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CO FORMATION IN THE METAL-RICH EJECTA OF SN 1987A

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ABSTRACT

We present a model for the formation of CO in the expanding metal-rich ejecta of SN 1987A. Our model is motivated by the presence of 4.6 μm and 2.3 μm emission bands in the spectrum of the supernova, ascribed, respectively, to the fundamental and first vibrational overtone of CO. The observations show that the CO expansion velocities are lower than ~ 2000 km s^{-1}, suggesting that the emission emanates from the inner, metal-rich, regions of the ejecta. In addition, we ascribe a 2.26 μm excess feature in the high-resolution IR spectra to the $v = 2 \rightarrow 0$ overtone of CO$^+$, and offer a possible identification of a 2.95 μm feature with the $v = 2 \rightarrow 0$ transition of electronically excited CO* ($a\ ^3\pi$). The concurrence of the CO$^+$ and CO*($a\ ^3\pi$) with the ground state of CO supports a scenario in which the formation, excitation and ionization of the CO molecule take place in a warm environment. If reaction rates used in this paper are even approximately correct, then the regions in which CO formation is taking place must be ionized to a substantially lower degree than regions which dominate the line emission of heavier metals. The infrared observations of SN 1987A represent the first evidence for the formation of CO in a warm ($T > 1500$ K), hydrogen-deficient environment, under conditions unique in the interstellar medium. Furthermore, our identification of CO* ($a\ ^3\pi$) is the first assignment of this species in an astronomical object outside the solar system.

Subject headings: infrared: spectra — line identification — molecular processes — stars: individual (SN 1987A) — stars: supernovae

I. INTRODUCTION

Ground-based and airborne infrared (IR) observations of SN 1987A lifted the veil on its expanding inner core region, revealing a large number of fine-structure IR emission lines originating from radioactive Co, and from various metallic elements such as Fe, Ni, Ar, and S, that were synthesized in the explosion (Rank *et al.* 1988; Moseley *et al.* 1988; Witteborn *et al.* 1989). One of the most exciting developments in the IR observations was the discovery of an IR excess, above the continuum photospheric emission, at 5 μm (Danziger *et al.* 1988; Feast 1988). Initially attributed to an infrared echo from a circumstellar dust shell (Allen, Whitelock, and Catchpole 1987), the 5 μm excess is now widely interpreted as due to the 4.6 μm fundamental vibration of CO (Catchpole 1987; Danziger 1988; Feast 1988). This interpretation is strengthened by the detection of the CO first overtone at 2.3 μm (McGregor and Hyland 1987; Elias *et al.* 1988; Witteborn *et al.* 1988). More recently, the 8.1 μm fundamental band of SiO has also been identified in near-infrared spectra of the supernova (Rank *et al.* 1988). Analysis of the high-resolution ($c\Delta\lambda/\lambda \sim 200$ km s^{-1}) observations of the SN with the Anglo-Australian Telescope (Spyromilio *et al.* 1988) suggests that the CO is expanding at velocities of ~ 500–2000 km s^{-1}. These velocities are too large for the CO to be associated with the slowly expanding ($v < 30$ km s^{-1}) circumstellar shell that gives rise to the narrow UV lines (e.g., Kirshner 1988 and references therein), suggesting that the CO emission emanates from the faster moving SN ejecta. Within the ejecta, it is of great importance to determine the location of the CO line-emitting layer, since, in ejecta with a stratified composition, that will determine the network of chemical reactions leading to the CO formation.

Since the ejecta are expanding homologously, with the outer layers expanding at higher velocities than the inner material, one way of determining the composition of the CO forming layer is to compare the CO expansion velocities with those of various other observed elements. As a first step, it is important to determine whether the CO is located in the hydrogen-rich envelope, or in the underlying metal-rich (mantle) ejecta. We therefore have to compare the velocity of the slowest moving hydrogen to the observed CO velocities. The question of determining the ejecta velocity at the base of the hydrogen envelope was addressed in some detail by Woosley (1988*a*). Infrared observations of lines in the Paschen and Brackett series of hydrogen (Phillips *et al.* 1988; Elias and Gregory 1989; data presented in Fig. 14 of Woosley 1988*a*) show that the velocities of the slowest moving hydrogen lines are near 2100 km s^{-1}. This suggests that the CO emission originates from the slower moving, metal-rich, ejecta of the SN. This region may have undergone some mixing and may therefore contain some hydrogen (Woosley, Pinto, and Weaver 1989; Nomoto *et al.* 1988). The mixed model 10HM of Woosley (1988) has ~ 0.2 $M_\odot$ of hydrogen mixed into the helium core. Even if this model is correct, it implies that, at best, CO has formed in an extremely hydrogen deficient environment.

The formation of CO in this H-poor environment is of considerable astrophysical interest since it is also devoid of any dust grains that, in the interstellar medium (ISM), enable molecule formation and CO shielding from dissociating UV radiation. The metal-rich ejecta of the SN offer, however, an attractive site for the formation of CO for the following reasons: (1) C and O are highly abundant species in these regions (e.g., Woosley 1988*a*); (2) CO may be effectively shielded from UV photons created in events following the Co-decay by UV-absorbing metals; finally (3) the CO formation rate in the mantle is sufficiently high to permit a detectable abundance to exist in dynamic equilibrium despite the various destruction mechanisms operating in this SN environment. The mechanisms leading to the formation of CO and other species in the general ISM have recently been reviewed by Turner (1987). The first step in the chain of CO-forming reactions requires the presence of dust grains which play a crucial role in the formation of H_2. It is obvious that none of the standard reactions contribute to CO formation in the SN mantle. An important contribution of this paper will therefore be the identification of various chemical reactions and physical processes that play a role in the formation and excitation of the CO molecule in the expanding mantle of SN 1987A. We note that qualitative similar results regarding the dominant formation and destruction mechanisms have been derived independently by Lepp *et al.* (1988) and McCray (1989).

We also propose that the excess 2.26 μm emission in the infrared spectrum of Spyromilio *et al.* (1988) represents the *R*-branch of the $v = 2 \rightarrow 0$ overtone transition in CO^+. Its *P*-branch is blended with, and broadens, the *R*-branch of the CO overtone. This identification solves a difficulty in the early analysis of the CO spectra (Elias *et al.* 1988), in which the CO^+ overtone was attributed to an extremely blueshifted ($v \approx 3000$ km s^{-1}) overtone of ground-state CO. This latter identification is problematic, since it implies blueshifts disconsonant with the velocities, less than 2000 km s^{-1}, which characterize the other material attributed to the expanding mantle.

A final contribution of the paper is the possible identification of the 2.95 μm feature, evident in the spectrum (Rank 1988) of the SN, with the $v = 2 \rightarrow 0$ transition in the electronically excited CO*($a\ ^3\pi$) metastable state of CO (hereafter designated as CO*). The fundamental band, whose center lies at 5.9 μm, is blended with the Humphreys γ recombination line which, consequently, appears wider than other hydrogen lines apparent in the spectrum. The $a\ ^3\pi$ band is complicated, and probably blended, on its red side, with the strong feature identified as Ni I. We can also not rule out the possibility that the feature is due to the CO-stretch mode of an unidentified gaseous species.

