

PREPRINTS
OF THE
STEWART OBSERVATORY
THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

NO. 54

CONDITIONS FOR CARBON MONOXIDE VIBRATION-ROTATION
LTE IN LATE STARS^{*}

by

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ABSTRACT

Collisional vibration and rotation transition rates are found for carbon monoxide due to H, H₂, He and electrons. These rates are compared to the radiative rates of transition in carbon monoxide to establish temperature-pressure regions in which Vibration-Rotation LTE is a good approximation and those regions in which possible non-LTE effects may occur. Comparison of these data with current late star model atmospheres indicates that possible vibrational non-LTE effects may occur in supergiants, but in all late star computed atmospheres rotational LTE should be a good approximation. The further question of total molecular LTE is examined and rate equations set up. Rough order of magnitude estimates are made on the conditions for total LTE in CO.

INTRODUCTION

Recent observations of the carbon monoxide infrared vibration-rotation bands in late stars (Johnson et al 1972, Thompson et al 1969, Connes et al 1968, Spinrad et al 1970, Johnson and Mendez 1970) have led to the speculation that the carbon monoxide population levels may not be in vibrational LTE (local thermodynamic equilibrium). Establishment of the conditions for carbon monoxide LTE is of great importance in the interpretation of these spectra. Discrepancies in the $^{12}\text{C}/^{13}\text{C}$ ratio obtained from CO spectra and CN spectra (Spinrad et al 1971) may be the result of non-LTE effects. It has also been shown that CO plays an important role in the determination of temperatures for late stars (Johnson 1972) and in the effective atmospheric opacity (Alexander and Johnson 1972). The above calculations have assumed LTE populations for CO, therefore deviations from LTE may have significant effects on the atmospheric structure of these stars.

VIBRATION-ROTATION LTE CONDITIONS

In steady state the net rate of change of the population of a state is zero. The state may be destroyed either by a radiative transition (absorption or spontaneous and induced emission) or by collision with another particle. In carbon monoxide the first allowed electronic state transition lies at an energy of approximately 8 eV, which corresponds to a wavelength of 1530Å. For late stars therefore transitions from the ground state to this electronic state will not play an important role in determining the population of the ground state levels. In hotter stars such as the sun this mechanism may be important, however. Due to the above, only vibration-rotation transitions will be considered in the radiative case. Similarly, the low temperature of late stars allows collisional excitation of the first electronic state to be neglected and only vibrational and rotational collisional transitions need be considered. The validity of these assumptions is discussed in a later section.

In order to determine whether the conditions for vibration rotation-LTE are met it is necessary to determine whether collisional or radiative transitions are dominant in determining the population of a state. If collisions dominate it is safe to use LTE in determining the vibrational and rotational level populations, if, however, radiative transitions dominate then LTE assumptions may be invalid. In the following, the radiative and collisional transition probabilities for the ground $X^1\Sigma^+$ state of CO are calculated and the transition rates compared for typical late star temperatures and pressures.

RADIATIVE TRANSITION RATES

For a purely rotational transition from an upper state with rotational quantum number J_u to a lower rotational state with rotational quantum number $J_l = J_u - 1$ the Einstein A coefficient is given by

$$A_{ul} = \frac{64\pi^4}{3h} \mu^2 w^3 (2J_l + 1)/(2J_u + 1) \quad (1)$$

where μ is the permanent dipole moment for CO ($\mu = 0.1$ Debye) and w is the wave number of the emitted radiation in cm^{-1} . Values of A_{ul} for CO are in the range of 10^{-7} - 10^{-8}sec^{-1} or of the order of one transition per year. In late stars pure rotational radiative transitions play no part in determining the populations of the energy levels.

Vibration-rotation radiative transition probabilities have been calculated by several people (Young 1968, Kunde 1967 and Chackerian 1970). For a vibration-rotation transition the Einstein A may be written as (Chackerian 1970)

$$A_{ul} = \frac{64\pi^4}{3h} w^3 (TM)^2 / g_u \quad (2)$$

where $g_u = 2J_u + 1$.

In (2) the transition moment TM is given by

$$(\text{TM})^2 = |m| \left[\int_0^\infty \psi_u(r) M(r) \psi_e(r) dr \right]^2 \quad (3)$$

where $m = J_\ell + 1$ for the R branch ($J_u = J_\ell + 1$) and $m = -J_\ell$ for the P branch ($J_u = J_\ell - 1$). The dipole moment function $M(r)$ has been expressed as a cubic polynomial by Young and Eachus (1966). In this work the transition moment has been calculated via the expression given by Chackerian (1970) which has been derived from the polynomial for $M(r)$

$$(\text{TM})^2 = |M(n)|^2 \frac{(V_\ell + n)!}{V_\ell! n!} |m| C(V_\ell, n) F(m, n) \quad (4)$$

where $n = V_u - V_\ell$ with V_ℓ and V_u representing the lower and upper state vibrational quantum numbers respectively. Other terms ($M(n)$, $C(V_\ell, n)$, $F(m, n)$) in (4) are defined in Chackerian's work and represent the dipole moment, the vibrational, and the rotational contributions to the matrix element respectively. It should be noted, however, that the values listed by Chackerian for $M(n)$ are really the values for $M(n)^2$. Alternatively the $A_{u\ell}$ values may be obtained from the tabulated absorption strengths $S_{\ell u}$ of Kunde (1967) in the following manner

$$A_{u\ell} = \frac{S_{\ell u} (8\pi c w^2 p Q)}{N_0 g_u} e^{E_\ell/kT} \left[1 - e^{-\frac{hcw}{kT}} \right]^{-1} \quad (5)$$

where p is the pressure, Q is the partition function, N_0 is the number density and E_ℓ is the energy of the lower state. Values obtained by the two methods agree 10% in the cases considered.

