radiative lifetime which is connected to $\sum R_e^2$ through equations (20) and (22). Equation (20) demonstrates that the measured decay time involves the total spontaneous transition from the excited state v' to all lower states v''. To obtain $A_{v'v''}$ for a particular vibrational transition, information about vibrational branching ratios $\left(\text{i.e., how } A_{v'} \text{ is partitioned among the } A_{v'v''}\right)$ is needed. But this requires, at least, knowledge of the relative variation of $\sum R_e^2$ between vibrational bands, which is not known a priori. To circumvent this difficulty, approximate vibrational branching ratios, expressed in terms of the Franck-Condon factors which are more readily calculated, are often employed. These quantities are obtained by substituting equation (22) into equation (20) yielding

$$A_{v'} = \sum_{v''} A_{v'v''} = \frac{1}{4\pi\epsilon_0} \frac{64\pi^4}{3h} \frac{1}{\left(2 - \delta_{0,\Lambda'}\right)(2S' + 1)} \sum_{v''} \lambda_{v'v''}^{-3} q_{v'v''} \sum R_e^2\left(\bar{r}_{v'v''}\right) \tag{24}$$

If $\sum R_e^2\left(\bar{r}_{v'v''}\right)$ is assumed to be constant, it can be factored from the summation to give

$$A_{v'} = \frac{1}{4\pi\epsilon_0} \frac{64\pi^4}{3h} \frac{\left\langle \sum R_e^2 \right\rangle}{\left(2 - \delta_{0,\Lambda'}\right)(2S' + 1)} \sum_{v''} \lambda_{v'v''}^{-3} q_{v'v''} \tag{25}$$

where $\left\langle \sum R_e^2 \right\rangle$ represents the average value of $\sum R_e^2$. The combination of equations (25) and (22), with the same assumption, then results in

$$\frac{A_{v'v''}}{A_{v'}} = \frac{\lambda_{v'v''}^{-3} q_{v'v''}}{\sum_{v''} \lambda_{v'v''}^{-3} q_{v'v''}} \tag{26}$$

or in terms of the measured lifetime

$$A_{v'v''} = \frac{1}{\tau} \frac{\lambda_{v'v''}^{-3} q_{v'v''}}{\sum_{v''} \lambda_{v'v''}^{-3} q_{v'v''}} \tag{27}$$

The band absorption oscillator strength follows immediately from equation (13)

$$f_{v'v''} = 4\pi\epsilon_0 \frac{m_e c}{8\pi^2 e^2 \lambda_{v'v''}} \frac{\left(2 - \delta_{0,\Lambda'}\right)(2S' + 1)}{\left(2 - \delta_{0,\Lambda''}\right)(2S'' + 1)} \frac{1}{\tau} \frac{q_{v'v''}}{\sum\limits_{v''} \lambda^{-3}_{v'v''} q_{v'v''}} \tag{28}$$

and the corresponding electronic oscillator strength is

$$f_{el}(\lambda) = \frac{f_{v'v''}}{q_{v'v''}} = 4\pi\epsilon_0 \frac{m_e c}{8\pi^2 e^2 \lambda_{v'v''}} \frac{\left(2 - \delta_{0,\Lambda'}\right)(2S' + 1)}{\left(2 - \delta_{0,\Lambda''}\right)(2S'' + 1)} \frac{1}{\tau} \frac{1}{\sum\limits_{v''} \lambda^{-3}_{v'v''} q_{v'v''}} \tag{29}$$

It should be noted that equation (29) is essentially equivalent to equation (16) since a constant value for $\sum R_e^2$ has been assumed. Although this equation is frequently used in the literature for converting radiative decay times to electronic oscillator strengths, it should, of course, be applied only to those transitions for which the conditions of its validity are reasonably met.

Equation (29) can be simplified further for electronic band systems where the wavelength variation along a v'' progression is small or the vibrational bands in the progression decrease rapidly in intensity (i.e., a nearly vertical transition in which $v' = v''$). (For these transitions, only the diagonal elements of the Franck-Condon factor array have appreciable values whereas the off-diagonal elements are zero or nearly equal to zero.) For these cases, the factor $\lambda^{-3}_{v'v''}$ can be replaced by an average value and removed from the summation. Application of the vibrational sum rule, $\sum\limits_{v''} q_{v'v''} = 1$, then gives

$$f_{el} \approx 4\pi\epsilon_0 \frac{m_e c \lambda^2_{av}}{8\pi^2 e^2} \frac{\left(2 - \delta_{0,\Lambda'}\right)(2S' + 1)}{\left(2 - \delta_{0,\Lambda''}\right)(2S'' + 1)} \frac{1}{\tau} \tag{30}$$

The CH molecule is an example where this equation can be used with some degree of confidence. Equation (30) is frequently employed to define an effective f_{el} for electronic transitions where it does not strictly apply.

The lifetime technique can also supply information about the transition moment variation by measuring τ for several excited states. This is generally accomplished by replacing $\sum R_e^2\left(\bar{r}_{v'v''}\right)$ in equation (24) with a truncated Taylor series expansion, and using the experimental values of τ in conjunction with calculated Franck-Condon factors to solve for the unknown coefficients.

Free-Bound Radiation

As its name implies, free-bound radiation occurs when a free electron combines with an ion and excess energy is emitted as a photon:

$$A^+ + e^- \rightarrow A + h\nu$$

Such processes are also referred to in the literature as recombination radiation and the inverse process as photoionization.

For a hydrogenlike atom the absorption cross section (for the inverse process above) may be expressed by a relatively simple equation (see, for example, ref. 2):

$$\sigma_n = \frac{64\pi^4}{3\sqrt{3}} \frac{e^{10} m_e Z^4 \lambda^3 G}{\left(4\pi\epsilon_0\right)^5 h^6 c^4 n^5} \qquad \left(\lambda \leqq \lambda_{th}\right) \tag{31}$$

when λ is in nm. Here σ_n is the cross section for photoionization from the nth quantum level and exists only for wavelengths less than the threshold wavelength λ_{th}.

In order to extend the above to nonhydrogenic species, several factors should be taken into consideration. For the absorption process, only allowed transitions between the parent atom and its ion should be included. In addition, the hydrogenic formula (eq. (31)) is inaccurate for transitions involving the ground state and lower-lying levels of the parent atom. It becomes increasingly more applicable for higher levels, or increasing values of n.

As is done in reference 12 an effective Z^2 is defined by

$$Z_{eff}^2 = \frac{n^2\left(E_U - E_L\right)}{R_Y} \tag{32}$$

The cross section then becomes

$$\sigma_n = \frac{16}{3\sqrt{3}} \frac{Ge^2}{4\pi\epsilon_0 c^2 m_e} \frac{\lambda^3\left(E_U - E_L\right)^2}{n} \tag{33}$$

where the value of the Rydberg constant $R_Y = \frac{2\pi^2 m_e e^4}{h^3 c\left(4\pi\epsilon_0\right)^2}$ has been used. For the hydrogenlike particle of ionization energy I_o,

$$\sigma_n = \frac{16}{3\sqrt{3}} \frac{Ge^2}{4\pi\epsilon_0 c^2 m_e} \frac{\lambda^3 I_o{}^2}{n^5} \tag{34}$$

The absorption coefficient is found by summing the product of σ_n and the particle number density of level n:

$$k_\nu = \sum_n N_n \sigma_n = \frac{N}{Q} \frac{32}{3\sqrt{3}} \frac{Ge^2 I_o{}^2}{4\pi\epsilon_0 c^2 m_e} \exp\left(-\frac{I_o}{kT}\right) \sum_n \frac{1}{n^3} \exp\left(-\frac{I_o}{n^2 kT}\right) \tag{35}$$

where the approximate hydrogenic upper-level degeneracy, $g_n = 2n^2$, has been used.

For purposes of shock-layer transfer calculations, the above formulation is considered adequate for C and O atoms for $n \geqq 3$. This applies to the wavelength range from the near UV into the IR. In this range other processes are generally more important (lines, bands, and ionic free-free). Comparison of the hydrogenic cross sections with more exact computations for C atoms are given in reference 13, where equation (35) gives absorption coefficients that deviate from the detailed calculations by no more than 45 percent between 300 and 600 nm.

As with the other radiative processes, detailed quantum theory calculations are difficult, and when extensive transfer calculations are to be made, a measure of empiricism is desirable. This is particularly important for the lower-lying levels – the deviation from hydrogenic cross sections is most severe, and for high temperatures these levels are among the most important contributors. Recourse to quantum theory for individual cross sections with subsequent development of empirical formulas appears to be the most expedient way of handling the problem.

For a photoionization process, quantum theory gives the following formula for the cross section (ref. 14):

$$\sigma_{nf} = \frac{8\pi^3}{3\lambda} \frac{1}{g_n} \sum_n \sum_f \left| \int \psi_f{}^* \left(\sum_\mu e_\mu r_\mu \right) \psi_n \, d\tau_e{}' \right| \tag{36}$$

where ψ_n is the wave function for the initial state of statistical weight g_n and ψ_f is the wave function for the final state of the original particles in which one of the electrons is free. The charge of the μth particle of the system is e_μ, and r_μ is the position vector of the particle with respect to the system center of mass.

The major part of the problem is embodied in the evaluation of the dipole matrix elements

$$X_{nf} = \int \psi_n{}^* \left(\sum_\mu e_\mu r_\mu \right) \psi_f \, d\tau' \tag{37}$$

The above formulation is referred to as the dipole length. An equivalent expression

$$X_{nf} = \frac{h^2}{4\pi^2 m_e E_{nf}} \int \psi_f{}^* \left(\sum_\mu e_\mu \overline{V}_\mu \right) \psi_n \, d\tau' \tag{38}$$

is called the dipole velocity formulation.

The various detailed calculations of specific cross sections involve a number of assumptions about the wave functions and the potential function which appears in the Schrödinger equation. It is not reasonable here to go into detail on these aspects, but rather to present results of a number of the calculations for comparison among themselves and with experiment.

Free-Free Radiation

Free-free radiation arises as a result of the process

$$A + e^- \rightarrow A + e^- + h\nu$$

$$A^+ + e^- \rightarrow A^+ + e^- + h\nu$$

in which a free electron, e^-, interacts with the coulomb field of another particle, A. The consequent change in energy of the electron results in an emitted photon. The cross section for the process is normally evaluated in units of cm^5, which when multiplied by the number density product $N_A N_{e^-}$ yields the linear absorption coefficient in reciprocal centimeters. Detailed quantum-mechanical calculations of these cross sections are complex. An excellent procedural outline on such calculations is given in the text by Armstrong and Nicholls (ref. 4).

The classical expression for the emission cross section of a free electron accelerated in the field of a particle of charge Z was developed by Kramers (see, for instance, ref. 2) and may be written:

$$\sigma_{ff} = \frac{1}{4\pi\epsilon_0} \frac{16\pi^2}{3\sqrt{3}} \frac{e^6}{hc^4\left(2\pi m_e\right)^{3/2}} \frac{\lambda^3 Z^2}{(kT)^2} \tag{39}$$

For λ in nm and T in K,

$$\sigma_{ff} = 1.35 \times 10^{-43} \frac{\lambda^3 Z^2}{T^{1/2}} \text{ cm}^5 \tag{40}$$

The corresponding emission coefficient is

$$j_{ff} = 1.63 \times 10^{-34} \frac{N_e\text{-}N_A Z^2}{\lambda^2 T^{1/2}} \exp\left(-\frac{14388000}{\lambda T}\right) \tag{41}$$

for λ in nm. For electrons interacting with ions, this expression appears to give reasonable results (ref. 15) and is considered to be sufficiently accurate for shock-layer transfer calculations.

For electrons interacting with neutral particles, it is tempting to measure or deduce an effective Z^2 by applying the Kramers equation (eq. (40)). This may be done to give rough order-of-magnitude cross sections for a limited temperature and frequency range. This has been done in reference 16 over an extensive wavelength-temperature range, but might be justified by the fact that free-free radiation from neutrals is not a significant process in the high-temperature radiance of equilibrium gas mixtures.

DISCUSSION AND RECOMMENDATIONS

Molecular Band Systems

C_2 Swan band system $d^3\Pi_g - a^3\Pi_u$.- Both experiment and calculation have been used to obtain oscillator strengths for C_2 Swan band system. Table I summarizes the experimental measurements (refs. 17 to 26), and the calculated values are presented in table II (refs. 27 to 32).

The experimental techniques which have been employed to measure the f-number include furnaces (emission and absorption), shock tubes (incident shock and reflected shock, emission and absorption), and lifetime measurements (phase shift and laser

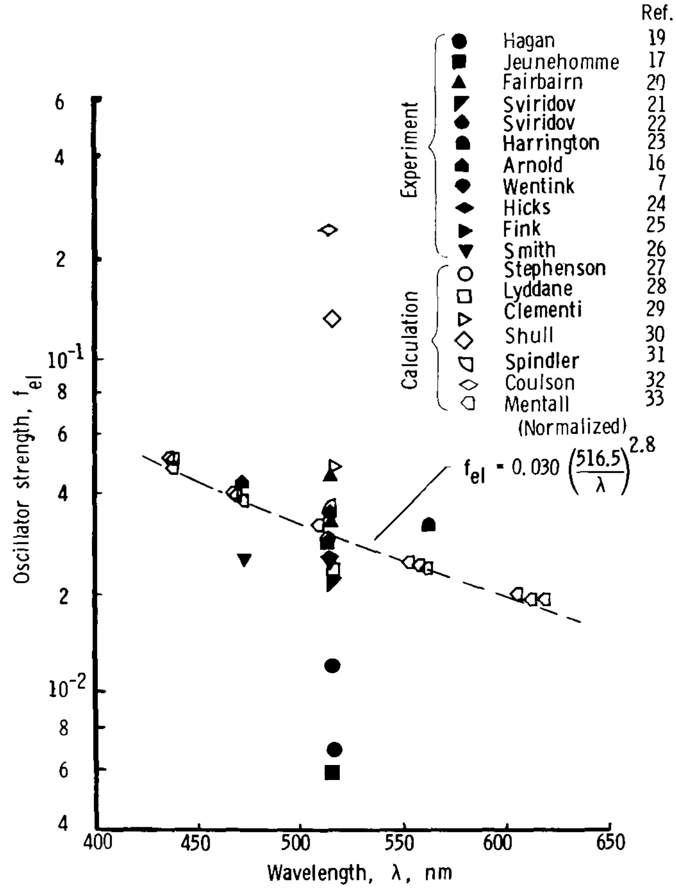


Figure 1.- Electronic oscillator strengths for C_2 Swan band system.

excitation). All the available data, experimental and calculated, are presented in figure 1. The experimental values of f_{el} extend from 0.006 to 0.043 while the calculations span a range from 0.024 to 0.24.

Note that most of the experimental data were evaluated at the (0,0) bandhead at 516 nm (all the calculated values in table II used approximately this wavelength). There is relatively little information regarding the variation with wavelength. Five of the most recent and most thorough sources (refs. 7, 20, and 22 to 24) report values of the f-number between 0.025 and 0.035 at the (0,0) bandhead. The correct value surely lies within this range. We have elected to select the mean of this range and recommend $f_{el}(0,0) = 0.030$.

As noted previously, only very limited data are available to indicate the variation of f-number with wavelength. Mentall and Nicholls (ref. 33) and Jeunehomme and Schwenker (ref. 17) have each developed empirical expressions for the variation of the transition moment with internuclear separation. These two relations differ slightly but are in essential agreement. The Mentall and Nicholls relation was used with the r-centroid values of reference 34 to determine the wavelength variation of oscillator strength, and this in turn was normalized to $f_{el}(0,0) = 0.030$. The result is shown in figure 1. As Arnold (ref. 20) points out, this method gives good relative agreement with his measurements at the $\Delta v = 0$ and $\Delta v = 1$ sequences. A simple expression that adequately defines this wavelength variation,

$$f_{el} = 0.030\left(\frac{516.5}{\lambda}\right)^{2.8}$$

(λ in nm) is shown on figure 1 and is our recommendation.