The identification of CO* is particularly important since it represents its first detection in an astronomical object outside the solar system. In the solar system, CO* has been observed in the Martian atmosphere, where its formation is attributed to the dissociative recombination of CO_2 (Conway 1981). In SN 1987A, CO* can only be formed in the creation of CO or via the impact of energetic electrons.

The remainder of this paper is organized as follows: first, we discuss the chemistry of CO, identifying various reactions for its formation and destruction in a warm H-deficient environment, and constructing models for the concurrent formation of CO^+ and CO* (§ II). While some of the relevant reaction rates are unmeasured and thus quite uncertain, we present a model which predicts, qualitatively, the observed temporal characteristics and relative intensities of the three electronic states of carbon monoxide observed in the emission spectra of SN 1987A. In § III we compare our model calculations to estimated CO and CO^+ abundances, derived from spectra taken at various epochs in the evolution of the SN. The astrophysical implications of our model and a brief summary of the paper are presented in § IV.

II. CO CHEMISTRY IN A WARM METALLIC ENVIRONMENT

The chemistry of CO in the mantle is determined by the abundances and ionization state of the various elements in the ejecta, its temperature and density evolution, and the evolution of the ambient radiation field. To model the CO formation we will adopt a simple model for the evolution of the mantle, assuming that it is expanding homologously with a constant outer velocity. The composition of the mantle is taken to be the 6 $M_\odot$ He-core of a 20 $M_\odot$ star, believed to be the progenitor of the SN (e.g., Woosley 1988*a*). The early breakout of the γ-rays and the hard X-ray component, as well as detailed fits to the bolometric SN lightcurve suggest that some mixing may have taken place in the expanding ejecta. Different degrees of mixing are employed by various authors (Woosley 1988*b*; Arnett 1988; Itoh *et al.* 1987). For simplicity, we will consider elemental abundances assumed for a 6 $M_\odot$ mantle which is completely mixed. Some hydrogen may also be admixed into the mantle, but we will ignore its presence in this paper since its abundance will probably be small compared to that of other elements such as He and O (see Fig. 3 in Woosley 1988*b*). Furthermore, our goal in this paper is to examine whether CO can form in a H-deficient environment on the dynamical time scale of the ejecta. Table 1 lists the abundances of the various elements in the mantle. At time t_d (in days) since the explosion, the volume comprising this material will be $2.7 \times 10^{39}(v_3 t_d)^3$ cm^3, where v_3 is the ejecta velocity in units of 10^3 km s^{-1}. The total number density in the ejected core material is therefore $n_0 = 2.7 \times 10^{17}(v_3 t_d)^{-3}$ atoms cm^{-3}, consisting of $\sim$80% He by number. At $t \gg 7d$, input to the radiation field is dominated by the radioactive decay of ^{56}Co. The gamma rays produced in the decay degrade through electron scattering and sequential atomic absorption and reemission processes to visual photons that produce the observed optical light curve (Hamuy *et al.* 1987; Catchpole *et al.* 1987). Beyond day 130 the rate of decline of the visual light curve matches to great accuracy the 114^d*e*-folding lifetime of ^{56}Co, implying 0.075 $M_\odot$ of explosively synthesized radioactive ^{56}Ni in the ejecta (Woosley 1988*b*; Itoh *et al.* 1988).

TABLE 1

ABUNDANCES OF MAJOR ELEMENTS IN THE MANTLE OF SN 1987A[1]

Element (A)	Mass m(A)/($M_\odot$)	Number[2] N(A)	Number Fraction
He	2.0	6.0 (56)	0.811
C	0.2	2.0 (55)	0.027
O	1.25	9.4 (55)	0.127
Ne	0.06	3.6 (54)	0.005
Mg	0.02	1.0 (54)	0.0014
Si	0.32	1.4 (55)	0.019
S	0.2	7.5 (54)	0.010
Ar	0.03	1.0 (54)	0.0014
Ca	0.02	6.0 (53)	0.0008
Fe	0.1	2.2 (54)	0.003
Total	4.2[3]	7.4 (56)	...

[1] Estimated for the 6 $M_\odot$ mass He core of SN 1987A (Woosley 1988*a*).

[2] Numbers in parenthesis indicate powers of 10.

[3] The remaining $\sim$1.8 $M_\odot$ presumably collapsed to form a compact object.

The radioactive energy input heats and ionizes the ejecta. While it is beyond the scope of this paper to provide detailed models of these processes in the SN, the details of the CO formation cycle might lend some insight into the ionization fraction of the various elements. Furthermore, temperatures and ionization states in portions of the ejecta at various epochs can be deduced from the IR observations of the SN. Infrared observations of fine structure lines obtained by Moseley *et al.* (1988; see also Rank *et al.* 1988) and Aitken *et al.* 1988) suggest a relatively low state of ionization overall. Denoting the ionization fraction of each element A by a parameter, $f(A^+) \equiv [A^+]/[A]$, we find from the data of Moseley *et al.* (1988) that $f(Fe^+) \approx 0.78$. The ionization state of carbon and oxygen atoms is discussed below in connection with our CO formation model. Helium is probably not appreciably ionized, i.e., $f(He^+) \ll 1$. The observations of Moseley *et al.* (1988) also suggest electron temperatures of ~ 6000 K and electron densities of $\sim 4 \times 10^8$ cm^{-3} in the metal-rich region of the SN, around day 265 after the explosion. The electron densities are in rough agreement with those required to produce the red-shifted wings observed in the high-resolution spectra of IR lines of Ni II and Ar II (Woosley, Pinto, and Weaver 1989).

In the following we consider the processes that are likely to dominate the formation and destruction of CO in this environment and demonstrate the feasibility of forming CO$^+$ and CO in the observed ratio at the epochs at which observations were performed.

a) Formation and Destruction Mechanisms

The rate at which a product X is formed by the interaction of species A and B can be written as $d[X]/dt = k[A][B]$, where $[A]$, $[B]$, and $[X]$ denote the concentrations (cm^{-3}) of the various species, and k (cm^3 s^{-1}) is a rate coefficient given by $\langle \sigma v \rangle$. Here σ is the reaction cross section, v is the relative velocity between the reactants, and the angle brackets denote a thermal average over the product. The collision between two species A and B creates a complex, $(AB)^*$, which will dissociate unless momentum and energy can be carried away by a collision with a third body, by radiation, or by fragmentation of the complex if either A or B is a molecule. For three-body reactions k is given in units of (cm^6 s^{-1}). The relative importance of the various stabilizing mechanisms depends on the timescales of the relevant reactions. Herbst (1980) showed that the rate of three-body association is proportional to the rate at which collisions with a third body stabilize the complex. This rate is largest for an ionic complex, and about equal to the Langevin collision frequency, $\Gamma_{\text{coll}} \approx 10^{-9}$ ns^{-1}. Simple radiative association, on the other hand, is proportional to the rate at which the product complex undergoes a radiative transition before dissociation. In CO$^+$, we estimate this rate to be $\Gamma_{\text{rad}} \approx 2 \times 10^7$ s^{-1}, by virtue of rapidly decaying electronic product states (Moran, Petty, and Hendrick 1969). A number density of greater than 10^{16} cm^{-3} is thus required before three-body association is more effective than radiative association in forming CO$^+$. The same considerations apply to the neutral CO complex as well. Radiative association will therefore play a more important role than three-body association in the formation of both CO$^+$ and CO, even at early times ($t > 3$ days).