For a typical transition in the (1, 0) fundamental ($\Delta V = n = 1$) band, such as the R(29) line, the Einstein A value is equal to $1.2 \times 10^2 \text{ sec}^{-1}$ or a factor of 10^9 - 10^{10} greater than the rotational rate. Values for the first overtone band $\Delta V = n = 2$ are reduced by a factor of approximately 10^2 from the fundamental values, thus a molecule is much more likely to undergo a

fundamental radiative transition than an overtone transition. Radiative vibration transition rates for a given level are therefore set equal to the fundamental transition rates.

COLLISIONAL TRANSITION RATES

Collisional rotational and vibrational transition rates of CO due to H, H₂, He and electrons are calculated in this section. Whenever possible, accurate experimental determinations of collisional transition rates are used in preference to theoretical calculations. This is due to the discrepancies between the observed and calculated rates for many collisional processes, e.g. Marriott (1964).

a. Vibrational Rates

Shock tube measurements of vibrational relaxation times have provided the best data to date on molecular collisional de-excitation rates. Millikan and White (1963) have reviewed a large portion of the shock tube data and found that the vibrational relaxation time τ_v could be fit to good accuracy by the following semi-empirical expression,

$$\ln_e (p\tau_v) = 1.16 \times 10^{-3} \mu^{1/2} \theta^{4/3} (T^{-1/3} - 0.015\mu^{1/4}) - 18.42 \quad (6)$$

where p is the pressure in atmosphere, μ is the reduced mass of the colliding system of gases in mole weights and θ is the energy of the vibrational transition energy in °K. This expression has nearly the same form as that derived from the Landau-Teller investigation of molecular collisions. The predicted and observed $T^{-1/3}$ dependence of $\ln\tau_v$ is shown in the formula (6) and may be derived from a simple application of Ehrenfest's principal (Herzfeld and Litovitz 1959). Equation (6) may be written in the form

$$p\tau_v = \exp [A(T^{-1/3} - 0.015\mu^{1/4}) - 18.42]. \quad (7)$$

Values of A have been specifically measured for the CO-H₂ and CO-He systems and are equal to 68 and 99 respectively (Millikan and White 1963). Equation (6) allows the A value for the CO-H system to be calculated and A is found to be 52.9. For the 1-0 vibrational de-excitation, θ_{CO} is taken as 3080°K by Millikan and White.

The de-excitation rate $C(u \rightarrow l)$ is related to the relaxation time τ_V by the following expression

$$C_V(u \rightarrow l) = [\tau_V(1 - e^{-\theta/T})]^{-1} \quad (8)$$

which reduces $C_V(u \rightarrow l) = \tau_V^{-1}$ for small T. The exponential term accounts for the possibility of excitation during the relaxation time. Equations (7) and (8) are used to compute the vibrational de-excitation rates used in this work for the action of H₂, He, and H on CO. It is estimated that these rates are accurate within 50% of the true rate. It should be noted that in the work of Pande (1968) on CO populations in the sun, the wrong expression for τ_V is given in the text. In that work the natural log of $p\tau_V$ is set equal to the expression of Millikan and White for the \log_{10} of $(p\tau_V)$. This is most probably a translation error as the correct de-excitation rate is eventually found.

Vibrational de-excitation of CO by electrons is calculated by two methods, each of which agree within 10%. In the first method a point-dipole cross section is assumed. This cross section is further discussed in detail below with respect to rotational de-excitation. As a check the cross section found experimentally by Phelps (1968) was approximated by a constant cross section σ equal to $4 \times 10^{-17} \text{ cm}^2$ for electron energies above the excitation threshold. A Maxwell-Boltzmann distribution of electron energies is assumed which gives an excitation rate C_V due to electrons in the case of a constant cross section

$$C_V(l \rightarrow u) = N_e \left(\frac{8}{m_e \pi} \right)^{1/2} (kT)^{-3/2} \int_{E_0}^{\infty} \sigma E e^{-E/kT} dE \quad (9)$$

where N_e equals the electron number density and E_0 the vibrational energy threshold. In order to find the de-excitation $C_v(u \rightarrow l)$ rate from the excitation rate $C_v(l \rightarrow u)$ given in (9) the simple formula (10) required by detail balancing is used

$$C(u \rightarrow l) = \frac{g_u}{g_l} e^{E_{ul}/kT} C(l \rightarrow u) \quad (10)$$

where E_{ul} is the energy difference between the upper and lower states (Mihalas 1970). As both the more complicated point-dipole cross section and the simple constant cross section give results for C_v which agree within 10% for all test cases, the constant cross section is used to reduce the calculational complexity.

At temperatures above about 2000°K the vibration resonant cross section centered at 2.1 eV for CO-electron collisions must be considered (Phelps 1968). This cross section is approximated by a constant cross section of $8 \times 10^{-16} \text{ cm}^2$ from 1.1 to 3 eV which is consistent with the observed cross section. At about 3500°K the resonant de-excitation becomes equal to the non-resonant de-excitation. It will be seen later, however, that electrons do not play a significant role in determining the vibrational populations for CO in late stars.

b. Rotational Rates

Experimental results for rotational relaxation times in molecules are not nearly as numerous as those for vibrational relaxation. Much of the data is obtained indirectly via collisional broadening studies of molecular lines in various gases. Direct measurements of collisional rotational transitions are only possible with the techniques of microwave spectroscopy.

Microwave studies of rotational transitions in CN (Evenson and Broida 1966) indicates that the efficiency of collisions in inducing rotational

transitions is almost unity. This is quite reasonable in terms of Ehrenfest's principal as the rotational period for molecules is quite low compared to the collision times for any reasonable temperature. Evenson and Broida also point out that very often collisions result in transitions involving rotational quantum jumps greater than ± 1 , thus the usual calculations which involve only dipole transitions ($\Delta J = \pm 1$) are not valid. From the results for CN it is found that a constant cross section equal that found from the optical diameter of broadening studies is a good approximation for the rotational collisional cross section.