CO fourth-positive band system $A^2\Pi - X^1\Sigma^+$.- The CO fourth-positive band system is the most important molecular radiator in shock-heated carbon dioxide. A number of investigators have reported its radiative properties using a variety of techniques; yet, considerable uncertainty remains as to its oscillator strength. The fact that the wavelength region is in the vacuum ultraviolet (110 to 280 nm) adds to the experimental difficulties. When observed in emission, the bands are mostly overlapped. Since the system's lower state is the ground state, it can be observed in absorption, and this technique has been used to advantage. An excellent summary of all carbon-monoxide bands is given in reference 35.

Figure 2 summarizes the f-number data available. Hexter (ref. 36) used the crystal field splitting of solid-state CO to determine a value of $f_{el} = 0.148$ at the (2,0) band, which is the most intense. In a similar manner, Brith and Schnepp (ref. 37) obtained a value of about 0.16. Lassettre and Silverman (ref. 38) used an electron impact technique to obtain $f_{el} = 0.24$. However, this experiment was performed again at higher resolution and a revised value of $f_{v'v''}(2,0) = 0.0429$ obtained. Using their relative intensity measurements, and the fact that $f_{el} = \sum_{v'} f_{v',0}$ they obtained $f_{el} = 0.195$. The prior value of $f_{el} = 0.24$ is not shown in figure 2, but the values for $v' = 0$ to 10 are shown from reference 39. Meyer and Lassettre (ref. 40) altered the experiment of reference 38 to permit measuring the electron impact spectra at zero scattering angle and obtained good agreement with the former result.

Vargin, Pasynkova, and Trekhov (ref. 41) measured the emission from the fourth-positive band system in an arc discharge in the wavelength region 221 to 230 nm and determined $f_{el} = 0.079$. Using a phase-shift technique, Hesser and Dressler (ref. 42) determined a lifetime of 10 ± 0.5 nsec for the $v' = 2$ transition. In reference 43, they report a revised value of 10.5 ± 1 nsec. In reference 44, Hesser interprets this measurement with the aid of relative emission data to derive $f_{v'v''}$ for $v' = 0$ to 5, $v'' = 0$ to 12. For this data, figure 2 shows $f_{el} = f_{v'v''}/q_{v'v''}$ using the Franck-Condon factors of reference 45.

Rich (ref. 46) used a shock tube to heat CO to about 5000 K, and measured absorption for a number of bands. His reported values of $f_{v'v''}$ have been converted to f_{el}

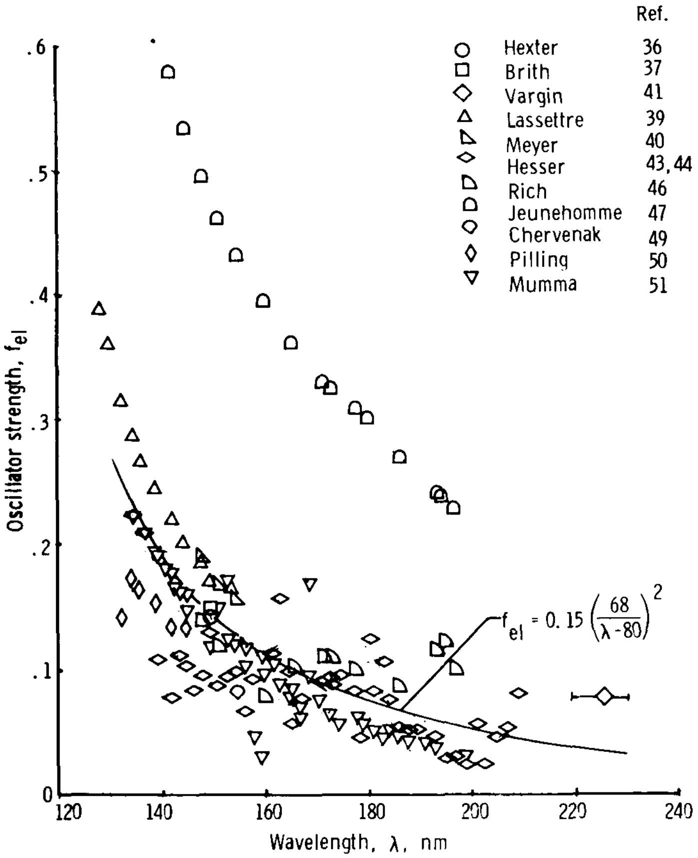


Figure 2.- Electronic oscillator strengths for CO fourth-positive band system.

and are shown on figure 2. Jeunehomme (ref. 47) measured a radiative lifetime of 10 ± 2 nsec, in good agreement with other investigators. However, he also performed extensive absorption and relative intensity measurements, shown on figure 2, which are higher than other measurements and for which he quotes an equivalent radiative lifetime of 2.5 ± 0.2 nsec. This discrepancy is not explained, but his absorption measurements were run at low density, and wall absorption may have been a problem. Penner (ref. 2) points out that wall absorption of CO can cause large errors in concentration, even for pressures 100 times greater than those in reference 47.

Radiative lifetime was also measured by Wells and Isler (ref. 48) using a level-crossing technique and they obtained $\tau = 9 \pm 1$ nsec for the $v' = 2$ state. No conversion to f-number was made in reference 48. Chervenak and Anderson (ref. 49) measured lifetimes for the first six vibrational levels ($v' = 0$ to 5) which ranged from 14.3 to 16.6 nsec. They report $f_{v'v''}(0,0) = 0.0097$ which would yield $f_{el} = 0.086$. Their longer lifetimes, as compared with those of references 42, 43, 47, and 48, are unexplained.

The curve-of-growth method was employed by Pilling, Bass, and Braun (ref. 50), who determined f_{el} for $v' = 3$ to 8 ranging from 0.128 to 0.175. Mumma, Stone, and

Zipf (ref. 51) using electron collision spectra, determined relative transition probabilities which they converted to an absolute scale by normalizing to other published values. On this basis they quote $f_{el} = 0.15$. Their transition probabilities have been converted to oscillator strengths and are included on figure 2.

Several experimenters have obtained oscillator strengths for this system near $f_{el} = 0.15$. In most of these cases the data were based on measurements on the (2,0) band ($\lambda = 147.7$ nm). The variation with wavelength has been studied by several of the investigators, and their findings are in essential agreement. In reference 51, the variation of transition moment with r-centroid was found to be $R_e = \text{Constant}(1 - 0.6\bar{r})$. Jeunehomme's power series in frequency closely approximated the same result. The recommended curve in figure 2,

$$f_{el} = 0.15\left(\frac{68}{\lambda - 80}\right)^2$$

(with λ in nm) has been selected to go through $f_{el} = 0.15$ at 148 nm and is in good agreement with the curve fits of references 51 and 47. It is also in general accord with other studies that covered a significant wavelength range. The evidence suggests the correct value of f_{el} lies within ±30 percent of the recommended curve.

CO^+ comet-tail band system $A^2\Pi_i - X^2\Sigma^+$.- The CO^+ comet-tail band system received its name from the fact that it is the most prominent band system observed in the tails of comets. It is also observed in fluorescent spectra from the atmosphere of Venus. The first investigator to present values of the band oscillator strength, $f_{v'v''}$, for a large number of bands was Nicholls (ref. 52). He combined radiative lifetime data of Bennett and Dalby (ref. 53) with the data of Robinson and Nicholls (ref. 54) to obtain absolute values of $f_{v'v''}$. However, the lifetime values of Bennett and Dalby have been challenged by Anderson, Sutherland, and Frey (ref. 55), whose more recent and presumably better values are significantly larger.

Whereas Nicholls used Franck-Condon factors based on Morse potentials, Jain and Sahni (ref. 56) analyzed the data of Robinson and Nicholls using Franck-Condon factors and r-centroids based on RKR potential functions. They then used Nicholls' technique and Bennett and Dalby's radiative lifetime data to calculate absolute values of $f_{v'v''}$.

Spindler and Wentink (ref. 57) obtained values of $f_{v'v''}$ from Bennett and Dalby's lifetime measurements by a much more direct technique than that used by Nicholls and Jain and Sahni. Despite the fact that Spindler and Wentink's Franck-Condon factors and r-centroids were calculated using Morse potentials, their work probably constitutes the best reduction of the data of reference 53. The values of $f_{v'v''}$ reported in reference 57 are, in most cases, about double those of Nicholls and Jain and Sahni.

Anderson, Sutherland, and Frey (ref. 55) calculated $f_{v'v''}$ values from lifetime measurements using a technique described by Anderson (ref. 58) which is similar to that used by Spindler and Wentink. They used their own lifetime measurements together with unpublished Franck-Condon factors and r-centroids calculated by Albritton (D. L. Albritton, Environmental Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colo.) using Rydberg-Klein-Rees potentials. Their values generally lie between those of Spindler and Wentink and those of Nicholls and Jain and Sahni, and are believed to be the best currently available. The values $f_{v'v''}$ from reference 55 have been converted to $f_{el}(\lambda) = f_{v'v''}/q_{v'v''}$ using the Franck-Condon factors due to Albritton.

The equation

$$f_{el} = 7.24 \times 10^{-3} \exp\left(-\frac{7.73 \times 10^{9} + 8.91 \times 10^{-4}\lambda^{5}}{\lambda^{4}}\right)$$

has been found to fit the results quite well. This function is shown in figure 3.

It should be noted that although the r-centroid approximation has been questioned by some investigators, its validity for the comet-tail system is demonstrated by the results of Krupenie and Benesch (ref. 59).

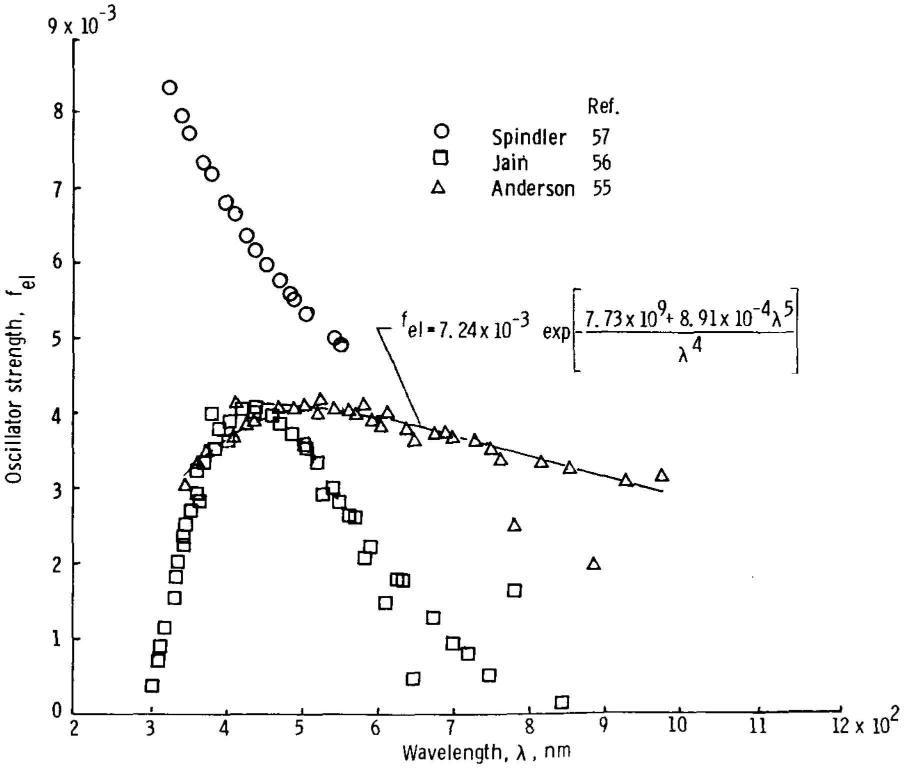


Figure 3.- Electronic oscillator strengths for CO^+ comet-tail band system.

CN violet band system $B^2\Sigma^+ - X^2\Sigma^+$.- The violet system of the CN radical has been extensively studied in the past (ref. 7 and refs. 60 to 75). Recently, Arnold and Nicholls (ref. 76) reviewed the work performed within the past decade, along with making their own measurement of the electronic transition moment. Their results and survey are recapitulated in table III. In addition, earlier sources not considered by them have been included. In order to facilitate comparisons between experimenters, the transition data have been converted to a wavelength-dependent electronic oscillator strength.

The results given by Dunham (ref. 60), White (refs. 61 and 62), and Tsang, Bauer, and Cowperthwaite (ref. 63) are probably not too reliable. Dunham stated that his f value was only tentative since his computed CN concentration was sensitive to the dissociation potential and vapor pressure assumed for carbon; Kudryavtsev (ref. 64) reviewed White's work (ref. 61) and expressed doubt as to whether the CN concentration was predicted correctly. In a subsequent paper, White (ref. 62) considered this question, and indicated that his previous estimate for the CN concentration may have been too high by a factor of 3 to 4 since he failed to account for secondary dissociation of CN by electrical discharge through C_2N_2. He therefore revised his earlier f value upward. In regard to the result deduced by Tsang, et al. (ref. 63), the authors claimed only an order of magnitude agreement with the true value.

Oscillator strengths deduced from shock-tube and ballistic range measurements are strongly dependent on the dissociation energy assumed for CN. This sensitivity is demonstrated by Fairbairn's results (ref. 65); as table III shows, a wide range of dissociation energies have been used. Consequently, the seemingly good agreement among the $f_{el}(\lambda)$ values obtained from recent shock-tube and ballistic range studies is somewhat deceptive. When corrected to a common dissociation energy, large disparities can occur.

Arnold and Nicholls (ref. 76) simultaneously determined the dissociation energy and the electronic transition moment by making measurements at widely separated temperatures. Their observations yielded an $f_{el}(\lambda)$ at 386 nm of 0.035 and a $D_{o,CN} = 7.89$ eV. Since they exercised considerable care in their measurements, this result has been used herein as a standard against which the other shock-tube results have been compared. Correction to $D_{o,CN} = 7.89$ eV can be accomplished by noting that (ref. 76)

$$f_{el}(\lambda) \propto \exp\left(-\frac{D_{o,CN}}{kT}\right)$$

where T is to be considered a constant (equal to the temperature actually observed during the absorption or emission measurement). Arnold and Nicholls have performed such a comparison and found that the f values obtained by Menard, et al. (refs. 66 and 67), Kudryavtsev (ref. 64), and Ambartsumyan, et al. (ref. 68) are lower than their result by about a factor of 2. Similarly Harrington's unpublished value reported by Wentink, et al. (ref. 7) is higher by approximately 40 percent. Reis' (ref. 69) and McKenzie and Arnold's (ref. 70) earlier measurements were found to agree well with the results of reference 76 when corrected to $D_{o,CN} = 7.89$ eV. Levitt and Parson's (ref. 71) value is low, but it should be noted that they assumed $f_{el} = 0.027$ was correct and employed measured CN emissions to deduce a dissociation energy which agrees well with the Arnold and Nicholls value.

Oscillator strengths found by the radiative lifetime technique are independent of dissociation energy uncertainties and, as table III shows, bracket the result found by Arnold and Nicholls. The electronic f-number given for Liszt and Hesser (ref. 72) is an average of their (0,0) band, (1,1) band, and (2,2) band f values converted to $f_{el}(\lambda)$ values, which were nearly constant. Liszt and Hesser tried to compare their phase shift results as closely as possible with those of Moore and Robinson in reference 73 (who were in good agreement with the earlier work of Bennett and Dalby in ref. 74) but were unable to reveal any reason for the disparity between the two measurements. After a review of all the results reported in table III, the present authors must agree with Arnold and Nicholls that the true electronic f-number lies in the range bounded by the lifetime results. Until additional measurements are made to narrow this range, it is recommended that Arnold and Nicholls' result be adopted as the mean value for the $\Delta v = 0$ sequence electronic f-number at 386 nm, with the radiative decay measurements providing the lower and upper limits of uncertainty.