To compare the relative importance of the various pathways (i) leading to the formation and destruction of CO and CO$^+$, we will define a rate R_i (in cm^{-3} s^{-1}), as

$$R_i(t) \equiv d[X]/dt\ , \tag{1}$$

where $[X]$ is the concentration of CO or CO$^+$ in the ejecta. For example, the CO formation rate by the three-body reaction is given by $R_{3n} = k_{3n}[\mathrm{C}][\mathrm{O}][\mathrm{He}]$. The various reactions for the formation and destruction of CO in an environment devoid of any hydrogen are listed in Table 2 and briefly discussed below.

i) *Three-Body Association*

The association process most amenable to laboratory quantification involves stabilization of the molecular product by means of collision with a neutral third body. The following two processes are likely to be the dominant three-body reactions in the SN mantle due to the overabundance of He in the ejecta:

$$\mathrm{C + O + He \rightarrow CO + He}\ , \tag{2}$$

and

$$\left.\begin{matrix} \mathrm{C^+ + O + He} \\ \mathrm{C + O^+ + He} \end{matrix}\right\} \rightarrow \mathrm{CO^+ + He}\ . \tag{3}$$

For the neutral three-body association rate (eq. [2]), we adopt a rate of $k_{3n} = 9.1 \times 10^{-22} T^{-3.08} \exp[2114/T]$ cm^6 s^{-1}, after Baulch *et al.* (1976), based on shock tube measurements of the analogous process in argon (Fairbairn 1969). Following the discussion by Herbst (1980), we adopt for the ionic three-body association reaction (eq. [3]) a rate of $k_{3i} = 100 \times k_{3n}$, which assumes that the electronically excited $(\mathrm{CO^+})^*$ stabilizes at a rate equal to the Langevin collision frequency of $\sim 10^{-9}$ ns^{-1}. In reaction (3), CO is likely to emerge as the charged species since its ionization potential (14 eV) is significantly lower than that of He (24 eV).

ii) *Radiative Association*

The rate of the ionic radiative association reaction,

$$\left.\begin{matrix} \mathrm{C^+ + O} \\ \mathrm{C + O^+} \end{matrix}\right\} \rightarrow \mathrm{CO^+} + h\nu\ , \tag{4}$$

denoted as $k_{\mathrm{RA};i}$, can be related to the three-body ionic association rate by

$$\begin{aligned} k_{\mathrm{RA};i}(\mathrm{cm^3\ s^{-1}}) &\approx (\Gamma_{\text{rad}}/\Gamma_{\text{coll}})k_{3i}\,n \\ &\approx 2 \times 10^{-3} T^{-3.08} \exp[2114/T] \\ &\approx 3 \times 10^{-14} \quad \text{at} \quad T = 4000\ \mathrm{K}\ , \end{aligned} \tag{5}$$

where Γ_{rad} and Γ_{coll} are, respectively, the radiative stabilization rate of the electronically excited states of CO$^+$ by fluorescence to the ground state and the two-body stabilization rate coefficient previously discussed above. This value of $k_{\mathrm{RA};i}$ is intermediate among known estimates for atomic and molecular radiative association rates. This process dominates CO$^+$ formation at later times, and at day 260, its formation rate is equal to

$$\begin{aligned} R(\mathrm{CO^+}) &\equiv (d/dt)[\mathrm{CO^+}] \\ &\approx 2 \times 10^{-7}\{f(\mathrm{C^+})[1 - f(\mathrm{O^+})] \\ &\quad + [1 - f(\mathrm{C^+})]f(\mathrm{O^+})\}\ \mathrm{cm^{-3}\ s^{-1}}\ , \end{aligned} \tag{6}$$

assuming a temperature of 4000 K.[1]

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[1] Lepp and Dalgarno (1989) have suggested that the ionic radiative association rate is substantially smaller than we have estimated. If so, another mechanism with a comparable rate is required to account for the observed abundance of CO$^+$ and CO in the ejecta.

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TABLE 2

IMPORTANT CO-FORMING REACTIONS IN THE MANTLE OF SN 1987A

Reaction	Rate Symbol	Rate Constant[a]	Reference
Three-body association:			
$C + O + M \rightarrow CO + M$	k_{3n}	$9.1 \times 10^{-22} T^{-3.08} \exp(2114/T)$	1
$C^+ + O + M \rightarrow CO^+ + M$	k_{3i}	$\sim 1 \times 10^{-19} T^{-3.08} \exp(2114/T)$	2
$C + O^+ + M \rightarrow CO^+ + M$	...	$\sim 1 \times 10^{-19} T^{-3.08} \exp(2114/T)$	2
Radiative association:			
$C + O \rightarrow CO + h\nu$	$k_{RA;n}$	$\sim 2 \times 10^{16} k_{3n}$	2
$C^+ + O \rightarrow CO^+ + h\nu$	$k_{RA;i}$	$\sim 2 \times 10^{16} k_{3i}$	2
$C + O^+ \rightarrow CO^+ + h\nu$	...	$\sim 2 \times 10^{16} k_{3i}$	2
Dissociation:			
$CO^+ + e \rightarrow C + O$	k_{ed}	$2 \times 10^{-7}(300/T)^{0.48}$	3
$CO^+ + e \rightarrow CO + h\nu$	$k_{er} \ll k_{ed}$	...	...
$M + CO \rightarrow C + O + M$	...	$1.5 \times 10^{6} T^{-3.52} \exp(-112700/T)$	1
$M^+ + CO \rightarrow C^+ + O + M$	k_{ce3}	1.4×10^{-9} (M = He)	4
$\rightarrow O^+ + C + M$		$\sim 1.4 \times 10^{-16}$	
Charge exchange reactions:			
$CO^+ + M \rightarrow CO + M^+$	k_{ce1}	$1.4 \times 10^{-10}(T/300)^{1/2}$ (M = O; ≠He)	2
$CO + M^+ \rightarrow CO^+ + M$	k_{ce2}	$2 \times 10^{-11}(T/5000)^{1/2} \exp(-4580/T)$ (M = O)	2
Photodissociation			
$CO + h\nu \rightarrow C + O$	$k_{\gamma d}[CO]$	($h\nu > 11.1$ eV)	...
$CO^+ + h\nu \rightarrow C + O$	$k_{\gamma d}[CO^+]$	($h\nu > 8.3$ eV)	...
Ionization:			
$CO + h\nu \rightarrow CO^+$	$k_{\gamma i}[CO]$	($h\nu > 14.0$ eV)	...
$CO + e \rightarrow CO^+ + h\nu + 2e$	k_{ei}	$<4 \times 10^{21}$	2

[a] Rate constants are given for $T \approx 300$ K. The rate at other temperatures scales as $T^{-1/2}$ unless the temperature dependence is explicitly given. Units are cm^3 s^{-1} for two-body reactions, and cm^6 s^{-1} for three-body reactions.