Optical diameters for CO have been measured by several workers (Crane-Robinson and Thompson 1962, Eaton and Thompson 1969) with results which lead to a cross section of $2 \times 10^{-15} \text{ cm}^2$ for small rotational quantum numbers and $1 \times 10^{-15} \text{ cm}^2$ for higher rotational quantum numbers. From the work of Crane-Robinson and Thompson the following cross sections are used for rotational transitions.

$$\begin{aligned} \sigma_R &= 2 \times 10^{-15} \text{ cm}^2 & J < 20 \\ \sigma_R &= \left(2 - \frac{J-20}{10}\right) \times 10^{-15} \text{ cm}^2 & 20 < J < 30 \\ \sigma_R &= 1 \times 10^{-15} \text{ cm}^2 & J > 30 \end{aligned} \quad (11)$$

An expression similar to (9) is then used to calculate the rotational transition rate. It is assumed that the collisional cross sections for H_2 , H, and He are equal to the cross section found from the Crane-Robinson and Thompson data for CO- H_2 broadening.

Finally the rotational de-excitation rate of CO due to electron collisions must be calculated. In this field extensive theoretical work has been done and is reviewed by Takayangi and Itikawa (1969). From this review the expressions for the point-dipole and point-quadrupole cross sections are

given below in equations (12) and (13) respectively.

$$\sigma_{PD}(J \rightarrow J+1) = \frac{8\pi}{3K_o^2} D^2 \frac{J+1}{2J+1} \ln \frac{K_o+K}{K_o-K} \quad (12)$$

$$\begin{aligned} \sigma_{PQ}(J \rightarrow J+2) = & \frac{8\pi}{15} \frac{K}{K_o} \frac{(J+1)}{(2J+1)} \frac{(J+2)}{(2J+3)} \left[Q^2 + \frac{\pi}{4} Q \alpha' K_o^{-1} (K_o^2 - \frac{\Delta K^2}{4}) \right. \\ & \left. + 9/32 \left(\frac{\pi}{4} \alpha' \right)^2 (K_o^2 - \frac{\Delta K^2}{2}) \right] \quad (13) \end{aligned}$$

In (12) and (13) K_o and K are the incoming and outgoing electron wave vectors respectively, $\Delta K^2 = K_o^2 - K^2$, D and Q are the dipole and quadrupole moments and α' is the nonspherical polarizability. If the approximation in (14) is used

$$\ln \frac{K_o+K}{K_o-K} = \ln \left[\frac{K^2}{B(J+1)} \right] - \frac{B(J+1)}{K^2} \quad K^2 \gg B(J+1) \quad (14)$$

where B is the rotational constant then the collisional excitation rates can be found via direct integration of (12) and (13) in (9). Equation (10) is then used to find the de-excitation rate. Results for the point-dipole and point quadrupole rates are given explicitly in (15) and (16)

$$C_{PD}(J+1, J) = N_e \left(\frac{512\pi}{9mkT} \right)^{1/2} \frac{(2J+3)(J+1)}{(2J+1)(2J+1)} D^2 e^{hcw/kT} \left[E_1 \left(\frac{E_o}{kT} \right) + \ln 4 e^{-E_o/kT} \right] \quad (15)$$

$$\begin{aligned} C_{PQ}(J+2, J) = & N_e \left(\frac{8\pi}{15} \right) \left(\frac{8}{m\pi} \right)^{1/2} \frac{(2J+5)(J+1)(J+2)}{(2J+1)(2J+1)(2J+3)} e^{hcw/kT} [Q^2 (kT)^{1/2} \\ & + \frac{\pi}{4} Q \alpha' \Gamma(5/2) kT + \frac{18}{32} \left(\frac{\pi \alpha'}{4} \right) (kT)^{3/2}]. \quad (16) \end{aligned}$$

E_1 in (15) represents the exponential function. In (16) it has also been assumed that $\frac{K}{K_o} \approx 1$ and that $K^2 \gg (4J+6)B$. w is the wavenumber of the energy difference between states. From the above equations the collisional rates for rotational and vibrational de-excitation of CO can be calculated for collisions with electrons, H, He and H_2 .

CONDITIONS FOR VIBRATION-ROTATION LTE

In order to establish a criterion for LTE in late stars, the ratio of radiative de-excitation via spontaneous emission versus the collisional de-excitation rate for the same state is calculated. If this ratio is much smaller than one, collisions control the population of the states and vibration-rotation LTE is valid. If the ratio is much greater than one the populations are radiatively controlled and non-LTE populations may evolve. This ratio neglects induced emission and absorption which are dependent on the radiation field and must be calculated in detail from model atmospheres. If the radiation field is simply an undiluted black body field at the temperature of the surrounding gas no non-LTE effects are present. Radiatively controlled populations simply allow the possibility of non-LTE effects for non-Planckian radiation fields.

a. Rotational LTE Conditions

In establishing conditions for rotational LTE, collisions due to electrons, H, H₂ and He are considered. From 1 we find that the pure radiative transition rate is extremely slow, on the order of about one transition per year. Equation (2), however, shows that a vibration-rotational transition occurs on the order of 100 times a second. A spontaneous vibration-rotation transition followed by a vibration-rotation absorption to the same vibrational state but a different rotational state ($\Delta J = \pm 2$) is therefore a much more effective way of radiatively changing a rotational state within a given vibrational state. The rate for radiatively de-exciting a rotational state has been set to $1/8 A(VJ, V-1 J-1)$ which allows for the possibility that once a radiative transition to a different vibrational state has occurred the molecule may be absorbed back to the same state giving no change or again radiatively de-excite to an even lower vibrational state, plus the fact that the

two transitions needed to change the rotational state take twice as long as a single transition. The important fact is that the effect of the pure rotational Einstein A is negligible in changing rotational states radiatively.