The variability of the electronic transition moment with internuclear separation was studied in references 77 to 80 and in a recent review by Klemsdal (ref. 81). Nicholls (ref. 77) claimed an appreciable variation of R_e, but his result disagrees substantially with all the other investigations which show little or no variation. Parthasarathi, Sastri, and Joshi (ref. 78) found R_e was practically constant even for high vibrational levels. Reis (ref. 69) indicated that the ratio of R_e for the $\Delta v = +1$ to $\Delta v = -1$ band sequence was 0.90, a value which compares well with Arnold and Nicholls' recent measurements

$$\frac{R_e(\Delta v = +1)}{R_e(\Delta v = -1)} = 0.90$$

The phase shift measurements of Moore and Robinson (ref. 73) also showed a slow variation of R_e

$$\frac{R_e(\Delta v = +1)}{R_e(\Delta v = -1)} \approx 0.94$$

Thus, based on a summary of prior work, the conclusion is that R_e is practically constant. Although the precise variation is yet to be determined, this assumption should be adequate for most radiative calculations. A constant transition moment, as discussed previously, implies $f_{el}(\lambda) \propto \lambda^{-1}$ so the present recommendation for the violet system is

$$f_{el} = 0.035 \frac{388}{\lambda}$$

CH molecule.- Data pertaining to the electronic oscillator strengths of the $A^2\Delta - X^2\Pi$, $B^2\Sigma^- - X^2\Pi$, and $C^2\Sigma^+ - X^2\Pi$ band systems of the CH radical are summarized in tables IV and V. These tables are felt to be reasonably complete, although the possibility of omissions cannot be excluded. To facilitate comparisons between theory and experiment, the data are grouped into experimental measurements and analytical calculations. Pertinent features of each experiment or calculation are included under the "Remarks" column. The wavelength to which the oscillator strength corresponds is also listed.

Except for Dunham's (ref. 60) and Linevsky's (ref. 82) absorption measurements, the experimental results were radiative decay measurements which have been converted to an equivalent electronic oscillator strength by means of the expression:

$$f_{el}(\lambda) = 4\pi\epsilon_0 \frac{m_e c\lambda^2}{8\pi^2 e^2} \frac{d'}{d''} \frac{1}{\tau}$$

where τ is the lifetime and λ is the (weighted) wavelength at which the measurement was made. In most cases, the values for λ and f_{el} listed in table IV are taken directly from the original sources. As pointed out in an earlier section, the above relationship must generally be used with caution; but for the CH bands, it should provide an excellent approximation to the electronic oscillator strengths since the assumptions involved in its derivation are fairly well met.

Dunham (ref. 60) measured the absorption by the $R_2(1)$ line of the (0,0) band of CH in a graphite tube maintained at 3130 K and derived a tentative f-number based upon a calculated CH concentration, which he stated was sensitive to the values adopted for the dissociation potential and vapor pressure of carbon. As can be seen, his result is about an order of magnitude larger than the more recent decay measurements and, since it is approximate, should not be given much weight.

Of the four lifetime measurements made on the $A^2\Delta - X^2\Pi$ system, only Jeunehomme and Duncan's (ref. 83) results are in disagreement. They did not provide any explanation for the discrepancy. Hesser and Lutz (ref. 84) have noted in a footnote to their paper that two lifetimes reported by Jeunehomme and Duncan in reference 83 were revised and have interpreted this as an indication that some problem was apparently encountered in the measurement of the A-state lifetime, which should therefore be disregarded. Without additional information on which to make a judgment, the present authors concur in this assessment.

The value $f_{el} = 0.0012$ given by Bennett and Dalby (ref. 85) for the B – X band system was based on a preliminary measurement of the $B^2\Sigma^-$ lifetime. This value is low by a factor of 2.5 in comparison with that for the other two decay measurements and with Linevsky's relative absorption measurement, and probably should not be given much weight. Since Bennett and Dalby used a 10 nm band pass centered at 390 nm, their observed B-state lifetime may have been influenced by emission from the atomic hydrogen line at 397 nm. Both Fink and Welge (ref. 25) and Hesser and Lutz (ref. 84) employed a narrower band pass (2 nm and 0.5 nm) and thus were able to exclude this foreign emission.

Linevsky's relative absorption measurement appears to be the only experimental data available on the $C^2\Sigma^+ - X^2\Pi$ band system. Hesser and Lutz (ref. 84) did measure the C-state lifetime but found that the data could not be represented by a single exponential decay. The possibility of radiative cascading from higher lying excited states was excluded because such states have not been observed in emission. Their observations were adequately described in terms of overlapping emissions from states with two distinct lifetimes, both of which were considerably smaller than the radiative decay time expected on the basis of Linevsky's f-number. This was interpretated as evidence for predissociation of the C-state.

Comparison between the theoretical predictions of f_{el} (refs. 86 to 88) and the corresponding experimental quantities show only an order of magnitude agreement. Huo (ref. 86) states that this is about the limit of accuracy achievable with a modern single configuration formulation. She also computed transition probabilities using the length and velocity forms of the transition operator in an attempt to determine which form was preferable to use with approximate wave functions. Since both forms gave results with comparable accuracy, no conclusion could be drawn.

None of the experimental studies listed in table IV specifically examined the variability of the electronic dipole-transition moment with internuclear separation. Huo (ref. 86), however, theoretically investigated the effect of electronic-vibrational interactions on the A – X transition and found the influence, for all practical purposes, to be negligible. Clearly, further studies are needed to define the variation of $R_e(r)$ for each band system.

Recommended values for the electronic oscillator strengths of the A – X, B – X, and C – X band systems of CH, based upon a review of the results contained in tables IV and V are given in the following table:

System	f_{el}	λ, nm
$A^2\Delta - X^2\Pi$	0.0053	431.4
$B^2\Sigma^- - X^2\Pi$	.003	387.1
$C^2\Sigma^+ - X^2\Pi$	.0063	314.3

The values for the A – X and B – X systems can be considered as being reasonably well established and, therefore, not subject to further large changes. However, the f_{el} for the C – X transition may have to be revised as more data become available.

CF molecule.- Electronic transition moment data for band systems of the CF radical are scarce. The only sources uncovered are the shock-tube studies made by Harrington and his colleagues (ref. 23) pertaining to the $A^2\Sigma^+ - X^2\Pi$ transition and the radiative decay measurements of Hesser and Dressler (ref. 43) and Hesser (ref. 44) for the $A^2\Sigma^+ - X^2\Pi$ and $B^2\Sigma - X^2\Pi$ systems. Due to a computational error, the f values originally given by Harrington et al. (ref. 23) for CF were too low by a factor of 10; revised f-numbers were reported in the errata of reference 23. The reader should be warned that the numbers actually quoted are emission (ems) oscillator strengths rather than absorption (abs) f values which are employed in this report. The relationship between the two is:

$$f_{ems} = \frac{d_L}{d_U} f_{abs}$$

Wentink and Isaacson (ref. 89) calculated equivalent electronic oscillator strengths using Hesser and Dressler's earlier lifetime measurements (ref. 43) and compared them with the corrected shock-tube results of Harrington et al. (ref. 23). The calculations were made assuming R_e = Constant. Reference 89 also tabulates Franck-Condon factors based on a Morse potential for the A – X and B – X band systems. In a later paper, Hesser (ref. 44) remeasured several of the excited-state lifetimes reported in his previous paper (ref. 43) employing an improved experimental technique. The new lifetime results for the A-state and B-state of CF were essentially identical to his old values. Hesser used these lifetimes in conjunction with the Franck-Condon factors of reference 89 to compute $f_{v'v''}$ arrays under the assumption that R_e is a constant. In addition, he assumed that 95 percent of the observed B-state lifetime was due to transitions into the ground state while the remainder was due to the spectroscopically unobserved B – A transition. A comparison of the various measured and calculated oscillator strengths is presented in table VI. Hesser's band f-numbers have been converted to $f_{el}(\lambda)$ values by dividing by the appropriate Franck-Condon factor taken from reference 89. Only f_{el}

corresponding to the 0 – 0 transition wavelength is listed for Hesser because, since he took R_e = Constant, the f_{el} at another wavelength can be obtained from the expression:

$$f_{el}(\lambda) = \frac{\lambda_{0,0}}{\lambda} f_{el}\left(\lambda_{0,0}\right)$$

As table VI shows for the A – X transition, there is reasonably good agreement between the f-numbers derived from Hesser's lifetime measurement and Harrington, Modica, and Libby's emission data on the basis of shock-tube determined CF_2 and CF heats of formation. It should be pointed out, however, that Harrington et al. also analyzed their data using JANAF heats of formation (joint Army, Navy, Air Force thermochemical tables) and obtained f-numbers that were a factor of 10 higher. Wentink and Isaacson (ref. 89) have argued that these latter values are unrealistically high. Moreover, oscillator strengths derived from lifetime data are independent of the thermochemical properties, and in this case, tend to favor the lower value. Until more measurements are made and more data become available, we recommend the following tentative values:

System	f_{el}	λ, nm
$A^2\Sigma^+ - X^2\Pi$	0.026	233
$B^2\Sigma^+ - X^2\Pi$	.016	202.5

Molecule	Heat of formation	
	J/mol	kcal/mol
CF_2	-1.66×10^5	-39.7
CF	2.06×10^5	49.2

The variation of electronic transition moment with internuclear separation is not known for these two band systems of CF. Harrington et al. computed f_{el} values from their measured emission data for the (0,0) band, (0,1) band, and (0,3) band sequences at 232.9, 237.7, and 254.7 nm of the A – X transition. An examination of the equation they used to theoretically predict the emitted intensity reveals that they essentially assumed R_e was constant. However, their reported f values display a much greater variation than expected on the basis of an inverse wavelength dependence $\left(\text{i.e., } R_e = \text{Constant}\right)$. This is perhaps an indication that R_e is variable, but further work is needed to clarify this point.

Since the Morse potential Franck-Condon factors given in reference 89 are apparently the only ones published, we recommend that they be used until more accurate arrays based on realistic potential functions become available.

Triatomic carbon C_3.- Data on the absorption spectrum of gaseous C_3 are extremely scarce. The few sources that have been uncovered in the literature range between the extremes of absorption measurements made at cryogenic temperatures (20 and 4 K) (refs. 90 to 94) and absorption measurements made in a graphite furnace characterized by temperatures in excess of 3000 K (ref. 95). The spectra obtained for these two situations differ significantly from one another. At extremely low temperatures, only transitions from the lowest vibrational level of the ground electronic state are observed and display a discrete line structure; at the temperatures found in a graphite furnace, the absorption spectrum shows a complex structure characterized by discrete transitions in the neighborhood of the Swings bands at 405 nm superimposed upon an underlying continuum. Brewer and Engelke (ref. 95) have demonstrated that the underlying continuous absorption is not a true continuum but involves transitions between the same two electronic levels that are responsible for the Swings bands. In fact, they were able to qualitatively explain their observed spectra in terms of a blending of many weak, closely spaced rotational lines into a pseudocontinuum, upon which a few rotational lines of particularly strong bands stood out. The subsequent rotational-vibrational analysis of gaseous C_3 by Gausset, Herzberg, Logerquist, and Rosen (ref. 96) has clarified the reason for the appearance of numerous rotational lines and hence C_3's spectral complexity. In both electronic states, C_3 is linear with a bending frequency in the ground level of approximately 70 cm^{-1}. The bending mode of the excited electronic state, on the other hand, was found to have a large Renner effect (i.e., interaction between the vibrational and electronic motions) which removes the degeneracy associated with this mode. The particular significance of these findings is that the absorption spectrum of C_3 should be strongly dependent on temperature. Consequently, extrapolation of results obtained from absorption measurements made at cryogenic temperatures to ablation-layer conditions will be difficult, if not impossible, without explicit knowledge of its temperature variation.

Interpretation of cryogenic measurements is also made difficult by so-called matrix or solid-state effects (refs. 90, 91, and 93). In this phenomenon, carbon vapor is trapped in an inert solid matrix, such as argon or neon, formed at extremely low temperatures, typically 20 K or lower. Although only the lowest vibrational level of the ground electronic state is populated at these low temperatures, thereby simplifying the spectral analysis, the solid matrix perturbs the trapped C_3 molecule, and such perturbations are easily detectable. For example, the observed absorption spectra are found to be shifted relative to the gaseous spectra by differing amounts, depending on the matrix employed. Weltner, Walsh, and Angell (ref. 90) noted subbands appearing in addition to the principal bands which they attributed to the existence of multiple matrix sites offering different environments.

The f-number of the 405 nm line group was reported in references 91 and 93, but these values disagree by approximately two orders of magnitude. This variance among f-numbers is probably indicative of their reliability. It is obvious that many more measurements, encompassing a wide range of temperatures, is needed to better define the absorption spectrum of C_3. In the interim, use of Brewer and Engelke's data (ref. 95) is recommended, since their measurements were made at a temperature typical of that expected in the ablation layer.

Figure 4 gives a plot of absorption cross section versus frequency, while table VII provides numerical values. These results were obtained by digitizing Brewer and Engelke's absorption curve and dividing by the value they gave for the C_3 concentration appropriate to their experimental conditions ($N = 3.268 \times 10^{16}$ cm^{-3}). The uncertainty in cross section is about a factor of 2 since this is the accuracy quoted by Brewer and Engelke for their estimate of the C_3 number density. This is exclusive of measurement and digitizing errors.

The reader should also note that the results presented in figure 4 and table VII pertain to a temperature of 3200 K and, in accord with previous comments, will vary with temperature.

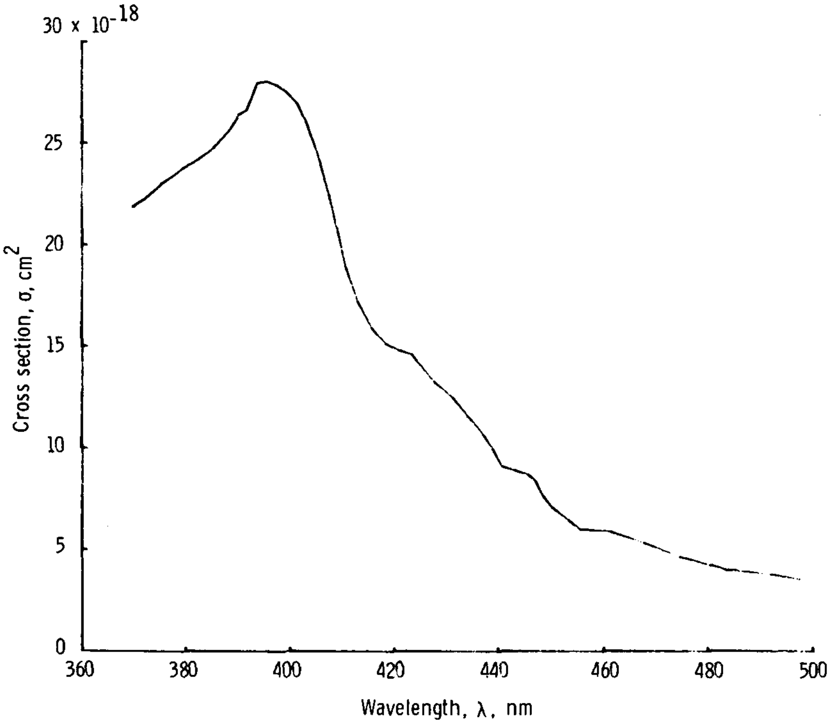


Figure 4.- Absorption cross section for C_3 (from Brewer and Engelke, ref. 95). $N = 3.268 \times 10^{16}$ cm^{-3}.