REFERENCES.—(1) Baulch *et al.* 1976; (2) *see text*; (3) Mitchell and Hus 1985; (4) Anicich and Huntress 1986.

The neutral analog of equation (4) is

$$C + O \rightarrow CO + h\nu . \tag{7}$$

Its reaction rate coefficient, designated $k_{RA;n}$, is ~ 100 times smaller than $k_{RA;i}$ since CO is statistically favored to form in the metastable triplet states which are too long-lived to stabilize the molecule before it redissociates. Thus for equation (7) we adopt $k_{RA;n} \approx 0.01 \times k_{RA;i}$. This rate is in agreement with the estimate of Julienne and Krauss (1973) for this reaction which was on the order of 10^{-17} cm^3 s^{-1}.

iii) *Radiative and Dissociative Recombination*

CO^+ is depleted primarily through interaction with abundant free electrons. An encounter between an electron and a CO^+ ion results in dissociation of the molecular ion,

$$CO^+ + e^- \rightarrow C + O . \tag{8}$$

A rate coefficient of $k_{ed} = 2 \times 10^{-7}(300/T)^{0.48}$ for this recombination process was derived in merged beam measurements by Mitchell and Hus (1985).

As is the case in other studied molecules, we assume that radiatively stabilized recombination,

$$CO^+ + e^- \rightarrow CO + h\nu , \tag{9}$$

is negligible with respect to dissociative recombination.

iv) *Charge Exchange*

A further mechanism considered for the depletion of CO^+ and formation of CO is the charge exchange reaction,

$$CO^+ + O \rightarrow CO + O^+ , \tag{10}$$

for which a rate, k_{ce1}, of 1.4×10^{-10} cm^3 s^{-1} has been measured (Fehsenfeld and Ferguson 1972) at 300 K. The reverse reaction is endothermic by 0.395 eV. The reaction cross section measured by Murad (1973) depends strongly on the source, and thus the excitation state, of the oxygen ion. For ground-state ions, the expected threshold is observed, above which the cross section reaches a plateau of order 0.5×10^{-16} cm^{-2} for kinetic energies up to 2–3 eV. We incorporate the threshold behavior and constant cross section over the temperature range of interest by adopting a rate of $k_{ce2} = 2 \times 10^{-11}(T/5000)^{1/2} \exp(-4580/T)$ cm^3 s^{-1}. From the temperature independence of the cross section for the reverse reaction we infer a $T^{1/2}$ law for the forward reaction as well.

The more rapid reaction

$$CO + He^+ \rightarrow C^+ + O + He , \tag{11}$$

with $k_{ce3} = 1.4 \times 10^{-9}(T/300)^{-1/2}$ cm^3 s^{-1} (Anicich and Huntress 1986), contributes negligibly to the depletion of CO because of the low abundance of He$^+$ in the ejecta.

v) *Electron Impact Excitation and Ionization*

Electrons bearing sufficient kinetic energy are capable of populating the electronically excited triplet states of CO, all of which decay rapidly to metastable CO*($a\ ^3\pi$). This process gives rise to emission of the Cameron band system extending from 1700 Å to 2600 Å. The threshold for this process,

$$CO(X\ ^1\Sigma) + e^- \rightarrow CO^*(a\ ^3\pi) + e^- , \tag{12}$$

is 6.01 eV, and the peak cross section, at 11 eV, is $1.1 \pm 8 \times 10^{-16}$ cm^2 (Ajello 1971).

More energetic electrons may leave CO in an ionized state, via the process:

$$CO + e^- \rightarrow CO^{+*} + 2e^- \rightarrow CO^+ + h\nu + 2e^- \ . \quad (13)$$

This process of electron impact ionization has a threshold of 14.0 eV and a peak cross section, at 100 eV, of 2.6×10^{-16} cm^2 (Rapp and Englander-Golden 1965).

Since hot electrons created through Comptonization of γ-rays at the SN core thermalize with the free electron gas before causing further ionization (Axelrod 1980), nearly all the electrons encountered by CO molecules are thermal. We can place a weak upper limit on the rate of electron impact ionization k_{ei} by neglecting the precise ionization spectrum and assuming that the maximum cross section obtains for all energies above threshold. For an electron temperature of 6000 K, this yields a limit of $k_{ei} < 4 \times 10^{21}$ cm^3 s^{-1}. The rate of triplet excitation by electron impact k_{et}, at $T_e = 6000$ K is $k_{et} = 8 \times 10^{-16}$ cm^3 s^{-1}.

vi) *Photodissociation and Photoionization*

The CO photodissociation rate per unit volume by UV radiation in the ejecta can be written as

$$R_{\gamma d} \equiv d[CO]/dt = F_{UV}\sigma_d[CO] \ , \quad (14)$$

where F_{UV} is the flux (in cm^{-2} s^{-1}) of incident UV radiation, and σ_d is the photodissociation cross section of CO or CO$^+$. The process has a threshold of 11.1 eV and 8.3 eV, for CO and CO$^+$, respectively, and implicit in our notation is a convolution of the cross section and the spectrum of the incident flux. Ultraviolet photons are continuously created by excitation of the atoms and ions in the expanding ejecta. Most of the excitation is caused by primary electrons slowing down in the helium-rich nebula. We have assumed that, as in Meyerott's (1978) analysis of a Type I supernova, the UV photons are created primarily by electron impact excitation of metastable He from the 1^1S ground state (McCray 1988). Another mechanism might be that of He II ionized by γ-rays from ^{56}Co decay recombining into an excited metastable state. This mechanism has been invoked by Graham (1988) in interpreting the 1.083 μm P Cygni profile which he attributes to population of the He 2^3S triplet state in the high-velocity envelope, and might come into play in the metal-rich mantle as well.

The He metastable 2^1S singlet state, at an excitation energy of 20.7 eV, decays radiatively to the ground state, with $A(2^1S \rightarrow 1^1S) = 51$ s^{-1}, by emission of two UV photons, with a broad spectrum peaked at ≈ 10 eV (Drake, Victor, and Dalgarno 1969). At high densities, however, the 2^1S state is coupled collisionally to the 2^1P state, with a transition rate $\sim 10^{-8}$ cm^3 s^{-1}. The 2^1P state, in turn, rapidly emits a 19.8 eV photon which can ionize, but not dissociate, a CO molecule. The effect of electron excitation of the metastable 2^3S triplet state is similar since, at high densities, it decays primarily via collisions to the 2^1S state at a rate of $\sim 2 \times 10^{-8}$ cm^3 s^{-1}. We define a quantity η_2 as the fraction of metastable decays proceeding via the two-photon channel. The value of η_2 is given by $\eta_2(t_d) = [1 + 10^{-8}n_0/A(2^1S \rightarrow 1^1S)]^{-1}$. Adopting an expansion velocity of 2000 km s^{-1}, we derive values of η_2 for days 100, 200, and 300 after the explosion of 0.13, 0.55, and 0.80, respectively.