Collisional rates for rotational de-excitation are much greater than those for vibration-rotation de-excitation and excitation, therefore, only pure rotational collisional rates need be considered. Table 1 lists the gas pressures and electron densities needed to make the ratio $A_{ij}/8C_{ij}$ equal to one for a few typical transitions from state i to j. Both the dipole and quadrupole rates are included in the electron collision rates. Since neither the Einstein A values or the collisional rates are strong functions of the rotational constant J, the entries in Table 1 typify the densities needed for rotational LTE in most states.

b. Conditions for Vibrational LTE

Vibrational radiative de-excitation rates are given simply as the sum of the Einstein A values for the P and R branch transition from a given vibrational state. This rate is then compared with the collisional rate derived from the relaxation times which have been averaged over all rotational states given by (7) and (8). Table 2 gives the values of N_e , P_H , P_{H_2} and P_{He} which make the ratio $[A(V, J, \rightarrow V-1, J-1) + A(V, J, \rightarrow V-1, J+1)]/C(V, V-1)$ equal to one. As before a few typical transitions have been used to show the trend of values. The pressures and temperatures needed to give vibrational LTE are significantly higher than those for rotational LTE due to the greater effectiveness of collisions in producing rotational transitions than vibrational transitions. It is therefore possible to have pressure temperature regions in which the rotational level populations of CO are in LTE but the vibrational populations are not.

EXAMINATION OF CONDITIONS FOR TOTAL MOLECULAR LTE

In the above work only the conditions for LTE in the internal vibration-rotation levels of the CO electronic ground state have been examined. Electronic, dissociative and ionizing transitions have been ignored and no attempt has been made to establish conditions for total LTE. The total rate equations for a state i of a molecule of CO are given in equations (17) and (18) in terms of the rates for leaving and entering the state i respectively.

Leaving state i :

$$\begin{aligned}
 N_{CO}^i & \left[\sum_{j<i} A_{ij} + \sum_{j\neq i} B_{ij} \right] \int_0^\infty \phi_\nu J_\nu d\nu + 4\pi \int_{\nu_0}^\infty \frac{\alpha_{dis}^i}{h\nu} J_\nu d\nu \\
 & + 4\pi \int_{\nu_0}^\infty \frac{\alpha_{ion}^i}{h\nu} J_\nu d\nu + \sum_{K=1}^4 N_K \left(\sum_{j\neq i} \Omega_{ij}^K \right) + \sum_{K=1}^4 N_K \Omega_{i, dis}^K \\
 & + \sum_{K=1}^4 N_K \Omega_{i, ion}^K + \sum_K N_K \Omega_{exch}^K \quad (17)
 \end{aligned}$$

Entering state i :

$$\begin{aligned}
 & \sum_{j>i} N_{CO}^j A_{ji} + \sum_{j\neq i} N_{CO}^j B_{ji} \int_0^\infty \phi_\nu J_\nu d\nu \\
 & + 4\pi N_{CO} N_0 \frac{Z_{CO}^i}{Z_C Z_O} \int_{\nu_0}^\infty \alpha_{dis}^i \left(\frac{2\nu^2}{c^2} + \frac{e^{-h(\nu-\nu_0)}}{h\nu} J_\nu \right) d\nu \\
 & + 4\pi N_{(CO^+)} N_e \frac{Z_{CO}^i}{Z_{(CO^+)} Z_e} \int_{\nu_0}^\infty \alpha_{ion}^i \left(\frac{2\nu^2}{c^2} + \frac{e^{-h(\nu-\nu_0)}}{h\nu} J_\nu \right) d\nu \\
 & + \sum_{K=1}^4 N_K \left(\sum_{j\neq i} N_{CO}^j \frac{g_j}{g_i} e^{-\frac{h\nu_{ij}}{kT}} \Omega_{ij} \right) + \sum_{K=1}^4 N_K N_{CO} N_0 \frac{Z_{CO}^i}{Z_C Z_O} e^{-\frac{(D_0 - E_i)}{kT}} \Omega_{i, dis} \\
 & + \sum_{K=1}^4 N_K N_e N_{(CO^+)} \frac{Z_{CO}^i}{Z_{(CO^+)} Z_e} e^{-\frac{(E_{ion} - E_i)}{kT}} \Omega_{i, ion} + \sum_K \sum_\ell N_K N_\ell \Omega_{exch, CO}^{K, \ell} \quad (18)
 \end{aligned}$$

As usual detailed balance arguments similar to those in Mihalas (1970) have been used in (17) and (18) to relate the spontaneous and induced rates to the absorption rates for a given process such as photodissociation. In (17) and (18) α^i_{dis} is the photodissociation cross section for state i , α^i_{ion} is the photoionization cross section, Ω^K_{ij} is the bound-bound collisional rate due to colliding particles K ($K = \text{H}, \text{H}_2, \text{He}, \text{e}$), Ω^K_i , dis and Ω^K_i , ion the collisional dissociation and ionization cross sections due to K respectively, Ω^K_{exch} is the exchange reaction rate of CO with K , (K any reaction molecule or atom), $\Omega^K, \ell_{\text{exch}, \text{CO}}$ is the exchange reaction rate of K and ℓ to form CO, Z_x is the total partition function of x (Z_x^i is the partition function for x in the i th level), $\nu_0 = D_0/h$, $\nu_0' = E^{\text{ion}}/h$ where D_0 and E^{ion} are the dissociation and ionization energies respectively, E_i is the energy of state i and the remaining symbols have their usual meaning.