Franck-Condon Factors

Franck-Condon factors based on Morse potentials are available for all of the band systems of interest here; for many of them, improved potential models such as the Rydberg-Klein-Rees (RKR) and Klein-Dunham (KD) potentials have been employed. Table VIII indicates sources (refs. 97 to 111, in addition to sources already mentioned) of tabulated Franck-Condon factors for the various band systems. Also, tables IX to XV reproduce limited arrays from certain of these references. The references selected based their calculations on either RKR or KD potential model.

Cross Sections for Free-Bound Continua

The available pertinent literature sources have been examined which deal with free-bound processes from neutrals as well as for positive and negative ions. Most important are those dealing with carbon and oxygen neutrals, since Venus entry shock-layer conditions are such that significant radiative transfer results from the emission due to electron capture. Of lesser importance, but worthy of inclusion in radiative transfer calculations, are the free-bound processes for the species C^+, C^-, and O^-.

Because of the large amounts of energy involved and the relatively high concentrations of C and O in the shock layer, transitions of the type:

$$A + h\nu \rightarrow A^+ + e^-$$

from the lower-lying levels of the parent atoms require special attention. These transitions occur for photon energies in the vacuum-ultraviolet region of the spectrum.

Oxygen atom cross sections have been extensively studied for Earth entry applications as well as for upper atmospheric photochemical processes. For oxygen the pertinent transitions and their corresponding photoionization edges are:

OI → OII	λ_{edge}, nm
^3P $^4S^0$	91.1
^3P $^2D^0$	73.2
^3P $^2P^0$	66.6
^1D $^2D^0$	82.8
^1D $^2P^0$	74.4
^1S $^2P^0$	85.8

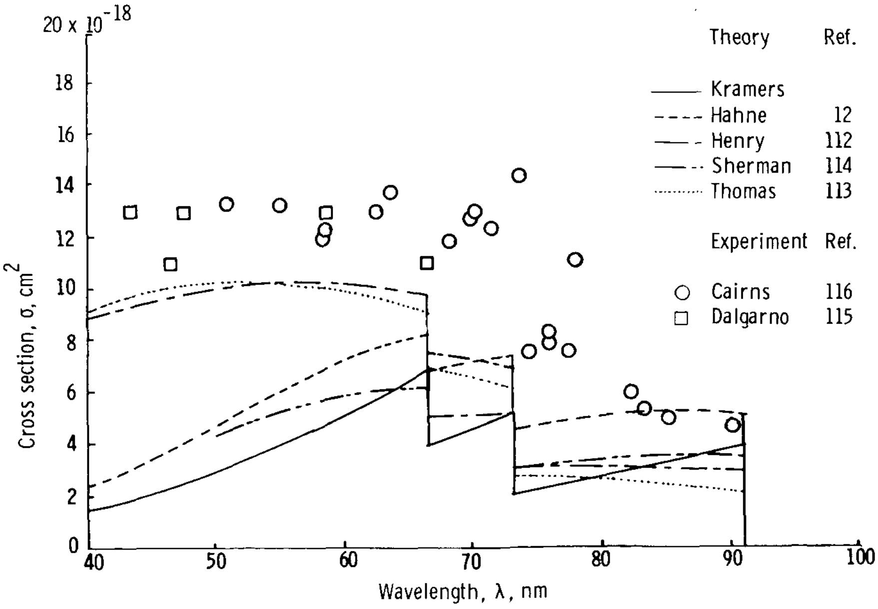
The transitions resulting from a single energy level in the parent atom result in cross sections which are atomic constants. For OI there are three such temperature-invariant cross sections of importance, all in the far ultraviolet ($\lambda < 100$ nm). Theoretical calculations of cross sections reported in the literature exhibit a variety of spectral dependence, primarily due to the different approximations and assumptions made in performing the computations. Use of more accurate wave functions should provide more reliable information.

Experimental data for the vacuum ultraviolet cross sections of oxygen are relatively scarce and generally of insufficient accuracy to indicate clearly the spectral variation. Plots of these cross sections for oxygen are given in figures 5(a), 5(b), and 5(c), showing the results of several authors (refs. 12 and 112 to 116). These plots exhibit the disparity of the various computations and how the experimentally obtained values compare with the various theories. In general, experimental values are somewhat higher than the computed cross sections. Reference 117 gives empirical curve fits to the data of reference 116.

References dealing with carbon atom photoionization are fewer in number than for the corresponding oxygen processes and are generally of more recent vintage. The relevant processes appear to be:

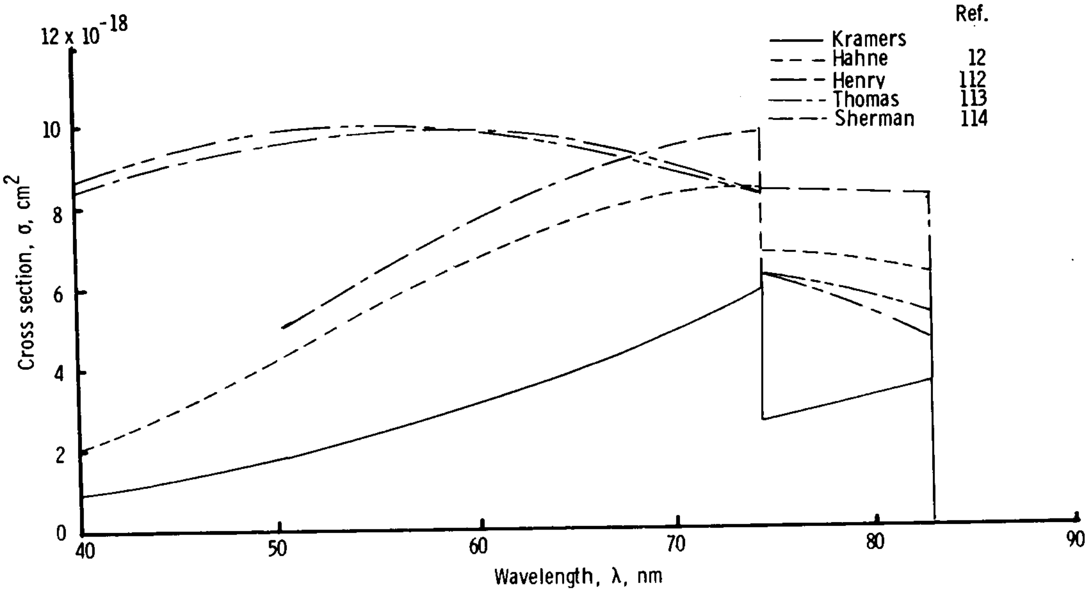
CI → CII	λ_{edge}, nm
^3P $^2P^0$	110
^3P ^4P	74.7
^1D $^2P^0$	123.9
^1S $^2P^0$	144.4
^5S ^4P	99.8

The transitions $^3P \rightarrow {}^4P$ and $^5S \rightarrow {}^4P$ have not been discussed in the literature, probably because of their relative unimportance in comparison with the others. A summary of the available sources is presented in figures 6(a), 6(b), and 6(c), showing results of references 112, 113, 118, and 119.

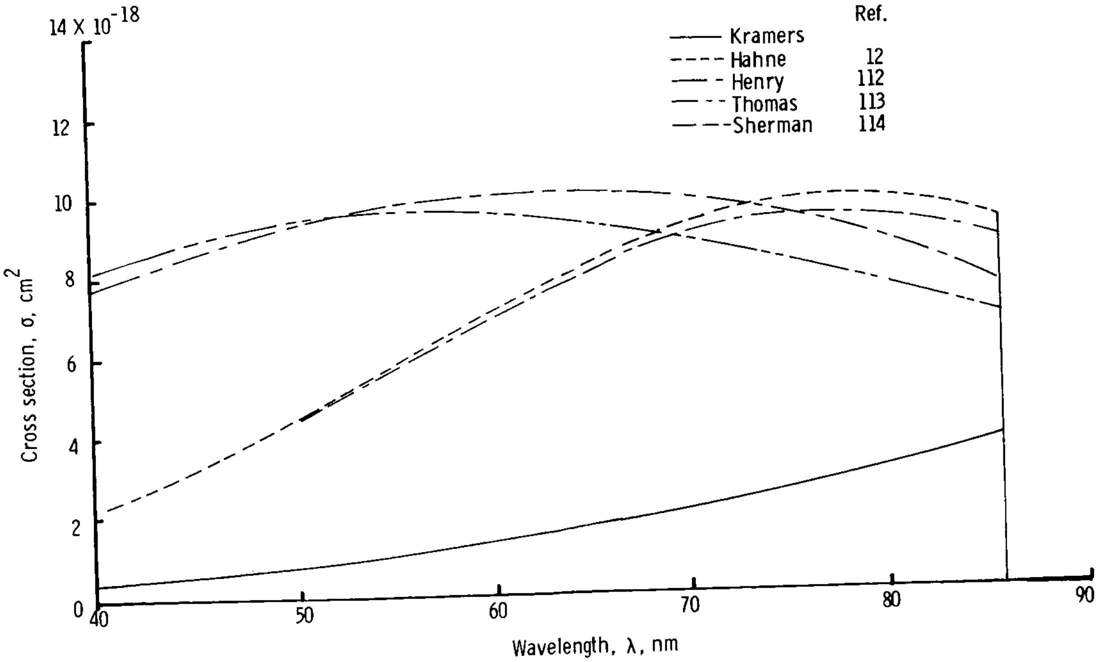


(a) $O(^3P) + h\nu \rightarrow O^+(^4S^0, {}^2D^0, {}^2P^0) + e^-$.

Figure 5.- Photoionization cross section of atomic oxygen.

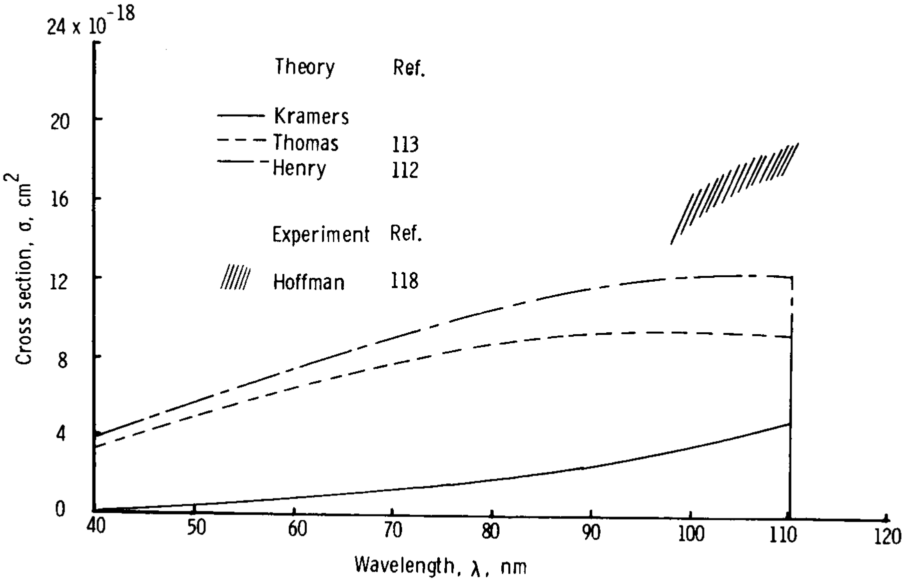


(b) $O(^1D) + h\nu \rightarrow O^+(^2D^0,\ ^2P^0) + e^-$.

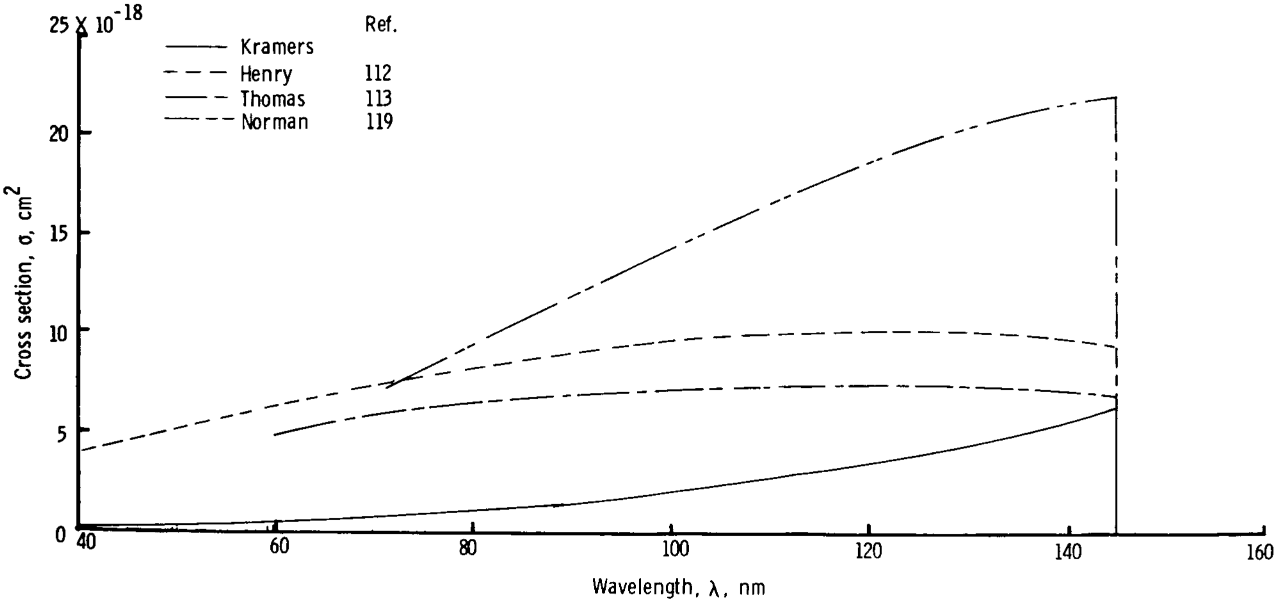


(c) $O(^1S) + h\nu \rightarrow O^+(^2P^0) + e^-$.

Figure 5.- Concluded.

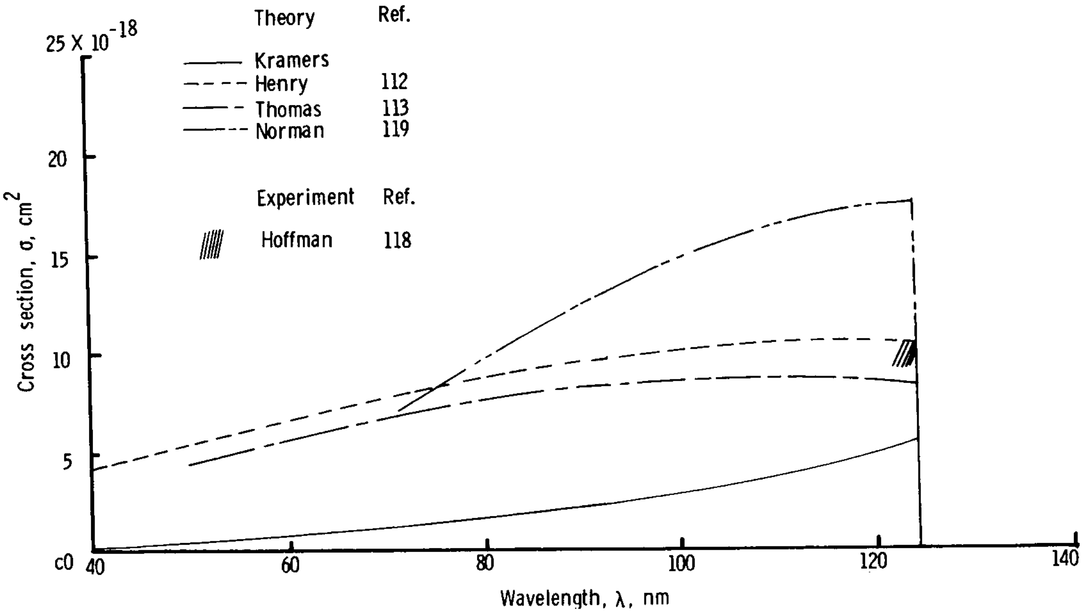


(a) $C\left(^2P\right) + h\nu \rightarrow C^+\left(^2P^0\right) + e^-$.