We estimate the UV flux in the ejecta from the observed distribution of Fe among its two major ionization states, Fe II, and Fe III. Implicit in this approach is the assumption that the CO is subjected to the same UV flux that maintains the ionization state of the metals. It has been brought to our attention by A. Dalgarno that recombination of Fe III is likely dominated by charge exchange with neutral oxygen, for which process we adopt a rate $\kappa(\mathrm{III} \rightarrow \mathrm{II})$ of 10^{-9} cm^3 s^{-1}. With this assumption, the UV flux can be written as

$$F_{UV} \approx \kappa(\mathrm{III} \rightarrow \mathrm{II})[O]\sigma_{ion}^{-1}[n_{\mathrm{III}}/n_{\mathrm{II}}] \ . \quad (15)$$

Using the Fe II and Fe III mass estimates derived by Moseley *et al.* (1988), we get an $(n_{\mathrm{III}}/n_{\mathrm{II}})$ ratio of ≈ 0.13. We point out that this ratio may be uncertain by a factor of ≈ 3 due to the optical depth effects discussed by Moseley *et al.* The estimated ionization cross section is $\sigma_{ion} \approx 10^{-17}$ cm^2. This leads to $F_{UV} \approx 10^{15}$ cm^{-2} s^{-1} for UV photons in excess of 16.18 eV. Fe II is ionized by all the photons emitted in the one-photon process, and only $\sim 12\%$ of those emitted in the two-photon decay, so that the Fe II ionizing flux needs to be multiplied by a factor of $(1 + \eta_2)/(1 - 0.76\eta_2)$ giving a total UV flux of $\approx 4 \times 10^{15}$ cm^{-2} s^{-1} on day 260 after the explosion. This flux should be regarded as an upper limit since other processes, such as electron impact, may contribute to the ionization of the mantle as well.

To obtain the time dependence of the UV flux, we assume that it scales linearly with the Co energy deposition rate. Were the decaying Co fully mixed and the photons streaming freely through the mantle, then we would expect the UV flux to vary inversely as the square of the mantle radius, and

$$F_{UV}(\mathrm{cm}^{-2}\ \mathrm{s}^{-1}) \approx 2.9 \times 10^{18}[(1 + \eta_2(t_d)]\ \exp(-t_d/114)/t_d^2 \ . \quad (16)$$

The CO photodissociation and photoionization yields versus photon energy have been reported by Cook, Metzger, and Ogawa (1965). From a threshold at 11.1 eV, the dissociation cross section σ_d reaches a peak of $\sim 2 \times 10^{-17}$ cm^2 at ~ 13.5 eV and drops off rapidly at the ionization threshold of 14.0 eV. Since dissociation occurs via discrete predissociating levels (van Dishoeck and Black 1988), the peak value employed constitues an upper limit. The photoionization cross section, σ_i, is of comparable magnitude to the photodissociation cross section and is constant, to within a factor of 2, from threshold to over 20 eV (Cook, Metzger, and Ogawa 1965). Thus 20% of the UV photons emitted via the two-photon channel can dissociate CO, while all of the photons emitted via the single photon channel, and an estimated 25% of those emitted in the two-photon process, can contribute to photoionization.

We find that the presence of molecular CO further constrains the UV flux to which the CO is exposed. If mixing is not complete, as our model seems to suggest, then UV absorbing metals such as Fe (Xu and McCray 1988) are apt to shield CO molecular regions from regions in which the UV flux can be considerably higher. To account for such shielding we introduce a shielding efficiency factor, η_{sh} which is left as a free parameter in the model, and a satisfactory solution is found for $\eta_{sh} = 1$.

The CO photodissociation rate can now be written as

$$R_{\gamma d} = 7 \times 10^{20}\eta_{sh}\eta_2\ \exp(-t_d/114)/t_d^2\sigma_d[CO] \ , \quad (17)$$

and its photoionization rate as

$$R_{\gamma i} = 2 \times 10^{21}\eta_{sh}(1 - 0.5\eta_2)\ \exp(-t_d/114)/t_d^2\ \sigma_i[CO] \ , \quad (18)$$

where we have surpressed the time dependence of η_2. For CO$^+$, the cross section σ_d in equation (17) should be replaced by the corresponding CO$^+$ value. In practice we have adopted the same dissociation rate for CO and CO$^+$, and we need not

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consider photoionization of CO$^+$, which has a threshold of 27.9 eV.

b) CO *Formation Model*

The equations governing the formation and destruction of CO and CO$^+$ in a H-deficient environment can be summarized as follows:

$$d[\mathrm{CO}]/dt = k_{\mathrm{ce1}}[\mathrm{CO}^+][\mathrm{O}] + k_{\mathrm{RA};n}[\mathrm{C}][\mathrm{O}] + k_{3n}[\mathrm{C}][\mathrm{O}][\mathrm{He}] + k_{\mathrm{er}}[\mathrm{CO}^+]n_e - \{k_{\gamma i} + k_{\gamma d} + k_{\mathrm{ce2}}[\mathrm{O}^+]\}[\mathrm{CO}] \quad (19)$$

and

$$d[\mathrm{CO}^+]/dt = \{k_{\mathrm{RA};i} + k_{3i}[\mathrm{He}]\}\{[\mathrm{C}^+][\mathrm{O}] + [\mathrm{C}][\mathrm{O}^+]\} + k_{\gamma i}[\mathrm{CO}] + k_{\mathrm{ce2}}[\mathrm{CO}][\mathrm{O}^+] - \{k_{\mathrm{ed}} n_e + k_{\mathrm{er}} n_e + k_{\gamma d} + k_{\mathrm{ce1}}[\mathrm{O}]\}[\mathrm{CO}^+] \,. \quad (20)$$

Rates involving [He$^+$] are negligibly small and have been omitted. The rate coefficients given in equations (18) and (19) above are summarized in Table 2.

To solve the equations (19) and (20) given above, we make the following set of simplifying approximations: (1) we neglect any depletion of atomic carbon (0.2 $M_\odot$) or oxygen (1.25 $M_\odot$) due to the formation of CO ($<10^{-4}$ $M_\odot$); (2) we also assume that the ionization state of the ejecta is low, i.e., that the various elements are at most, singly ionized. Furthermore, (3) since the reaction rates proceed much faster than the dynamical changes in the ejecta, we can safely assume that we are in a steady state situation, and set $d[\mathrm{CO}]/dt = d[\mathrm{CO}^+]/dt = 0$ at each time step. The temporal evolution of the CO and CO$^+$ abundance in the ejecta is then ascribed to the t_d^{-3} decrease in the density of reactant species, as well as the $\sim t_d^{-2}$ exp [$-t_d/114$] behavior of the UV flux, and hence the photodissociation rate, in the ejecta. The temperature governing the rates of chemical reaction is left as a free parameter and its effect has been studied in our model calculation.