Given equations (17) and (18) there are two questions to be asked: first are any of the terms in (17) or (18), not considered previously in the vibration-rotation case, significant relative to those already considered and may possibly affect the vibration rotation populations; second what do these equations tell us about the conditions for electronic, ionization and chemical equilibrium. It is evident that since many of the terms depend on the mean intensity J_ν a sufficiently pathological J_ν will always be able to produce a dominant term. An order of magnitude can be gained however by setting J_ν equal to the Planck function B_ν at some temperature T , then evaluating the term to see how much J_ν must deviate from B_ν before the term becomes significant. A typical value for B_ν used below is that of a 4000°K black-body. This is because 4000°K is reasonably close to T_{eff} for many late stars and is a temperature at which vibration rotation LTE is a good approximation.

ELECTRONIC TRANSITIONS

The first allowed transition from the CO ground state ($X^1\Sigma^+$) is to the $A^1\Pi$ state at an energy of 8.03 eV. Transitions between these states form the CO Fourth Positive band system in the vacuum ultraviolet shortward of 1550 Å. Transitions from the ground singlet state to the several lower lying triplet states ($a^3\Pi$ 6eV, $a'^3\Sigma^+$ 6.8eV, $d^3\Delta_1$ 7.5eV, $e^3\Sigma^-$ 7.9eV) are forbidden. Einstein A values for the CO Fourth Positive system have been measured by Mumma, Stone and Zipf (1971). The largest A value is measured for the (0, 2) band and is equal to $5.16 \times 10^7 \text{ sec}^{-1}$. Einstein A values for individual lines in a band are given by

$$A_{A^1\Pi, V', J' \rightarrow X^1\Sigma^+, V'', J''} = A_{A^1\Pi, V', X^1\Sigma^+, V''} \frac{S_{J'J''}}{2J'+1} \text{ sec}^{-1} \quad (19)$$

where $S_{J'J''}$ is the appropriate Honl-London factor which obeys the normalization

$$\sum_{J''} S_{J'J''} = 2J'+1. \quad (20)$$

The value of $5.16 \times 10^7 \text{ sec}^{-1}$ can be used therefore as the maximum A value for a single Fourth Positive band transition.

From the above data the terms due to electronic transitions in (17) and (18) may be evaluated. To evaluate the electronic contribution to the second term in (17) let J_ν be represented by the Planck function B_ν for a 4000°K blackbody. The term may then be written as

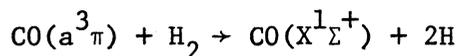
$$B_{ij} \int \phi_\nu J_\nu d\nu = \frac{c^2}{2h\nu_{ij}^3} \frac{g_j}{g_i} A_{ji} B_\nu(4000^\circ\text{K}) \quad (21)$$

where the expression relating the Einstein A_{ij} and B_{ji} has been used. When the expression for the Planck function is used in (21), along with the valid approximation that $\exp(h\nu_{ij}/kT) + 1 \approx \exp(h\nu_{ij}/kT)$, equation (21) becomes

$$B_{ij} \int \phi_\nu J_\nu d\nu = \frac{g_j}{g_i} A_{ji} e^{-h\nu_{ij}/kT} \text{ sec}^{-1} \quad (22)$$

Evaluation of this term yields an absorption rate of about 4×10^{-3} if $g_j \approx g_i$. This is also the rate of spontaneous emission from the $A^1\pi V'=0, J'$ state to the $X^1\Sigma^+ V''=2, J''$ state if the levels are populated via a Maxwell-Boltzmann distribution at 4000°K . In order for these rates to be comparable to the vibration-rotation rates of about 10^2sec^{-1} either the radiation field or the $A^1\pi$ populations would have to exceed the 4000°K LTE intensities or populations by about 5×10^4 . Unless these conditions are met radiative electronic transitions have little effect on the ground state vibration-rotation populations.

In order to investigate the criterion for CO electronic LTE the collisional electronic transition rates due to H, He, H_2 and e must be found. No collisional decay rates for the $A^1\pi$ state due to He, H_2 or H have been measured. Decay or quenching rates for the first excited electronic state ($a^3\pi$) have been measured however. Since the $a^3\pi \rightarrow X^1\Sigma^+$ transition is forbidden the $a^3\pi$ state is fairly stable against radiative decay and collisional rates may be measured. Measurements at 300°K for quenching due to H_2 yields rates of K_{H_2} of $1.6 \times 10^{-10} \text{cm}^3 \text{molecules}^{-1} \text{sec}^{-1}$ (Slanger and Black 1971) where $N_{\text{H}_2} K_{\text{H}_2}$ gives the rate of quenching. The mechanism of relaxation is via H_2 dissociation.



This should also be mechanism by which the higher energy $A^1\pi$ state is relaxed therefore some extrapolation may be made. If the collisional cross section σ for this reaction is independent of energy the quenching rate K_{H_2} may be written as

$$K_{\text{H}_2} = \left(\frac{8kT}{\mu\pi}\right)^{1/2} \sigma \quad (23)$$

where k is the Boltzmann constant and μ is the reduced mass of the CO-H₂ system. For $T = 300^\circ\text{K}$ equation (23) yields a value for σ equal to $8.4 \times 10^{-16} \text{ cm}^2$. As a first order approximation let the cross section for A ¹ π H₂ quenching be constant and equal to the a³ π cross section. In terms of the pressure of H₂ (P_{H_2}) in dynes/cm² the electronic collision relation rate for the A ¹ π state may be written as

$$N_{\text{H}_2} \Omega_{\text{A } ^1\pi \rightarrow \text{X } ^1\Sigma^+} = 6.7 \times 10^4 P_{\text{H}_2} T^{-1/2} \text{ sec}^{-1} \quad (24)$$