(b) $C\left(^1S\right) + h\nu \rightarrow C^+\left(^2P^0\right) + e^-$.

Figure 6.- Photoionization cross section for atomic carbon.



(c) $C(^1D) + h\nu \rightarrow C^+(^2P^0) + e^-$.

Figure 6.- Concluded.

The cross section for the process:

$$C^+(^2P) + h\nu \rightarrow C^{++}(^1S) + e^-$$

is of lesser importance due to the short wavelength threshold $\left(\lambda_{edge} = 50.86 \text{ nm}\right)$. Results of Henry (ref. 112) are presented in figure 7 along with a Kramers' calculation. Cross sections for the O^+ processes have even shorter wavelength thresholds, and are not considered to be of sufficient importance to include in radiative transfer calculations.

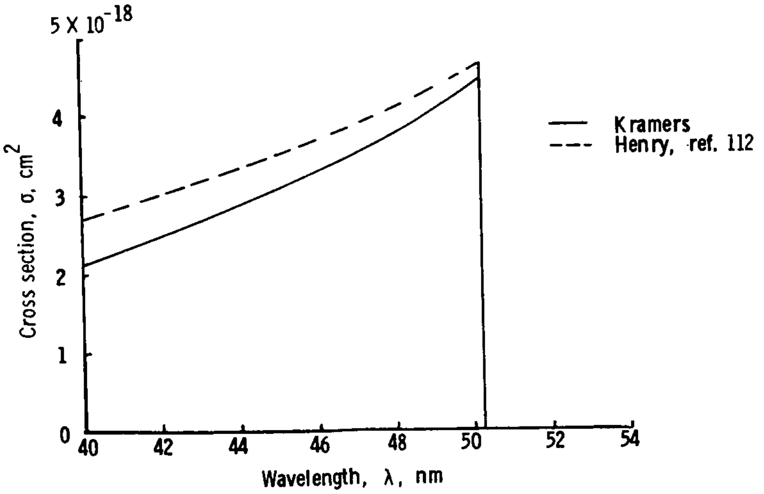


Figure 7.- Photoionization cross section for carbon ion, $C^+(^2P) + h\nu \rightarrow C^{++}(^1S) + e^-$.

For all of the carbon and oxygen free-bound vacuum ultraviolet cross sections, the work of Henry (ref. 112) appears to offer most consistency in that the cross-section formulas give a good compromise to the various theoretical calculations. These formulas compare with the existing measurements better than most of the theories, and are presented in reference 112 in a convenient formulation for inclusion in radiative transfer computations. Furthermore, there is a scarcity of recent vacuum ultraviolet measurements using latest techniques; and it is felt that, at the present time, detailed calculations of individual free-bound cross sections have a better reliability than do most of the measurements. For these reasons, the recommendation is that these cross-section formulas be used for the transitions involved.

Some representative calculations have been made for the carbon and oxygen vacuum-ultraviolet free-bound transitions. The general formula of reference 112:

$$\sigma(\lambda) = \sigma_{\text{edge}}\left[\alpha\left(\frac{\lambda}{\lambda_0}\right)^{s} + (1 - \alpha)\left(\frac{\lambda}{\lambda_0}\right)^{s+1}\right] \tag{42}$$

has been used to generate absorption coefficients for the combined pertinent transitions and the corresponding spectral radiance. The values of the empirical constants as given in reference 112 and used in the calculations are:

Transition	s	α	σ_{edge}, cm^2
$C(^3P) - C^+(^2P)$	2.0	3.317	12.19×10^{-18}
$C(^1D) - C^+(^2P)$	1.5	2.789	10.30
$C(^1S) - C^+(^2P)$	1.5	3.501	9.59
$C^+(^2P) - C^{++}(^1S)$	3.0	1.950	4.60
$O(^3P) - O^+(^4S)$	1.0	2.661	2.94
$O(^3P) - O^+(^2D)$	1.5	4.378	3.85
$O(^3P) - O^+(^2P)$	1.5	4.311	2.26
$O(^1D) - O^+(^2D)$	1.5	6.829	4.64
$O(^1D) - O^+(^2P)$	1.5	4.800	1.95
$O(^1S) - O^+(^2P)$	1.5	5.124	7.65

Figures 8 and 9 show the absorption coefficient per particle, or total cross section, for oxygen and carbon at temperatures of 8000 and 12 000 K. It is evident that this spectral quantity is notably insensitive to temperatures in this range.

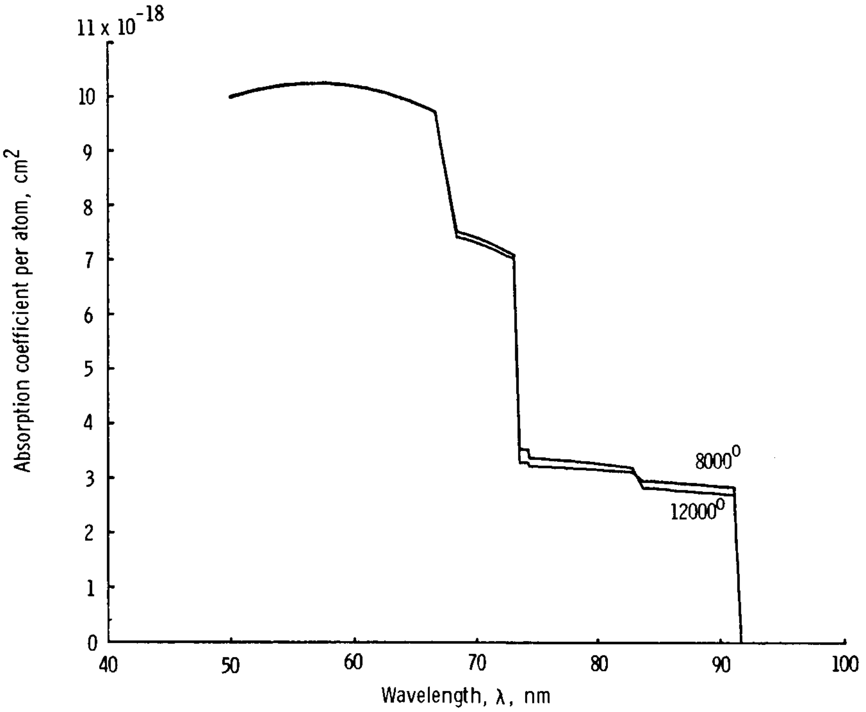


Figure 8.- Absorption coefficient per particle for free-bound transitions of oxygen.

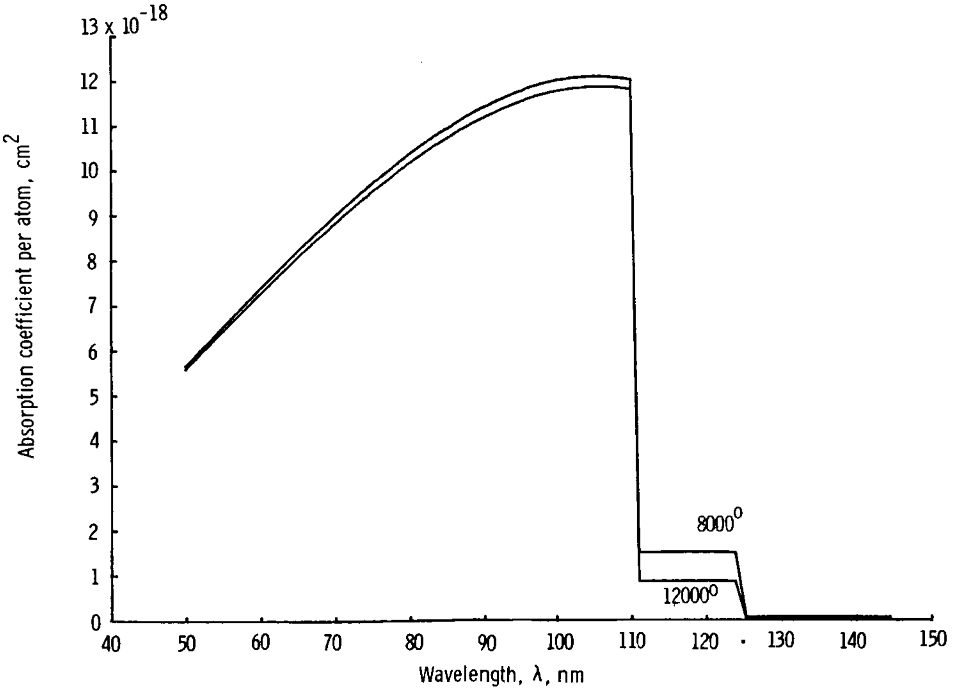


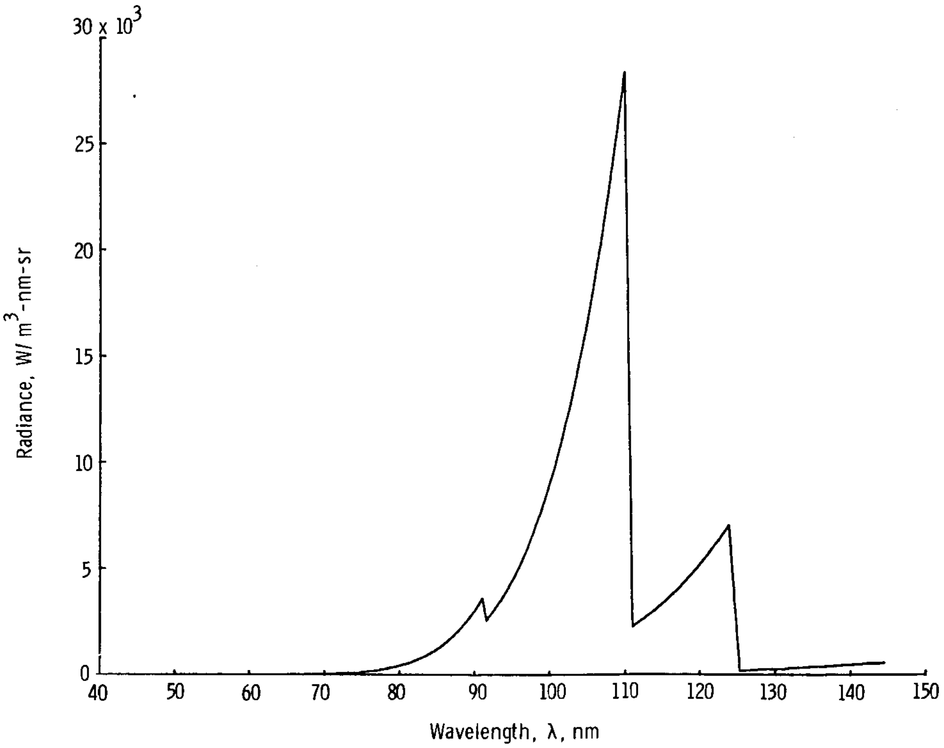
Figure 9.- Absorption coefficient per particle for free-bound transitions of carbon.

Figures 10(a), 10(b), and 10(c) show some representative radiance calculations for the carbon and oxygen transitions in the vacuum ultraviolet of temperatures of 8000, 10 000, and 12 000 K. The number densities of C and O used are those corresponding to equilibrium conditions in thermally excited CO_2 at a pressure of 1.013×10^5 N/m^2 (1 atm). The outstanding feature of the radiance calculations is the dominance of the carbon transitions. This is due to the influence of the Planck function as used in Kirchhoff's Law. Since these temperatures are representative of Venus entry shock-layer conditions, more importance must be given the carbon transitions for shock-heated CO_2.

Even though negative ion concentrations are small, bound-free photodetachment processes warrant some attention since the cross sections are relatively large over considerable portions of the spectrum. The relevant processes are:

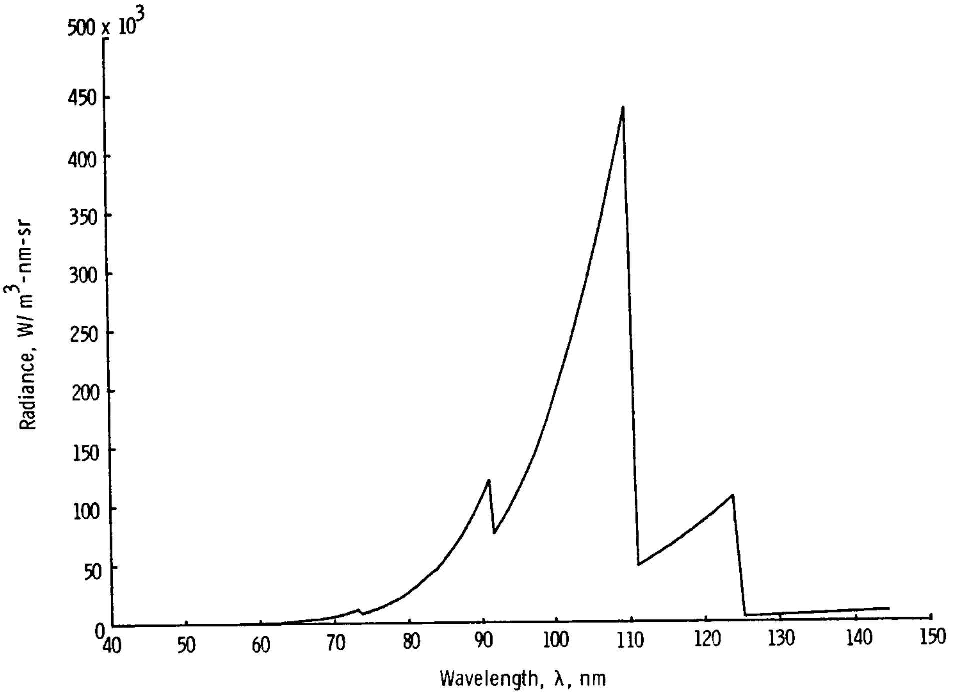
$$C^- + h\nu \rightarrow C + e^- \qquad \left(\lambda_{edge} = 990 \text{ nm}\right)$$

$$O^- + h\nu \rightarrow O + e^- \qquad \left(\lambda_{edge} = 855 \text{ nm}\right)$$

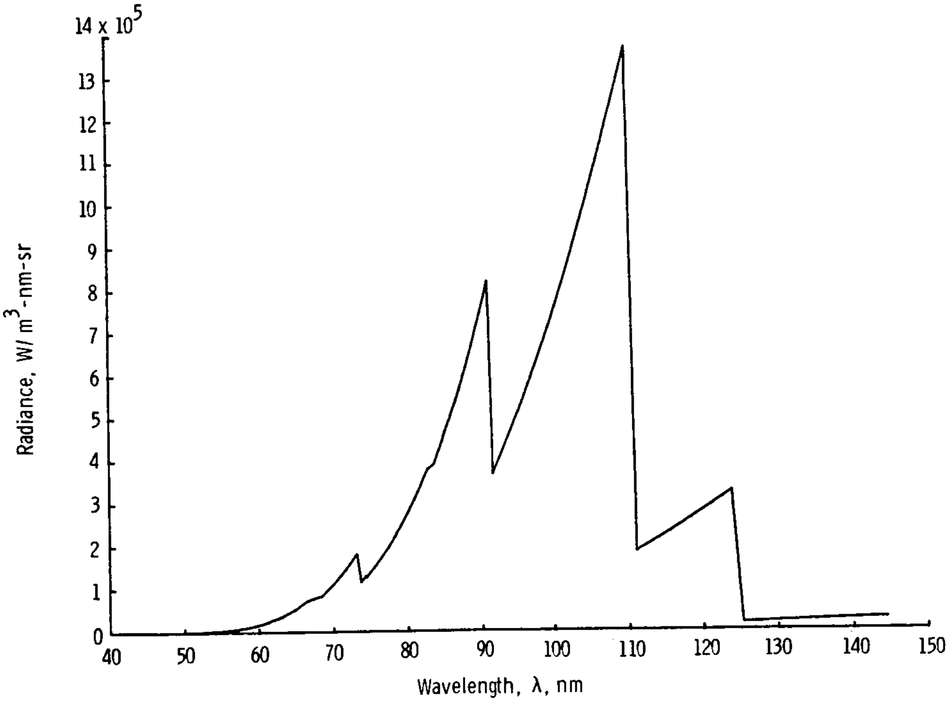


(a) T = 8000 K; 1 atm pressure.