We find that the overall abundance of [CO] + [CO$^+$] is dominated by recombinative dissociation of CO$^+$ (reaction 8), and that, if our assumed formation rates are correct, then the fractional electron density *in the regions in which CO is being formed* cannot exceed 0.1%, or $n_e < 3 \times 10^7$ cm^{-3} at day 200. Since our mixed model assumes that atomic oxygen constitutes $\sim$10% of the density by number, we infer that $f(\mathrm{O}^+) \leq 1\%$. The ionization fraction of carbon, however, is not strongly constrained.

Figure 1 depicts the behavior of the rate R_i of the various reactions (i) as a function of gas temperature for an ejecta density of 4×10^9 cm^{-3}, corresponding to $t_d = 200$ days, and ionization fractions $f(\mathrm{C}^+) = 0.4$ and $f(\mathrm{O}^+) = 0.01$. While no rigorous optimization of parameters was performed, our calculations demonstrate that CO and CO$^+$, in proportions of approximately unity, can indeed be formed in the SN mantle

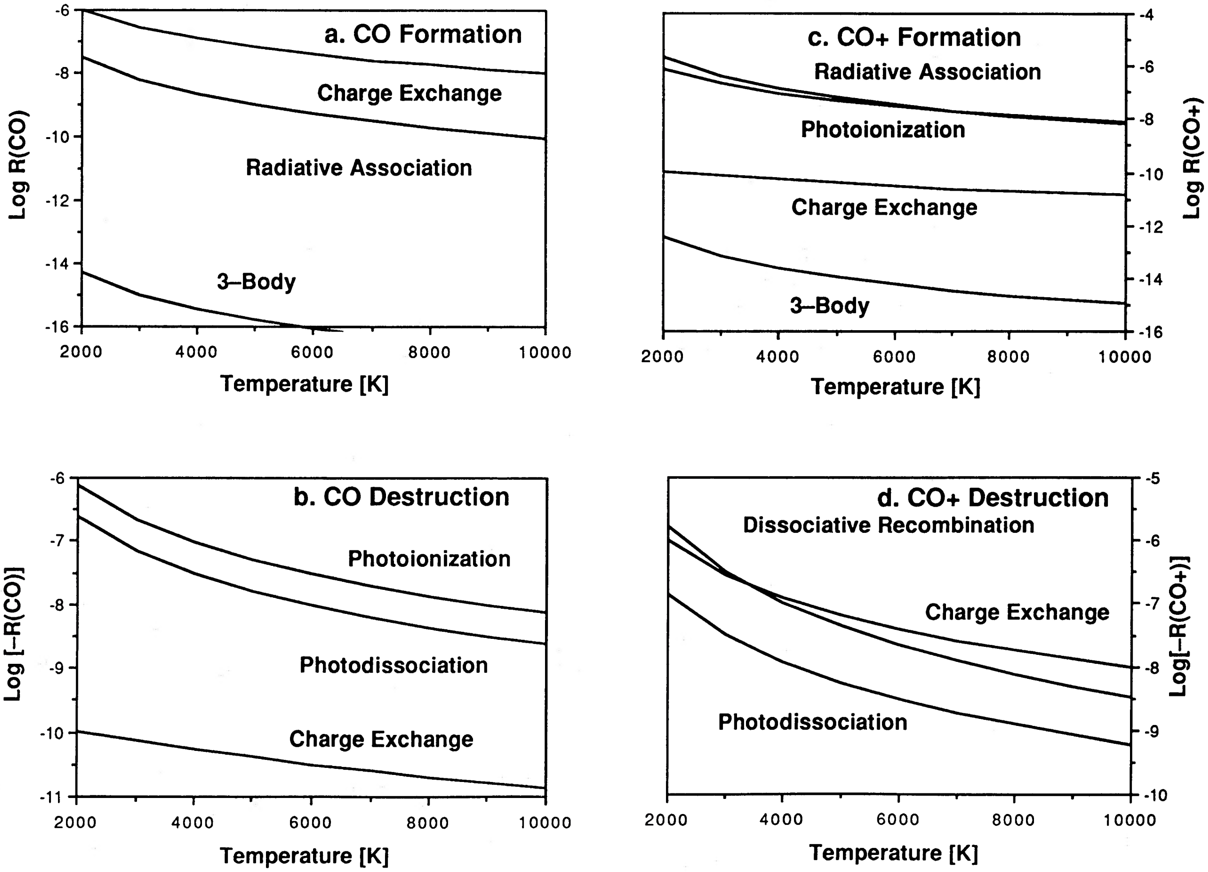

FIG. 1.—(*a*) Reactions leading to the formation of CO are depicted as a function of gas temperature for a constant number density of $n_0 = 4.2 \times 10^9$ cm^{-3}. (*b*) Same as (*a*) for reactions leading to the destruction of CO. (*c*) Same as (*a*) for reactions leading to the formation of CO$^+$. (*d*) Same as (*a*) for reactions leading to the destruction of CO$^+$.