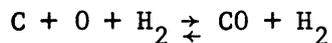
For $T = 4000^\circ\text{K}$ this rate becomes $1.06 \times 10^3 P_{\text{H}_2}$. A typical H₂ pressure at this temperature is about 10^3 dynes/cm^2 which yields a collision rate of about 10^6 sec^{-1} . This rate is a factor of 50 below the radiative rate of $5 \times 10^7 \text{ sec}^{-1}$ therefore this naive analysis predicts that the population of the A ¹ π state of CO will be radiatively controlled rather than collisionally controlled. A more exact analysis will have to await better values for the CO (A ¹ π) H₂ collisional cross sections. Slanger and Black have shown that atomic collisions are not effective in CO(a³ π) relaxation thus collisions with H and He are not considered here. Mumma, Stone and Zipf have found that the electron collision cross sections are of the order of $2 \times 10^{-18} \text{ cm}^2$ at maximum thus electrons should also have little effect on the CO electronic populations in late stars.

Dissociation

One of the reasons that CO plays an important role in late stars is its high dissociation energy of 11.1 eV from the ground state. Photodissociation therefore occurs via vacuum ultraviolet photons shortward of 1200Å. The photodissociation cross section α_{dis} in the third terms of (17) and (18) has been measured by Cook, Metzger and Ogawa (1965). They find that the maximum cross section of $1.2 \times 10^{-17} \text{ cm}^2$ occurs at about 920Å

and falls off to less than 10^{-18} cm^2 as the dissociation edge at 1120\AA is approached. In order to evaluate the third term in (17) the mean intensity J_ν is again set to B_ν (4000°K) and α_{dis} is set to a constant equal to 10^{-17} cm^2 . Evaluation of this term then yields a photodissociation rate of $1.2 \times 10^{-6} \text{ sec}^{-1}$ which is negligible relative to the vibration rotation rates in (17). The spontaneous and induced photorecombination rates in the third term of (18) yield a similar recombination rate if the abundance of C and O versus CO is in chemical equilibrium at 4000°K . In order for either photodissociation or photorecombination to be significant in determining the population of the $X^1\Sigma^+$ vibration rotation levels either the mean intensity at 1200\AA would have to be 10^8 that of a 4000°K blackbody or the (C and O)/CO abundance ratio would have to be 10^8 times the chemical equilibrium value at 4000°K .

The question of whether or not chemical equilibrium is a good approximation can be determined by evaluating the sixth and last terms of (17) and (18). These terms represent the collisional three body and exchange reactions for association and dissociation respectively. Three body reactions are represented by the sixth terms of (17) and (18). An example of this reaction is

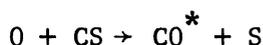


in which the H_2 molecule carries off the energy instead of a photon as in photorecombination considered above. Tsuji (1964) has considered the three body reactions and found that reaction rates K are of the order of $10^{-33} \text{ cm}^6 \text{ particle}^{-2} \text{ sec}^{-1}$ which gives a total rate for the above reaction of

$$\frac{d[\text{CO}]}{dt} = 10^{-33} [\text{C}][\text{O}][\text{H}_2] \quad (23)$$

where [A] represents the number density of particle A. For a solar composition atmosphere at 4000° and P_g about 10^3 the abundance of C, O, and H_2 are of the order 10^{11} , 10^{12} , and 10^{12} respectively which gives a rate of about 10^2 molecules per sec. The total CO abundance is about 10^{12} therefore the lifetime of a CO molecule at equilibrium is about 10^{10} seconds. Three body recombination is therefore relatively ineffective in maintaining CO chemical equilibrium under these conditions.

A more effective way of maintaining chemical equilibrium is through exchange reactions such as



and



the first of which has a K value at room temperature of about $4 \times 10^{-11} \text{ cm}^3 / \text{molecule}^{-1} \text{ sec}^{-1}$ (Foster 1972). From Tsuji the rate constant goes as

$$K = p Z e^{-E_A/kT} \quad (24)$$

where

$$Z = 2[A][BC](\sigma_A + \sigma_{BC})^2 \left\{ \frac{(M_A + M_{BC})^2 2\pi kT}{M_A M_{BC}} \right\}^{1/2} \quad (25)$$

for the reaction $A + BC \rightarrow AB + C$, p is the steric factor and E_A is the activation energy. The activation energy for $O + CS \rightarrow CO^* + S$ should be about $D_0(CO) - E(CO^*) - D_0(CS)$ where D_0 is the dissociation energy and $E(CO^*)$ is the energy of the excited state of CO which is formed ($X^1\Sigma^+$, $V = 12, 13$). This yields about 0-.2 eV depending on whether $V = 12$ or 13. Under the assumption that E_A is negligible the rate at 4000°K becomes about 4 times the rate at 300°K due to the increase in Z . At 4000°K and $p = 10^3 \text{ dynes/cm}^2$ the density of O and CS are 10^{12} and 10^7 respectively therefore the rate of formation of CO is 1.6×10^9 molecules/sec. For a CO density of 10^{12} this yields a

CO relaxation time of 10^3 seconds which is much greater than the photorecombination rate or three body reaction rate but not enough to alter the vibration rotation population.