Figure 10.- Radiance of heated CO_2 due to free-bound transitions of atomic carbon and oxygen.



(b) T = 10 000 K; 1 atm pressure.



(c) T = 12 000 K; 1 atm pressure.

Figure 10.- Concluded.

Fortunately, experiment and theory appear to agree quite well for both ions, as can be seen on figures 11 and 12. Figure 11 shows the O^- cross section as computed from references 120 and 121, and the measurements of reference 122. The C^- data of reference 123 shows some differences at long wavelengths between measurement and theory, but the discrepancy should not seriously affect overall radiative transfer. The dipole velocity calculations of references 124 and 125 are in good agreement. Henry (ref. 124) illustrates the difference in the dipole-length and dipole-velocity formulations, and the data at the shorter wavelengths suggest that the latter formulation is preferable. The present recommendation is to use the calculation of Cooper and Martin (ref. 121) for both C^- and O^- photodetachment.

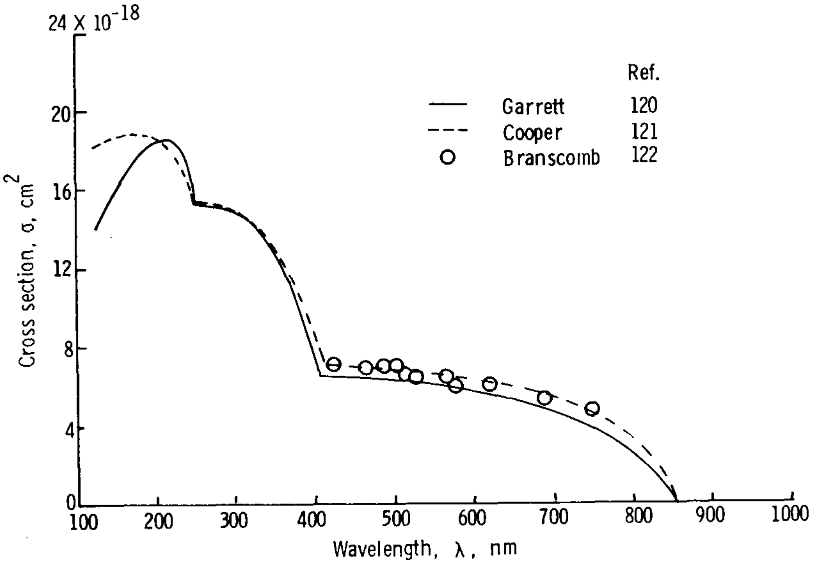


Figure 11.- Cross section for detachment of the negative oxygen-ion.

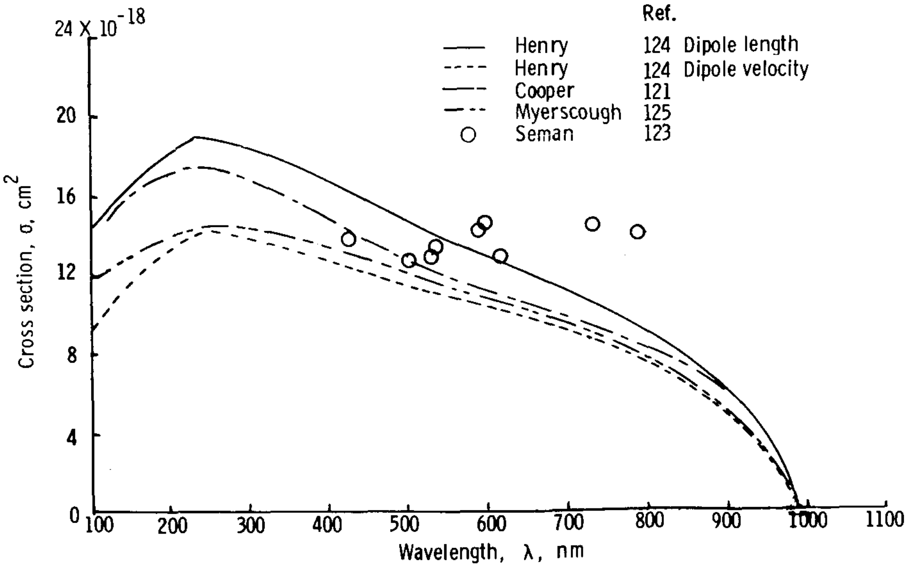


Figure 12.- Cross section for detachment of the negative carbon-ion.

Atomic Lines

Transition probabilities for carbon and oxygen lines can be obtained from Wiese, Smith, and Glennon (ref. 126) who have carefully surveyed sources in the literature and compiled recommended f-numbers. Data may be found for many more lines than are important in radiative heating calculations. Wilson and Nicolet (ref. 127) have applied specified criteria to screen those transitions which ought to be included and have supplemented the NBS tables of reference 126 with calculated f-numbers for additional lines. Reference 127, therefore, presents a good compilation for use in radiation calculations, but the values from reference 126, which are based on experimental measurement, are to be preferred. Also, references 128 to 130 present additional experimental transition probabilities for carbon lines. The recommended transition values, tables XVI to XIX, were thus obtained by combining the above sources. It should be noted that reference 126 is indicated in the tables even though this is not the prime source for certain experimentally determined transitions. The sources of these experiments may be obtained by referral to reference 126.

For cases where absorption becomes important, a knowledge of the line width and absorption shape is required. Tables of line half width and line shift data are included in reference 127, based on the theory of electron impact broadening as set forth by Griem (ref. 3). This broadening mechanism leads to a Lorentz, or dispersion profile, and for lines which are optically very thick indicates that for practical problems a substantial amount of energy is contained in the line wings. In situations where moderate to high ionization occurs and line radiation contributes less than about 15 to 20 percent of the total radiant transfer, electron impact broadening theory should yield acceptable results. In other situations, a more detailed analysis is required – other broadening mechanisms become important and lead to different line widths and profiles. For example, in gases composed primarily of neutral atoms and relatively few electrons, Doppler and resonance effects are the dominant broadening mechanisms. A good description of these effects is found in reference 131, where a detailed analysis for NI atomic line radiation is presented. In this paper it is also shown that for line series associated with high quantum numbers, mathematical simplifications may be made which treat these line series as a continuum. (See also ref. 132.)

Cross Sections for Free-Free Continua

An excellent survey of theoretical methods for computing the radiation from free-free transitions is given by Johnson in reference 133. Several theoretical studies are available in the open literature, for example, references 134 to 139.

Experiments show that ion-electron interactions (Kramers' radiation) are adequately described by applying a correction for quantum effects (Gaunt factor) to the semiclassical

Kramers' cross section. (See refs. 140 to 142.) No evidence has been found that significant improvement in the cross section for Kramers' radiation can be made by departing from this relatively simple calculation. Thus it is recommended that cross sections be obtained by using Kramers' cross sections and appropriate Gaunt factors, as obtained in reference 138.

The scattering of electrons by neutrals (neutral bremsstrahlung) is more complicated, since the effective scattering force is produced by polarization of the atom by the incident electron. References 134, 136, 139, and 143 show that, for oxygen and nitrogen, theory and experiment are in poor agreement for this process. Experimental results are usually formulated as effective values of Z^2 for use in Kramers' formula, but Kramers' formula does not correctly describe the wavelength or temperature dependence. For oxygen, the experimental cross sections (refs. 143 and 144) are about 2 percent as large for the neutral as for the ion. No experimental data have been found for carbon. For many cases it may be appropriate to neglect the neutral bremsstrahlung. When it is deemed necessary to include neutral bremsstrahlung, experimental data close to the desired thermodynamic state will be required for reasonably accurate cross sections.

SUMMARY OF RECOMMENDATIONS

As a result of the survey of published measurements and calculations, the values recommended for use in radiative heating calculations for Venus entry are

Molecular band systems:

C_2 Swan	$f_{el} = 0.030\left(\frac{516.5}{\lambda}\right)^{2.8}$
CO fourth positive	$f_{el} = 0.15\left(\frac{68}{\lambda - 80}\right)^{2}$
CO^+ comet tail	$f_{el} = 7.24 \times 10^{-3} \exp\left(-\frac{7.73 \times 10^{9} + 8.91 \times 10^{-4}\lambda^{5}}{\lambda^{4}}\right)$
CN violet	$f_{el} = 0.035 \frac{388}{\lambda}$
CH A – X	$f_{el} = 0.0053$
CH B – X	$f_{el} = 0.003$

CH C – X $f_{el} = 0.0063$

CF A – X $f_{el} = 0.026$

CF B – X $f_{el} = 0.016$

(The above relations use λ in nm.)

Free-bound continua:

For both carbon and oxygen photoionization use the cross-section formula of Henry (ref. 112); for photodetachment of C^- and O^-, use the calculations of Cooper and Martin (ref. 121).

Atomic lines:

Use f-numbers as compiled in tables VIII to XI.

Free-free continua:

Ion-electron interactions are adequately described by the Kramers formulation with the Gaunt factors from Karzas and Latter (ref. 138). Neutral-electron interactions may usually be neglected, but, if included, they must be based on experimental data close to the desired thermodynamic state.

APPENDIX

OTHER BAND SYSTEMS OF C_2, CN, CO, AND CO^+

Some data have been collected concerning other band systems of C_2, CN, CO, and CO^+. These other band systems have, in general, been studied less extensively than those discussed in the main body of this report and, in most radiative heating calculations, they have been neglected. (The red system of CN is usually considered for Earth entry, but for Venus atmospheric models with little nitrogen, it is frequently neglected.) The possible importance of these "minor" band systems has not been investigated, so the extent of the errors incurred by neglecting them are not known. The brief, not necessarily inclusive, summary of absolute intensity studies which follows represents the extent of the work which has been uncovered for these band systems. No recommendations as to best values are made.

C_2 Phillips System $A^1\Pi - X^1\Sigma^+$

For the Phillips system, a value of $f_{el} = 0.0165$ at the (0,0) bandhead ($\lambda = 1210$ nm) is given by Wentink et al. (ref. 7). Clementi (ref. 29) calculated a value of $f_{el} = 0.0027$ with hybridization considered. Hicks (ref. 24) reported a ratio of

$$\frac{f(2,0)_{\text{Phillips}}}{f(1,0)_{\text{Swan}}} = 0.468 \pm 0.028$$

which was based on experimental measurements. Using the present recommendation for the Swan system, Hicks' result would yield $f_{el} = 0.025$ for the Phillips system.

C_2 Deslandres-d'Azambuja System $C^1\Pi_g - A^1\Pi_u$

For the C – A band system, a value of $f_{el} = 0.0061$ at the (0,0) bandhead was reported by Wentink et al. (ref. 7) based on radiative lifetimes measured in laser blow-off experiments. Shull (ref. 30) and Clementi (ref. 29) calculated f-numbers considering hybridization and reported values of 0.17 and 0.065, respectively. In reference 27, Stephenson did not consider hybridization and computed a value of 0.039.

C_2 Freymark System $E^1\Sigma_g{}^+ - A^1\Pi_u$

Wentink et al. (ref. 7) estimated from calculations a radiative lifetime of 33 ns for the Freymark system from which they compute $f_{el} = 0.011$ at the (0,0) band.

C_2 Fox-Herzberg System $e^3\Pi_g - a^3\Pi_u$

Sviridov et al. (ref. 22) estimated an upper limit for $f_{el} < 0.011$. Wentink et al. (ref. 7) gave a calculated value of $f_{el} = 0.00312$. Clementi (ref. 29) calculated $f_{el} = 0.8184$.

C_2 Mulliken System $D^1\Sigma_u^+ - X^1\Sigma_g^+$

Wentink et al. (ref. 7) give a probable lower bound as $f_{el} = 0.0203$ for the Mulliken system. Clementi (ref. 29) calculated $f_{el} = 0.1025$ using a value of 8.5 percent of hybridization. Smith (ref. 26) obtained $f_{el} = 0.055$ in a lifetime measurement.

C_2 Ballik-Ramsay System $b^3\Sigma_g^- - a^3\Pi_u$

Clementi (ref. 29) reports a calculated $f_{el} = 0.0066$ of the Ballik-Ramsay system.

CN Red System $A^2\Pi_i - X^2\Sigma^+$

The variation of the transition moment of the CN red system was determined from relative intensity measurements by Dixon and Nicholls (ref. 145). Wentink, Isaacson, and Morreal (ref. 146) measured a lifetime of 3.5 μsec from which they quoted a corresponding band oscillator strength $f_{v'v''} = 0.0037$. Jeunehomme (ref. 147) measured lifetimes of 6.4 to 7.4 μsec and calculates $f_{v'v''} = 0.0034$. The inconsistency of these two sets of data is attributed by Jeunehomme to neglect of a degeneracy term in the former result, and he states the Wentink, Isaacson, and Morreal result should be interpreted as $f_{v'v''}(0,0) = 0.0074$. Schadee (ref. 5) used the Dixon and Nicholls measurements, normalized to Jeunehomme's result at the (0,0) bandhead and obtained a wavelength variation of $f_{el}(\lambda)$. His result can be closely approximated by $f_{el} = 7/\lambda$ (λ in nm).

CO Cameron Band System $a^3\Pi_r - X^1\Sigma^+$

The $a^3\Pi$ state of CO is metastable, and transition to the singlet ground state is forbidden because of spin change. The a – X transition is observed, however, because of spin-orbit mixing with the A-state. A wide range of lifetimes and f-numbers are quoted in the literature (refs. 148 to 158) as shown in table AI. A best value of f_{el} appears to be about 6×10^{-7} at the (0,0) band. This value was obtained by Hasson and Nicholls (ref. 153) and is in good agreement with the value obtained by Fairbairn (ref. 152) and the calculation by James (ref. 158). Very little trend in f_{el} with wavelength was observed by Lawrence and Seitel (ref. 155) for $v' = 0$ to 5, $v'' = 0$, so a constant oscillator strength appears justified.

TABLE AI.- CO CAMERON BAND SYSTEM $a^3\Pi - X^1\Sigma$

Source	Reference	Lifetime or oscillator strength	Comment
Hansche	148	$\tau \approx 10$ µsec	Rough estimate
Meyer, Smith, and Spitzer	149	$\tau = 100$ µsec to 3 msec	Matrix
Donovan and Husain	150	$\tau = 12$ msec	Prediction
Borst and Zipf	151	$\tau = 1$ msec	Electron beam
Fairbairn	152	$f_{el} = 5.5 \times 10^{-7}$	Absorption
Hasson and Nicholls	153	$f_{0,0} = 1.62 \times 10^{-7}$ $^a\left(f_{el} = 5.53 \times 10^{-7}\right)$	Absorption
Lawrence	154	$\tau = 7.5$ msec	
Lawrence and Seitel	155	$f_{el} \approx 6 \times 10^{-7}$	Relative to reference 155 data
Johnson and Van Dyck	156	$\tau = 10$ to 60 msec	Time of flight
Slanger and Black	157	$\tau = 4.4$ msec	Photon absorption
James	158	$f_{0,0} = 1.63 \times 10^{-7}$ $^a\left(f_{el} = 5.56 \times 10^{-7}\right)$	Calculated

[a] Calculated using Franck-Condon factor of reference 106.