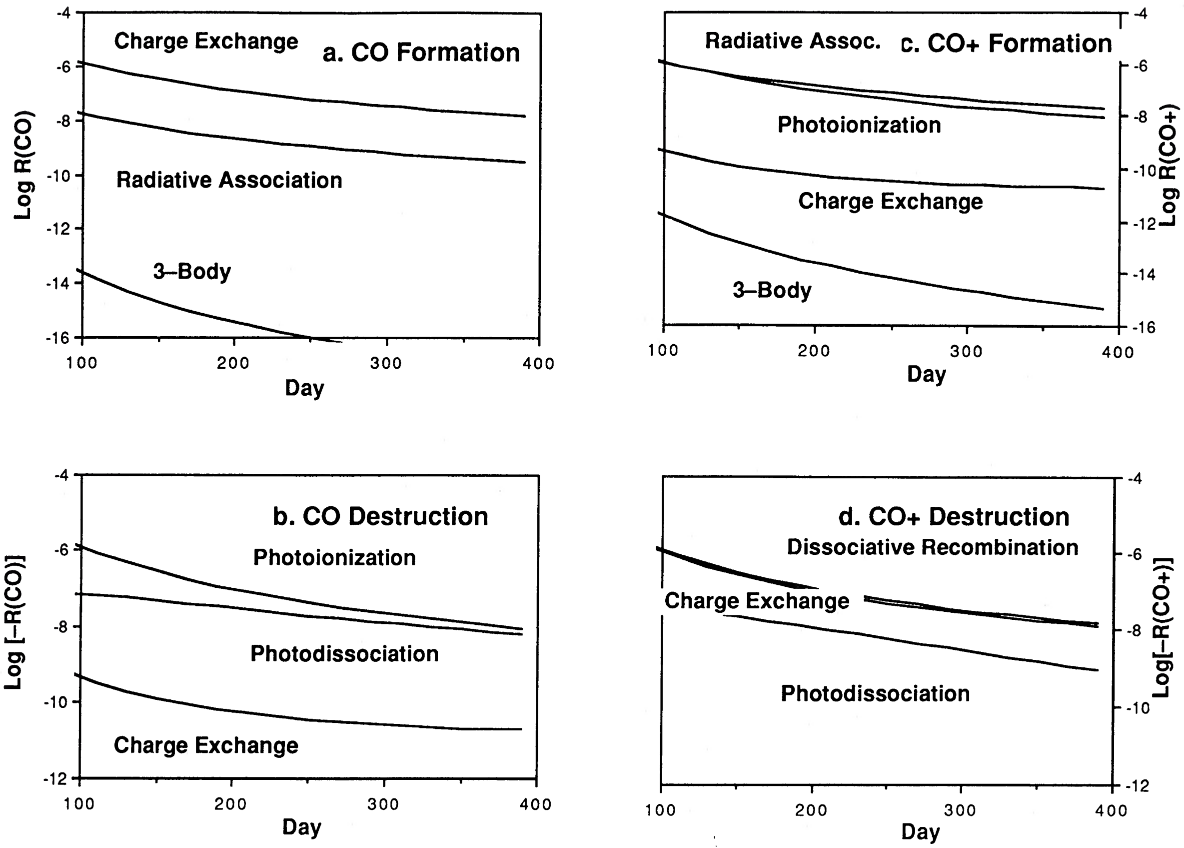

FIG. 2.—(*a*) Reactions leading to the formation of CO are depicted as a function of time for a constant gas temperature of $T = 4000$ K. (*b*) Same as (*a*) for reactions leading to the destruction of CO. (*c*) Same as (*a*) for reactions leading to the formation of CO$^+$. (*d*) Same as (*a*) for reactions leading to the destruction of CO$^+$.

by the processes enumerated above. Similarly, in order to maintain a CO$^+$ abundance consistent with observations and with the lower estimates of band intensity due to Marian *et al.* (1988), we can place an upper limit of 0.1% on the fractional electron density in the immediate vicinity of the molecular material. Continuum measurements by Moseley *et al.* (1988) provide a measure of $n_e^2 V$, where V is the volume comprising the ionized heavy elements, from which an estimated electron density $n_e \geq 10^8$ cm^{-3} is derived at $t_d = 270$ days. This corresponds to an ionization fraction of close to 12%, a value two orders of magnitude higher than the limit placed by dissociative recombination of CO$^+$ according to our model. This, again, supports a picture in which microscopic mixing has not occurred and that a high ionization fraction characterizing the inner core material does not extend into the region of molecule formation.

Figure 2 depicts R_i at temperature $T = 4000$ K as a function of time, again under the set of assumptions that $f(\mathrm{C}^+) = 0.4$ and $f(\mathrm{O}^+) = 0.01$. Figure 2*a* shows that CO formation is dominated by charge exchange between CO$^+$ and neutral O (eq. [10]). This remains true even for nearly complete ionization of the minority species. CO destruction is dominated, under all conditions, by UV photoionization, so that the observed [CO$^+$]/[CO] ratio serves to constrain the ambient photoionizing UV flux. CO$^+$ is formed predominantly by radiative association of ionized and neutral atomic partners (equation [4]), as shown in Figure 2*c*, with dissociation by thermal electrons (eq. [8]) governing its destruction (Fig. 2*d*).

Calculated mass abundances of CO and CO$^+$ are shown in Figure 3 as a function of time at a constant temperature of 4000 K. The discrete points correspond to CO abundance estimates by Spyromilio *et al.* (1988) based on fits to infrared observations during the period of days 200–350. The lower CO abundance at earlier times is attributable to the harder UV spectrum since higher densities favor the deexcitation of metastable He via the single 19.8 eV photon radiative channel. Results for $t_d < 100$ days are not shown since our model does not account for higher kinetic temperatures, electron densities, and UV flux which likely characterized that epoch.

c) Formation of Metastable CO*

Radiative coupling of the singlet CO ground state to the electronically excited triplet states [of which CO*($a\ ^3\pi$), with a term energy of 6.02 eV, is the lowest lying] is forbidden by spin conservation. CO* excitation is therefore a collisional process. For electron densities of less than 10^9 cm^{-3} and temperatures $T_e < 7000$ K, we can place an upper limit of $\sim 10^{-6}$ s^{-1} on the rate of CO* excitation by electron impact. This rate is significantly smaller than the CO* ($a\ ^3\pi$) creation rate during the CO formation process, either in the CO$^+$ charge exchange or the CO radiative association process. We will assume that CO is formed both in the ground state singlet and excited metastable triplet states with a statistical distribution of the end products favoring the formation of triplets by a factor of 3. The fraction of CO that is formed as CO* is therefore $0.75 f^*$, where f^* is the fraction of the formation collisions that occur at relative ener-

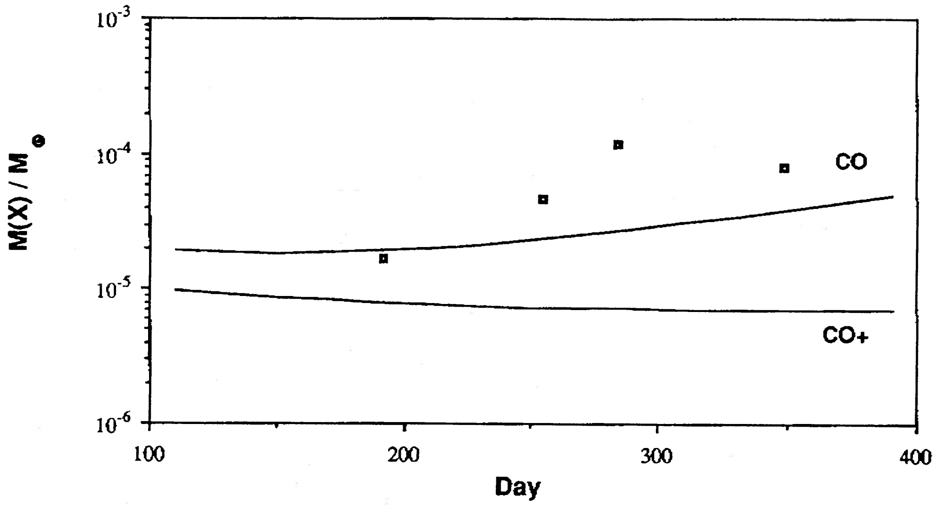

FIG. 3.—Adopting a constant gas temperature of 4000 K, the figure depicts the evolution of the CO and CO^+ abundances in the He-core of SN 1987A as functions of time. Points indicate CO abundances inferred by Spyromilio *et al.* (1988).