The rate of destruction of CO can be estimated from the $\text{CO} + \text{N} \rightarrow \text{CN} + \text{O}$ reaction. An activation energy of 3.1 eV is found from the dissociation energies of 11.1 eV and 8.0 eV for CO and CN respectively. No published rate constants are known for this reaction but from Tsuji (1964) the rate can be estimated by $K \approx 10^{-10} e^{-E_A/\theta}$ where $\theta = 5040/T$. This formula yields a rate constant of $2 \times 10^{-12} \text{ cm}^3/\text{molecule}^{-1} \text{ sec}^{-1}$ for the reaction. For the same conditions as used above the nitrogen abundance is on the order of 10^{11} cm^{-3} . A CO / lifetime of 5 sec is then found from the above equations in the same manner as for the creation rate of CO. Again this rate is much higher than the photodissociation rate but not high enough to affect the vibration rotation populations. Exchange reactions therefore are very effective in maintaining chemical equilibrium and chemical LTE should hold in most late stars as was concluded by Tsuji (1964).

IONIZATION

The remaining terms in (17) and (18) refer to ionization. Photoionization cross sections α_{ion} have been determined by Cook, Metzger, and Ogawa (1965) for the region between 600 and 1000Å. Shortward of the ionization edge at 14 eV the photoionization cross section has a maximum value of $1.9 \times 10^{-17} \text{ cm}^2$. In the same manner as with the photodissociation rate the photoionization rate for CO in a 4000°K blackbody field is computed to be $2 \times 10^{-10} \text{ sec}^{-1}$ which has no effect on the vibration rotation populations. If the ratio of $N_e N_{\text{CO}^+}/N_{\text{CO}}$ is given by the usual Saha equation then the

radiative recombination rate should be equal to the ionization rate, therefore, recombination does not affect the vibration rotation populations.

The collisional ionization rate can be estimated by letting the ionization cross section for electrons on CO be equal to the electronic excitation cross section of about 10^{-18} cm^2 (used above). This cross section yields an ionization rate of $6 \times 10^{117} N_e \text{ sec}^{-1}$ for a temperature of 4000°K and an ionization threshold of 14.01 eV. Typical electron densities for $P_g = 10^3$ T = 4000°K are on the order of 10^{11} cm^{-2} which yield an ionization rate of $6 \times 10^{-6} \text{ sec}^{-1}$. This rate is much greater than the photoionization rate but not significant relative to vibration rotation transition rates, therefore, CO ionization LTE should be a good approximation for late stars.

The above has been a very qualitative examination of the total LTE conditions for CO. No significant effects have been found which would affect the vibration rotation population of the ground electronic state. The original conditions derived in the first part of the paper can therefore be used with some confidence. Conditions for total CO LTE will depend heavily on collisional cross sections measurements for electronic excitations which are not currently available. It is evident however that as to internal energy distribution, rotational LTE is the most likely, with vibrational and electronic LTE successively less likely. Ionization and chemical LTE is a relatively good approximation for late stars.

COMPARISON WITH LATE STAR MODEL ATMOSPHERES

New model atmosphere calculations for both M and C stars have been carried out by Alexander and Johnson (1972). These atmospheres include molecular opacity due to CO and CN but have assumed LTE to hold for molecules throughout the atmosphere. Inclusion of CO opacity in these models has resulted in a cooling of the outer atmosphere in many cases relative to models without CO opacity (Johnson 1972).

In Figures 1, 2 and 3 the pressure and temperature at which the radiative and collisional vibrational rates are equal for the CO (1, 0) R(30) line is plotted over the pressure temperature relations for various model atmospheres of Alexander and Johnson (1972). Regions to the left (lower pressure) of the equal rate line are regions in which non-LTE CO vibrational populations may occur. For many of the $\log g = 0$ models significant amounts of the atmosphere extend to the left of the equal rate line. These regions may account for the suspected non-LTE CO populations discussed earlier in the paper. For $\log g = 1$ stars, no significant vibrational non-LTE regions are evident from the model atmospheres which would imply that normal giants should have LTE CO populations. In all of the computed atmospheres the collisional rate due to atoms and molecules is much higher than that due to electrons for the possible non-LTE regions. Contributions to collisional de-excitation via electrons is therefore not included in the figures.

There are no regions in any of the computed atmospheres which have pressures low enough for rotational CO non-LTE populations to occur. There is some evidence, however, that rotational CO non-LTE populations have been observed in the (2, 0) band of Alpha Herculis (Johnson et al 1972). It is possible that when the conditions of hydrostatic equilibrium imposed on the model atmosphere calculations are relaxed to provide for the outflow of matter observed for Alpha Herculia (Weymann 1963) that an extended low pressure atmosphere will be found in which rotational non-LTE may be found.

SUMMARY

Collisional rates for both rotational and rotation-vibration transitions in CO have been calculated for H, H₂, He and electrons. These rates have been compared to the radiative transition rates in order to establish conditions for LTE populations. Tables 1 and 2 give the results for several transitions. Comparisons of the conditions required for LTE with conditions in late star model atmospheres indicates that many log g = 0 stars may have non-LTE vibrational populations but not non-LTE rotational populations.

ACKNOWLEDGEMENTS

The author would like to acknowledge extremely helpful discussions with Dr. Don Hall of Kitt Peak National Observatory and Dr. Hollis Johnson of Indiana University during the course of this investigation.