CO Hopfield-Birge System $B^1\Sigma^+ - X^1\Sigma^+$

For the Hopfield-Birge B – X band system, Lassettre and Silverman (ref. 38) quoted an integrated oscillator strength $f_{el} = 0.03$ based on electron scattering. Later work, reference 39, suggested this should be reduced by the factor 0.727. Meyer et al. (ref. 159) measured electron impact spectra and obtained $f_{el} = 0.0224$. Hesser (ref. 44) measured a radiative lifetime of 25 nsec. The system is narrow in wavelength, as are several other ultraviolet systems of CO, so a wavelength-dependence of the oscillator strength is not required.

CO Hopfield-Birge System $C^1\Sigma^+ - X^1\Sigma^+$

For the Hopfield-Birge C – X band system, Lassettre and Silverman's (ref. 38) electron scattering measurements led to an estimated $f_{el} = 0.28$, but they state this value may not be too reliable. By the same reasoning as was applied to the B – X transition, Lassettre and Skerbele (ref. 39) conclude the earlier value should be reduced by the factor 0.727. Meyer, Skerbele, and Lassettre (ref. 159) reported a value $f_{el} = 0.33$. Hesser, in reference 44, reported an experimental radiative lifetime $\tau = 1.4$ nsec.

CO Third-Positive Band System $b^3\Sigma^+ - a^3\Pi_r$

Barrow et al. (ref. 160) measured the relative intensity of the vibrational bands in the third-positive band system but made no absolute measurements. Robinson and Nicholls (ref. 161) measured relative intensities and fit the relation

$$R_e = \text{Constant}(-1 + 0.943\bar{r})$$

to their data through the use of calculated r-centroid values. Tawde and Patil, in reference 162, performed a similar analysis using the data of reference 160 and obtained

$$R_e = \text{Constant}(1 - 0.6433\bar{r})$$

Schwenker (ref. 163) measured a radiative lifetime of 86 nsec from which he quotes $f_{el} = 8.9 \times 10^{-3}$. Fowler and Holzberlein (ref. 164) measured $\tau = 40$ nsec while Moore and Robinson (ref. 73) measured 97 nsec.

CO Angstrom Band System $B^1\Sigma^+ - A^1\Pi$

Robinson and Nicholls (ref. 161) measured relative intensities for the $v' = 0$ progression of the Angstrom band system. Fowler and Holzberlein (ref. 164) obtained $\tau = 75$ nsec, while Moore and Robinson (ref. 73) quoted a transition probability for the $v' = 0$ progression:

$$A_{BA} = 1.11 \times 10^7 \text{ sec}^{-1}$$

which would correspond to a radiative lifetime of 90 nsec. Using this latter value and the Franck-Condon factors given in reference 73, equation (29) yields:

$$f_{el} = 0.03$$

CO Asundi Band System $a'\,{}^3\Sigma^+ - a\,{}^3\Pi_r$

The Asundi bands extend through most of the visible, but are not very intense. Wentink et al. (ref. 7) performed extensive lifetime measurements and concluded a best fit was obtained for a constant transition moment, which corresponded to $f_{el}(0,0) = 1.56 \times 10^{-3}$.

CO$^+$ First-Negative Band System $B^2\Sigma^+ - X^2\Sigma^+$

Experimentally determined values of the radiative lifetime for various levels of the first-negative band system have been reported in references 43, 44, 163, and 165 to 168. All of the sources with the exception of references 163 and 165, obtained lifetimes in the range 44 to 60 nsec. The variation of the transition moment with r-centroid has been studied in references 169 to 172 without a conclusive determination, but the variation of R_e would appear to be small. By using the lifetime measurements of Hesser (ref. 44), Isaacson et al. (ref. 169) calculated $f_{el} = 0.0144$, assuming a constant transition moment. They obtained $f_{el} = 0.0192$ for a varying transition moment. However, in view of the apparent small variation of the transition moment, the former value $\left(f_{el} = 0.0144 \text{ at the } (0,0) \text{ bandhead}\right)$ seems preferable.

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TABLE I.- MEASURED ELECTRONIC f-NUMBERS FOR C_2 SWAN BAND SYSTEM

Source	Date	Reference	Wavelength of measurement, nm	f_{el}	Method
Arnold	1968	18	516.5 471	0.035 ± 0.005 .043 ± .006	Shock tube (emission)
Fairbairn	1966	20	509 to 529	0.033 ± 0.012	Shock tube (emission)
Fink and Welge	1967	25		0.022	Phase shift
Hagan	1963	19	516	0.007 ± 0.004	Furnace (emission and absorption)
Harrington, Modica, and Libby	1966	23	516	0.028 ± 0.009	Shock tube (emission)
Hicks	1957	24	516	[a]0.026	Furnace
Jeunehomme and Schwenker	1965	17		0.006	Laser excitation
Smith	1969	26	471	0.025 ± 0.003	Phase shift
Sviridov, Sobolev, and Sutovskii	1965	21		0.022 ± 0.008	Shock tube (emission)
Sviridov, Sobolev, and Novgorodov	1966	22		0.028 ± 0.009	Shock tube
Wentink, Marram, Isaacson, and Spindler	1967	7		0.0133	Laser excitation

[a] Original value of 0.034 adjusted by Fairbairn.

TABLE II.- CALCULATED f-NUMBERS FOR C_2 SWAN BAND SYSTEM

Source	Date	Reference	f_{el}	Remarks
Clementi	1960	29	0.048	Considers hybridization
Coulson and Lester	1965	32	0.24	A general estimate based on hybridization and orthogonalization
Lyddane and Rogers	1941	28	0.024	
Shull	1951	30	0.13	Considers hybridization
Stephenson	1951	27	0.029	
Spindler	1965	31	0.0357	Based on Jeunehomme and Schwenker's lifetime measurement (ref. 17)

TABLE III.- MEASURED ELECTRONIC f-NUMBERS FOR CN VIOLET BAND SYSTEM

Source	Date	Reference	Assumed D_o, eV	Wavelength of measurement, nm	Bandpass, nm	$f_{el}(\lambda)$	Experimental method
Arnold and Nicholls	1973	76	7.89	358 386 417 421.5	4.7 4.7 4.7 2.35	0.031 ± 0.005 .035 ± .005 .033 ± .005 .034 ± .005	Shock tube (incident shock, emission)
Dickerman	1969	75	8.1	388	1.5	0.033 ± 0.003	Shock tube (incident shock, emission)
Levitt and Parsons	1969	71	7.8 ± 0.2	421.5	7.5	0.027	Shock tube (incident shock, emission)
Kudryavtsev	1968	64	7.54	388 and 421.5	(a)	0.030 ± 0.004	Shock tube (reflected shock, absorption)
Ambartsumyan, Ionov, and Kon'kov	1968	68	7.5	388	1.5 (approx)	0.027 ± 0.006	Shock tube (reflected shock, absorption)
Thomas and Menard	1966	66	7.7	421.6	3.2	0.027	Shock tube (incident shock, emission)
Menard, Thomas, and Helliwell	1967	67		358	3.2	.027	
McKenzie and Arnold	1967	70	8.2	421.6	2.9	0.023 ± 0.003	Shock tube (incident shock, emission)
Harrington	1967	7	7.5 7.6	------------	-----------	0.026 ± 0.0066	Shock tube (emission)
Reis	1965	69	8.2	358 417	10 (approx) 10 (approx)	0.019 ± 0.004 .020 ± .004	Ballistic range (emission)
Fairbairn	1964	65	8.35 7.6	420 (approx)		0.016 ± 0.008 .031 ± .015	Shock tube (reflected shock, emission)
Tsang, Bauer, and Cowperthwaite	1962	63	7.95	388.3 421.6	0.75 .75	0.013 .008	Shock tube (incident shock, absorption)
White	1940	61		388.3	(a)	0.026 ± 0.006	Absorption measurements at room temperature CN formed by electric discharge through C_2N_2
White	1940	62		388.3	(a)	0.1 ± 0.05	Reanalysis of data in earlier paper
Dunham	1941	60	-------	387.4	(a)	0.07	Absorption measurement in a high temperature graphite furnace (2300 K)
Liszt and Hesser	1970	72		388	0.6	0.039 ± 0.004	Lifetime
Moore and Robinson	1968	73		388	0.5	0.028 ± 0.003	Lifetime
Bennett and Dalby	1962	74		390	10	0.027 ± 0.003	Lifetime

[a] Rotational line analysis.

TABLE IV.- MEASURED ELECTRONIC f-NUMBERS FOR CH BAND SYSTEMS

Source	Date	Reference	$A^2\Delta - X^2\Pi$		$B^2\Sigma^- - X^2\Pi$		$C^2\Sigma^+ - X^2\Pi$		Remarks
			f_{el}	λ, nm	f_{el}	λ, nm	f_{el}	λ, nm	
Bennett and Dalby	1960	85	0.0049 ± 0.0005	427	0.0012 ± 0.0004	[a]400			Interrupted electron beam radiative lifetime measurement; spectral resolution of approximately 10 nm.
Fink and Welge	1967	25	0.0052 + 0.0004	430	0.0028 ± 0.0005	388.8			Radiative lifetime measurement using phase shift technique; spectral resolution of 2 nm.
Jeunehomme and Duncan	1964	83	0.0093	431.4 (approx)					Interrupted electron beam radiative lifetime measurement; spectral resolution of approximately 5 to 10 nm.
Hesser and Lutz	1970	84	0.0059	431.2	0.0033	387.1			Radiative lifetime measurement using phase shift technique; spectral resolution of approximately 0.5 to 0.8 nm.
Dunham	1941	60	0.06	430					Absorption measurement on $R_2(1)$ line made in a high temperature (approximately 2800 °C) graphite furnace.
Linevsky	1967	82			0.003	385 (approx)	0.0063	314.3 (approx)	Absorption measurements made on selected rotational lines in a graphite furnace ($T \approx 3000$ K); measured $\frac{f_{BX}}{f_{AX}} = 0.62$ and $\frac{f_{CX}}{f_{AX}} \approx 1.26$; ratios put on absolute basis using $f_{AX} = 0.005$.

[a] Wavelength calculated from equation (30) using quoted f value and measured lifetime.

TABLE V.- CALCULATED ELECTRONIC f-NUMBERS FOR CH BAND SYSTEMS

Source	Date	Reference	$A^2\Delta - X^2\Pi$		$B^2\Sigma^- - X^2\Pi$		$C^2\Sigma^+ - X^2\Pi$		Remarks
			f_{el}	λ, nm	f_{el}	λ, nm	f_{el}	λ, nm	
Stephenson	1951	87	0.008	432					One-electron approximation with dipole length form at transition moment.
Hurley	1959	88	0.014		0.012		0.0092		Intra-atomic correlation correction using dipole length form.
Huo	1968	86	0.0036 or 0.0046	431.5 (approx)	0.0027 or 0.001	385 (approx)	0.0048 or 0.0032	341.3 (approx)	Active electron approximation using dipole length or dipole velocity.

TABLE VI.- MEASURED ELECTRONIC f-NUMBERS FOR CF BAND SYSTEMS[a]

Source	Date	Reference	Transition	Wavelength of measurement, nm	Bandpass, nm	f_{el}	Method
Harrington, Modica, and Libby	1965	23	$A^2\Sigma^+ - X^2\Pi$	232.9 237.7 254.7	5.6 (approx) 5.6 (approx) 5.6 (approx)	[b]0.026 ± 0.0075 .018 ± .0065 .0195 ± .0055	Shock tube (reflected shock, emission)
Hesser and Dressler	1966	43	$A^2\Sigma^+ - X^2\Pi$ $B^2\Sigma^+ - X^2\Pi$	233 202.5	0.8 .8	[c]0.0271 [d].0167	Lifetime (phase shift)
Hesser	1968	44	$A^2\Sigma^+ - X^2\Pi$ $B^2\Sigma^+ - X^2\Pi$	233 202.5	0.8 .8	[e]0.0244 [f].0161	Lifetime (phase shift)

[a] State and wavelength assignments are those used in references 44 and 89. Assignment of B state as $^2\Sigma^+$ state is uncertain; therefore, statistical-weight factor entering lifetime—oscillator-strength conversion is uncertain. Oscillator strengths given for B – X transition assume the upper state is $^2\Sigma^+$.

[b] Emission oscillator strengths quoted in the errata of reference 23 converted to absorption f values using $f_{LU} = \frac{2}{4} f_{UL}$.

[c] Electronic f-number calculated in reference 89 assuming τ for $\nu' = 0$ same as for $\nu' = 1$ ($\tau = 19$ nsec), which was measured, and using $q_{0,0} = 0.1064$.

[d] Electronic f-number calculated in reference 89 using measured τ(19 nsec) and $q_{0,0} = 0.6765$.

[e] Calculated using $f_{el} = \frac{f_{v'v''}}{q_{v'v''}}$ where $f_{0,0} = 2.6 \times 10^{-3}$ and $q_{0,0} = 0.1064$.

[f] Calculated using $f_{el} = \frac{f_{v'v''}}{q_{v'v''}}$ where $f_{0,0} = 1.09 \times 10^{-2}$ and $q_{0,0} = 0.6765$.

TABLE VII.- C_3 ABSORPTION CROSS SECTION

$[T = 3200\text{ K};\ N = 3.268 \times 10^{16}\text{ cm}^{-3}]$

λ, nm	σ, cm^2	λ, nm	σ, cm^2
497.51	3.508E-18	415.80	1.590E-17
492.13	3.745E-18	413.05	1.722E-17
486.38	3.988E-18	410.68	1.893E-17
480.31	4.240E-18	409.16	2.064E-17
474.61	4.626E-18	407.50	2.248E-17
467.73	5.317E-18	405.68	2.419E-17
461.25	5.864E-18	403.39	2.591E-17
455.58	5.979E-18	401.61	2.693E-17
453.31	6.444E-18	399.36	2.755E-17
450.25	7.066E-18	397.46	2.787E-17
448.43	7.658E-18	395.57	2.806E-17
447.03	8.378E-18	393.86	2.797E-17
445.63	8.689E-18	393.08	2.744E-17
443.07	8.885E-18	391.85	2.665E-17
440.72	9.073E-18	390.32	2.641E-17
438.98	9.946E-18	388.80	2.576E-17
437.25	1.067E-17	385.36	2.476E-17
434.22	1.157E-17	382.26	2.416E-17
431.41	1.237E-17	379.22	2.370E-17
427.72	1.325E-17	375.37	2.299E-17
423.37	1.460E-17	372.72	2.238E-17
420.87	1.480E-17	369.96	2.191E-17
418.41	1.514E-17		

TABLE VIII.- SOURCES OF FRANCK-CONDON FACTORS

Band system	Reference source employing –	
	Rydberg-Klein-Rees or Klein-Dunham potential	Morse potential
C_2 Swan	34, 31	97, 98, 99, 100, 101
C_2 Deslandres-d'Azambuja	7	97
C_2 Mulliken		97, 99, 100
C_2 Phillips	31	97, 98, 99, 100
C_2 Fox-Herzberg B – X	7, 34	97, 99, 100
C_2 Ballik-Ramsay b – a		99, 100
CF		89
CH A – X	102	100, 103
CH B – X	102	100, 103
CH C – X	102	7, 100
CN violet	31	10, 97, 100, 101, 103, 104, 105
CN red	31	101, 104
CO fourth positive	7, 106	40, 98, 100, 107, 108
CO triplet	106	109
CO third positive		98, 110
CO Angstrom		98, 110
CO Cameron	106	45, 100, 111
CO Asundi	106	100, 111
CO^+ comet-tail	56, 106	52, 100, 111, 57
CO^+ first negative	56, 106	45, 52, 100

TABLE IX.- FRANCK-CONDON FACTORS FOR C_2 SWAN BAND SYSTEM

[From reference 31]

v'' v'	0	1	2	3	4	5	6	7
0	0.7213	0.2206	0.0476	0.0088	0.0015	0.0002	0.0000	0.0000
1	.2506	.3371	.2803	.0999	.0254	.0054	.0010	.0002
2	.0272	.3742	.1381	.2621	.1377	.0453	.0119	.0027
3	.0008	.0659	.4255	.0477	.2112	.1572	.0647	.0202
4	.0000	.0022	.1055	.4446	.0143	.1576	.1592	.0782
5	-----	.0000	.0028	.1341	.4585	.0046	.1137	.1525
6	-----	-----	.0002	.0019	.1492	.4831	.0042	.0804
7	-----	-----	.0000	.0008	.0001	.1413	.5192	.0103

TABLE X.- FRANCK-CONDON FACTORS FOR CH A – X BAND SYSTEM

v'' v'	0	1	2	3
0	[a]0.9930 [b].9996 [c].9923	----- 0.0002 .0071	----- 0.0000 .0005	----- 0.0000 -----
1	------ 0.0002 .0074	0.9867 .9986 .9843	----- 0.0001 -----	----- 0.0000 -----
2	----- 0.0000 .0002	----- 0.0001 -----	0.9894 .9947 -----	----- 0.0028 -----
3	----- 0.0000 -----	----- 0.0000 -----	----- 0.0032 -----	----- 0.9819 -----

[a] Reference 102 (RKR).

[b] Reference 103 (Morse).

[c] Reference 100 (Morse).

TABLE XI.- FRANCK-CONDON FACTORS FOR CH B – X BAND SYSTEM

v'' v'	0	1	2	3
0	[a]0.8623 [b].5937 [c].7042	0.1187 .0006 -----	0.0179 .1691 .0278	----- 0.0525 -----
1	0.1231 .0013 .1557	0.5538 .2176 .1239	0.2110 .0167 -----	0.0967 .1116 -----
2	------ 0.1845 .0379	----- 0.0166 -----	----- 0.0004 -----	----- 0.0162 -----
3	------ 0.0000 .0077	----- 0.2174 -----	----- 0.0012 -----	----- 0.0745 -----

[a]Reference 102 (RKR).
[b]Reference 103 (Morse).
[c]Reference 100 (Morse).

TABLE XII.- FRANCK-CONDON FACTORS FOR CH C – X BAND SYSTEM

v'' v'	0	1	2	3
0	[a]0.9995 [b].9997 [c].9997	---------- 1.57×10^{-5} ----------	---------- 2.35×10^{-4} ----------	---------- 6.29×10^{-6} ----------
1	------ ------ ------	0.9979 ---------- .9963	---------- ---------- ----------	---------- ---------- ----------
2	------ ------ ------	---------- ---------- ----------	0.9860 ---------- .9740	---------- ---------- ----------
3	------ ------ ------	---------- ---------- ----------	---------- ---------- ----------	0.9487 ---------- .9046

[a]Reference 102 (RKR).
[b]Reference 100 (Morse).
[c]Reference 7 (Morse).

TABLE XIII.- FRANCK-CONDON FACTORS FOR CN VIOLET BAND SYSTEM

[From reference 31]

v'' v'	0	1	2	3	4	5	6	7
0	0.9179	0.0760	0.0058	0.0003	0.0000	-----	-----	-----
1	.0809	.7795	.1240	.0143	.0012	0.0001	0.0000	0.0000
2	.0012	.1417	.6754	.1550	.0239	.0026	.0002	.0000
3	.0000	.0028	.1905	.5929	.1745	.0342	.0046	.0005
4	-----	.0000	.0043	.2318	.5279	.1825	.0452	.0071
5	-----	.0000	.0001	.0054	.2668	.4824	.1781	.0554
6	-----	-----	.0000	.0002	.0050	.2933	.4583	.1640
7	-----	-----	-----	.0000	.0007	.0032	.3095	.4554

TABLE XIV.- FRANCK-CONDON FACTORS FOR CO FOURTH POSITIVE BAND SYSTEM

[From reference 106]

v'' v'	0	1	2	3	4	5	6	7
0	0.1140	0.2640	0.2850	0.1950	0.0947	0.0346	0.0099	0.0023
1	.2200	.1540	.0023	.0800	.1950	.1840	.1050	.0424
2	.2340	.0104	.0947	.1130	.0035	.0627	.1680	.1640
3	.1830	.0246	.1150	.0001	.0943	.0788	.0000	.0754
4	.1180	.0954	.0289	.0642	.0606	.0099	.1010	.0443
5	.0666	.1290	.0017	.0903	.0004	.0855	.0164	.0396
6	.0342	.1170	.0413	.0347	.0509	.0347	.0295	.0682
7	.0165	.0858	.0841	.0003	.0741	.0014	.0703	.0005

TABLE XV.- FRANCK-CONDON FACTORS FOR CO$^+$ COMET-TAIL BAND SYSTEM

[From reference 106]

v' \ v''	0	1	2	3	4	5	6	7
0	0.0423	0.1520	0.2500	0.2520	0.1740	0.0864	0.0322	0.0091
1	.1130	.1930	.0812	.0005	.0918	.1910	.1770	.1000
2	.1670	.0987	.0028	.1080	.0856	.0004	.0726	.1740
3	.1800	.0141	.0726	.0705	.0036	.0969	.0630	.0010
4	.1590	.0045	.0961	.0010	.0765	.0371	.0188	.0988
5	.1220	.0414	.0498	.0305	.0581	.0079	.0788	.0063
6	.0850	.0789	.0067	.0703	.0039	.0620	.0151	.0419
7	.0549	.0952	.0034	.0586	.0140	.0485	.0116	.0567

TABLE XVI.- LINES OF NEUTRAL CARBON CI

Line	Wavelength, nm	Energy, eV	f-number	Reference code (a)
1	1973.7	.628	1.06E-01	1
2	1858.3	.667	9.85E-01	1
3	1788.6	.693	1.52E-01	1
4	1786.0	.694	1.03E+00	1
5	1753.2	.707	1.04E+00	1
6	1688.6	.734	7.40E-01	2
7	1603.5	.773	1.14E+00	1
8	1502.5	.825	1.81E-01	1
9	1461.7	.848	1.86E-01	1
10	1454.8	.852	2.75E-01	1
11	1441.2	.860	7.24E-01	1
12	1270.0	.976	1.59E-01	1
13	1259.1	.985	2.49E-01	2
14	1235.8	1.003	1.63E-01	1
15	1220.0	1.016	1.66E-01	1
16	1177.1	1.053	2.31E-01	1
17	1175.5	1.055	7.00E-01	2
18	1166.4	1.063	9.60E-01	2
19	1164.1	1.065	1.32E-01	2
20	1145.8	1.082	1.75E-01	1
21	1133.0	1.094	6.30E-01	2
22	1069.5	1.159	2.54E-01	1
23	1069.5	1.159	5.00E-01	2
24	1041.6	1.190	1.34E-02	1
25	1012.4	1.225	2.62E-01	2
26	960.1	1.291	1.00E-01	2
27	833.5	1.487	3.20E-02	4
28	828.0	1.497	1.90E-02	1
29	750.3	1.652	2.10E-02	1
30	716.9	1.729	2.20E-02	1
31	667.5	1.857	2.40E-02	1
32	660.7	1.876	1.00E-02	1
33	658.8	1.882	8.46E-03	3
34	631.4	1.964	2.50E-02	1
35	579.8	2.138	1.06E-03	3
36	538.0	2.304	7.47E-03	3
37	505.2	2.454	1.11E-02	3
38	504.1	2.459	1.02E-03	4
39	493.2	2.514	4.27E-03	3
40	482.6	2.569	4.40E-04	3
41	481.7	2.574	4.52E-04	3
42	477.0	2.599	4.74E-03	3

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[a] Reference codes 1, 2, 3, and 4 are references 127, 126, 128, and 129, respectively.

TABLE XVI.- LINES OF NEUTRAL CARBON CI – Continued

Line	Wavelength, nm	Energy, eV	f-number	Reference code (a)
43	493.2	2.514	4.74E-03	4
44	437.1	2.836	1.69E-03	3
45	426.9	2.904	1.05E-03	3
46	247.8	5.003	9.40E-02	2
47	193.1	6.421	8.20E-02	2
48	176.7	7.016	1.41E-02	1
49	175.1	7.081	1.20E-01	2
50	165.7	7.482	1.70E-01	2
51	160.6	7.720	5.34E-03	1
52	160.5	7.725	3.67E-02	1
53	156.1	7.942	9.10E-02	2
54	154.4	8.030	1.97E-03	1
55	154.3	8.035	2.60E-03	1
56	151.3	8.194	1.16E-02	1
57	151.1	8.205	1.47E-03	1
58	149.3	8.304	7.40E-03	1
59	149.3	8.304	9.07E-04	1
60	148.1	8.371	1.10E-02	2
61	148.0	8.377	5.01E-03	1
62	147.0	8.434	1.42E-02	1
63	146.3	8.474	9.30E-02	2
64	145.9	8.498	7.00E-03	2
65	143.1	8.664	1.30E-01	2
66	135.7	9.136	5.26E-03	1
67	135.6	9.143	3.62E-02	1
68	132.8	9.336	3.80E-02	2
69	131.2	9.450	1.93E-02	1
70	131.2	9.450	2.55E-03	1
71	129.0	9.611	1.14E-02	1
72	128.8	9.626	1.43E-03	1
73	127.8	9.701	1.95E-02	1
74	127.8	9.701	3.80E-03	2
75	127.7	9.709	6.30E-02	2
76	127.5	9.724	7.22E-03	1
77	127.5	9.724	8.85E-04	1
78	126.5	9.801	4.88E-03	1
79	126.0	9.840	2.90E-02	2
80	119.2	10.401	7.19E-03	1
81	119.1	10.410	4.95E-02	1
82	115.7	10.716	2.63E-02	1
83	115.7	10.716	3.47E-03	1
84	114.0	10.875	7.05E-01	1
85	114.0	10.875	1.55E-02	1
86	113.9	10.885	1.95E-03	1
87	112.8	10.991	9.80E-03	1
88	112.8	10.991	1.20E-03	1
89	101.8	12.179	1.05E+00	1
90	94.5	13.122	2.70E-01	2
91	91.1	13.605	2.95E-01	1

[a] Reference codes 1, 2, 3, and 4 are references 127, 126, 128, and 129, respectively.

TABLE XVII.- LINES OF NEUTRAL OXYGEN OI

Line	Wavelength, nm	Energy, eV	f-number	Reference code (a)
1	5484.5	.226	1.90E-01	1
2	5274.5	.235	1.97E-01	1
3	1820.1	.681	9.72E-01	1
4	1799.0	.689	9.84E-01	1
5	1609.7	.770	2.15E-03	1
6	1591.1	.779	2.17E-03	1
7	1402.1	.884	1.63E-01	2
8	1255.8	.987	1.61E-01	1
9	1245.7	.995	1.62E-01	1
10	1128.9	1.098	7.50E-01	2
11	1095.0	1.132	1.73E-01	2
12	926.3	1.338	9.00E-01	2
13	844.9	1.467	8.98E-01	2
14	777.6	1.594	9.22E-01	2
15	736.5	1.683	1.62E-02	2
16	701.5	1.767	3.98E-02	2
17	641.9	1.931	1.48E-02	2
18	615.1	2.016	6.64E-02	2
19	596.2	2.080	3.97E-03	1
20	532.7	2.327	1.40E-02	2
21	443.9	2.793	5.60E-03	2
22	391.4	3.168	2.29E-03	2
23	371.6	3.336	1.28E-02	1
24	334.0	3.712	1.43E-02	1
25	130.5	9.500	3.10E-02	2
26	121.7	10.187	1.30E-01	2
27	115.2	10.762	9.00E-02	2
28	112.6	11.011	1.85E-02	1
29	105.0	11.808	4.89E-03	1
30	104.6	11.853	1.99E-02	1
31	102.7	12.072	1.00E-02	2
32	101.9	12.167	1.88E-03	1
33	99.8	12.427	3.50E-02	2
34	99.0	12.524	4.70E-02	2
35	98.0	12.654	5.24E-03	1
36	97.6	12.702	2.13E-02	1
37	97.3	12.738	1.54E-02	1
38	96.0	12.915	7.01E-02	1
39	95.3	13.008	2.01E-03	1
40	95.0	13.051	1.05E-02	1
41	93.8	13.223	1.88E-02	1
42	93.7	13.232	2.22E-02	1

[a] Reference codes 1 and 2 are references 127 and 126, respectively.

TABLE XVII.- LINES OF NEUTRAL OXYGEN OI – Concluded

Line	Wavelength, nm	Energy, eV	f-number	Reference code (a)
43	93.7	13.236	6.57E-03	1
44	93.0	13.334	4.27E-03	1
45	92.5	13.397	2.93E-03	1
46	92.2	13.450	1.50E-02	2
47	91.8	13.501	5.60E-03	1
48	91.4	13.559	4.97E-03	1
49	91.3	13.585	4.94E-02	1
50	89.5	13.856	2.14E-03	1
51	89.2	13.898	3.35E-02	1
52	88.3	14.033	5.82E-03	1
53	87.9	14.108	3.70E-02	2
54	87.8	14.116	3.85E-02	1
55	86.2	14.386	2.23E-03	1
56	85.9	14.428	2.61E-02	1
57	83.1	14.925	2.50E-02	1
58	81.7	15.181	2.54E-02	1
59	81.2	15.276	6.91E-03	1
60	81.2	15.276	7.70E-03	2
61	80.5	15.405	1.22E-02	1
62	78.8	15.726	6.52E-03	1
63	78.4	15.810	1.44E-02	1
64	77.6	15.979	6.62E-03	1
65	77.2	16.064	2.43E-02	1
66	77.1	16.078	2.49E-03	1
67	76.9	16.120	9.71E-03	1
68	75.9	16.335	2.53E-03	1
69	75.7	16.376	1.64E-02	1
70	73.5	16.873	2.83E-02	1
71	72.6	17.084	2.32E-02	1
72	70.2	17.671	7.32E-03	1
73	69.8	17.757	1.61E-02	1
74	68.8	18.026	2.79E-03	1
75	68.6	18.068	1.09E-02	1

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[a] Reference codes 1 and 2 are references 127 and 126, respectively.

TABLE XVIII.- LINES OF IONIZED CARBON CII

Line	Wavelength, nm	Energy, eV	f-number	Reference code (a)
1	392.0	3.163	1.43E-01	5
2	283.7	4.370	1.33E-01	5
3	251.1	4.937	1.36E-01	5
4	133.5	9.287	2.70E-01	2
5	103.6	11.967	5.90E-02	2
6	90.4	13.713	5.20E-01	2
7	85.8	14.443	4.60E-02	2
8	80.8	15.340	1.23E-01	1
9	68.7	18.039	2.60E-01	2
10	65.1	19.039	4.88E-01	1
11	64.2	19.321	1.65E-01	1
12	63.6	19.494	1.05E-02	1

[a] Reference codes 1, 2, and 5 are references 127, 126, and 130, respectively.

TABLE XIX.- LINES OF IONIZED OXYGEN OII

Line	Wavelength, nm	Energy, eV	f-number	Reference code (a)
1	83.3	14.880	4.30E-01	2
2	79.7	15.566	7.00E-02	2
3	71.8	17.258	2.50E-01	2
4	67.3	18.427	6.30E-02	2
5	64.4	19.252	1.50E-01	2

[a] Reference code 2 is reference 126.

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