TABLE 1
 ROTATIONAL EQUAL RATE PRESSURES AND DENSITIES

Upper Level	Temperature	$\log P_{H_2}$ (dynes/cm ²)	$\log(P_H)$	$\log(P_{He})$	$(N_e) \text{ cm}^{-3}$
V=0 J=10	500	-2.69	-2.84	-2.54	2.9×10^9
	1000	-2.53	-2.68	-2.38	3.6
	1500	-2.44	-2.59	-2.29	3.9
	2000	-2.37	-2.53	-2.22	3.7
	2500	-2.33	-2.48	-2.17	3.2
	3000	-2.28	-2.43	-2.13	2.7
	3500	-2.25	-2.40	-2.10	2.3
	4000	-2.22	-2.37	-2.07	2.1
	4500	-2.20	-2.35	-2.04	1.9
	5000	-2.17	-2.32	-2.02	1.7
V=0 J=30	500	-2.43	-2.58	-2.28	4.3×10^9
	1000	-2.25	-2.40	-2.09	5.5
	1500	-2.15	-2.30	-1.99	5.8
	2000	-2.08	-2.23	-1.93	5.3
	2500	-2.03	-2.18	-1.87	4.3
	3000	-1.98	-2.13	-1.83	3.5
	3500	-1.95	-2.10	-1.80	3.0
	4000	-1.92	-2.07	-1.77	2.5
	4500	-1.89	-2.04	-1.74	2.3
	5000	-1.87	-2.02	-1.72	2.1
V=1 J=30	500	-2.14	-2.29	-2.29	8.2×10^9
	1000	-1.96	-2.11	-2.11	1.1×10^{10}
	1500	-1.86	-2.01	-2.01	1.1×10^{10}
	2000	-1.79	-1.94	-1.94	1.0×10^{10}
	2500	-1.74	-1.89	-1.89	8.4×10^9
	3000	-1.70	-1.85	-1.85	6.9
	3500	-1.66	-1.81	-1.81	5.7
	4000	-1.63	-1.78	-1.78	4.9
	4500	-1.61	-1.76	-1.76	4.4
	5000	-1.58	-1.73	-1.73	4.0

TABLE 2

VIBRATIONAL EQUAL RATE PRESSURES AND DENSITIES

Upper Level	Temperature	$\log P_{H_2}$	$\log(P_H)$	$\log P_{He}$	N_e
V=1	500	3.55	2.89	4.87	5.4×10^{10}
J=10	1000	2.76	2.27	3.73	6.7
	1500	2.34	1.94	3.15	6.9
	2000	2.07	1.71	2.76	6.2
	2500	1.85	1.54	2.47	5.1
	3000	1.68	1.39	2.24	4.2
	3500	1.54	1.27	2.05	3.6
	4000	1.42	1.17	1.89	3.1
	4500	1.31	1.08	1.75	2.8
	5000	1.22	1.00	1.63	2.5
V=1	500	3.54	2.88	4.87	5.4×10^{10}
J=30	1000	2.76	2.69	3.73	6.6
	1500	2.34	1.94	3.15	6.9
	2000	2.06	1.71	2.76	6.1
	2500	1.85	1.53	2.47	5.1
	3000	1.68	1.39	2.24	4.2
	3500	1.54	1.27	2.05	3.5
	4000	1.41	1.17	1.89	3.1
	4500	1.31	1.08	1.75	2.7
	5000	1.21	1.00	1.63	2.5
V=2	500	3.82	3.17	5.15	1.0×10^{11}
J=30	1000	3.04	2.55	4.01	1.3×10^{11}
	1500	2.63	2.22	3.43	1.3×10^{11}
	2000	2.35	1.99	3.04	1.2×10^{11}
	2500	2.13	1.82	2.75	9.9×10^{10}
	3000	1.96	1.67	2.52	8.1
	3500	1.82	1.55	2.33	6.9
	4000	1.70	1.45	2.17	6.0
	4500	1.59	1.36	2.03	5.3
	5000	1.50	1.28	1.91	4.8

TABLE 3

Model No.	T(°K)	log g	Chemical Comp.
A1	3000	0.0	Solar
A2	3000	0.0	C/H=5.30E-5, N/H=1.40E-3 O/H=6.00E-5 (C/O=0.88)
A3	3000	1.0	C/H=4.79E-5, N/H=2.10E-3 O/H=5.98E-5, (C/O=0.80)
A5	3200	0.0	C/H=5.30E-5, N/H=1.46E-3 O/H=1.06E-5, (C/O=5)
A6	3200	0.0	C/H=5.30E-5, N/H=1.42E-3 O/H=3.53E-5, (C/O=1.50)
A7	3200	0.0	C/H=5.30E-5, N/H=1.43E-3 O/H=5.89E-5 (C/O=0.90)
A8	3600	1.0	Solar
A10	3600	1.0	C/H=5.30E-5, N/H=1.39E-3 O/H=9.10E-5, (C/O=0.58)
A11	3600	1.0	C/H=5.30E-5, N/H=1.43E-3 O/H=5.00E-5, (C/O=1.06)

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FIGURE CAPTIONS

Figure 1 The pressure-temperature points at which the collisional de-excitation rate of the $V=1, J=30$ state is equal to the radiative rate is plotted. P_H, P_{H_2} , and P_{H_e} refer to collisional de-excitation due to H_1, H_2 and H_p respectively. The letters A1, A2, V1717, and A3 refer to model atmosphere calculations of Alexander and Johnson (1972) given in Table 3. Areas to the left of the lines, P_H, P_{H_2} and P_{H_e} are areas where possible non-LTE effects may occur.

Figure 2 The pressure-temperature points at which the collisional de-excitation rate of the $V=1, J=30$ state is equal to the radiative rate is plotted. P_H, P_{H_2} and P_{H_e} refer to collisional de-excitation due to H_1, H_2 and H_p respectively. The letters A5, A6 and A7 refer to model atmosphere calculations of Alexander and Johnson (1972) given in Table 3. Areas to the left of the lines, P_H, P_{H_2} and P_{H_e} are areas where possible non-LTE effects may occur.

Figure 3 The pressure-temperature points at which the collisional de-excitation rate of the $V=1, J=30$ state is equal to the radiative rate is plotted. P_H, P_{H_2} and P_{H_e} refer to collisional de-excitation due to H_1, H_2 and H_p respectively. The letters A8, A11, A10 refer to model atmosphere calculations of Alexander and Johnson (1972) given in Table 3. Areas to the left of the lines, P_H, P_{H_2} and P_{H_e} are areas where possible non-LTE effects may occur.