gies in excess of 6 eV. For a Maxwellian distribution of energies in the center of mass of the colliding CO and O projectiles, we get that at temperatures of ≈ 4000 K, $f^* \approx 5 \times 10^{-7}$. The radiative lifetime of the $a\,^3\pi$ state, averaged over its $\Omega = 0$, 1, and 2 manifolds, has been measured as 9.5 ± 0.63 ms (James 1971), compared to typical lifetimes of the singlet states of 10^{-8} s. Recent laboratory measurements in both the microwave (Saykally 1986; Yamamoto and Saito 1988) and infrared (Davies and Rothwell 1985) have provided an accurate set of molecular parameters for the state. Molecules formed in higher lying triplet or singlet states rapidly fluoresce to the $a\,^3\pi$ and $X\,^1\Sigma$ states, respectively. A determination of the abundance ratio of [CO*] to [CO] would thus establish the ratio of the CO* lifetime with respect to fluorescence to that of CO with respect to its predominant destruction mechanism.

III. COMPARISON WITH OBSERVATIONS

The first reported detection of CO in SN 1987A was in both the fundamental and overtone vibrational bands, at 4.6 μm and 2.3 μm, in 1987 June (Danziger *et al.* 1987). CO^+ was first identified in the spectra of Spyromilio *et al.* (1988). In hindsight, we can see that the CO^+ overtone is apparent in the Cerro Tololo spectra of 1987 May and June (Elias *et al.* 1988). We also point out that the very earliest IR spectra of the SN obtained with the CVF at ESO La Silla between days 5 and 15 (Bouchet *et al.* 1987), exhibit a single spectral point at 2.28 μm, elevated by $\sim 2\ \sigma$. This feature could be due to the presence of either CO, CO^+, or a blend of the two. The implications of such a CO feature, if present, are unclear since the spectral resolution of the observation does not allow us to determine from what region the emission would arise.

In analyzing the evolution of the 2.3 μm feature, we note that the centers of the $2 \rightarrow 0$ bands of ground state CO and CO^+ lie at 2.35 μm and 2.306 μm (Rao 1950), respectively. The rates for spontaneous decay from $v = 2 \rightarrow 0$ are $A = 1.0\ s^{-1}$ and $A = 1.8\ s^{-1}$ for CO and CO^+, with values calculated for individual vibrational-rotational transitions given by Kirby-Docken and Liu (1978) and Rosmus and Werner (1982), respectively. While we know of no measurement of the CO^+ overtone band intensity, more recent calculations (Marian *et al.* 1988), brought to our attention by J. Spyromilio, suggest that the CO^+ band intensity is ~ 5 times weaker than that calculated by Rosmus and Werner (1982).

The time evolution of the CO^+ and CO abundances, as well as the evolution of their respective rotational and vibrational distributions can be derived from the high-resolution spectra taken at the Anglo-Australian Telescope (Spyromilio *et al.* 1988), as well as from those taken at ESO La Silla (Danziger *et al.* 1988). Oliva, Moorwood, and Danziger (1987) derive a CO mass of $\sim 3 \times 10^{-4}\ M_\odot$ on day ~ 220. Combined with the mass estimates of Spyromilio *et al.* (1988), we see that the CO^+ and CO abundances between days 200 and 350 remained approximately constant (given the sensitivity of the mass estimates to the assumed vibrational temperature), and comparable, with a value $\sim 10^{-5}$–$10^{-4}\ M_\odot$.

Decreasing emission in the $2 \rightarrow 0$ bands is due to vibrational cooling of the CO. The rate constant for vibrational relaxation of CO, given by Scoville, Krotkov, and Wang (1980) for CO-H_2 and applicable to collisions between partners for which there is no long-range chemical interaction, is $q = 3.7 \times 10^{-11}$ $cm^3\ s^{-1}$. This would imply that the distribution of population among the vibrational states of CO is no longer characteristic of the kinetic temperature of the gas when a critical density of $\sim A/(q\tau) \approx 4 \times 10^{10}\ cm^{-3}$ is reached. Here τ is the optical depth in the CO fundamental band. Assuming an expansion velocity of 2000 km s^{-1}, and adopting a nominal value of $5 \times 10^{-5}\ M_\odot$ for the CO mass (assumed to be distributed uniformly throughout the mantle), and a vibrational temperature of 2000 K, we get that densities above the critical value obtain only until day 47. A precise determination of the CO, CO^+ masses after this day therefore requires an estimate of how the distribution of vibrational populations evolved during the time that both have been observed. Cooling is clearly evident since the higher-v band heads apparent in the spectra of days 223–228 (Danziger *et al.* 1987) are absent in the day 349 spectrum of Spyromilio *et al.* (1988).

IV. SUMMARY AND ASTROPHYSICAL IMPLICATIONS

We have presented in this paper important reactions for the formation and destruction of CO in the metal-rich ejecta of SN 1987A. The important CO formation and destruction reactions are $CO^+ + O \rightarrow CO + O^+$ (charge exchange reaction), and

$CO + h\nu \rightarrow CO^+ + e$ (photoionization), respectively. The important CO^+ formation and destruction reactions are $C^+ + O \rightarrow CO^+ + h\nu$ (radiative association), and $CO^+ + e \rightarrow C + O$ (dissociative recombination), respectively. Our association of the CO and CO^+ emission with the metal-rich regions of the ejecta is based on the observation that the CO expansion velocities are lower than those of the hydrogen at the base of the H-envelope.

In our model CO^+ is the first molecule to form in the SN ejecta, and its formation is followed by that of CO. Our picture of CO^+ undergoing constant binary association and conversion, via charge exchange, to CO, while CO is being ionized and CO^+ dissociated by electron collisions, is supported by the tentative identification of CO^* ($a\ ^3\pi$) in the spectrum of the SN. In our proposed reaction network, the formation of CO^* is a natural byproduct of the CO formation process.

Our model further suggests that the relative abundance of neutral and ionized CO is modulated by the trapped flux of ionizing radiation via photoionization. The relative CO and CO^+ abundances can therefore be used to constrain the UV flux in the molecule-forming regions of the ejecta, and we find that it is comparable to that required to maintain the Fe ionization fractions in the ejecta. Similarly, the fractional electron density in the molecule-forming regions cannot exceed 0.1% in order for the observed CO^+ abundance to survive in the face of recombinative dissociation.

It is interesting to examine to what extent the detection of CO, CO^+, and CO^* in the spectrum of SN 1987A can be used to constrain the physical conditions in the ejecta. The observed CO and CO^+ abundances do not strongly constrain the temperature which characterizes the rate of chemical reactions accounting for their formation. The early absence of CO and gradual emergence of a substantial flux in the CO^+ overtone can be attributed to high temperatures and consequently slow rates of association in the early expanding mantle. Temperatures in the range of 1500–6000 K account for the observed CO production in the epoch after day 200. The fact that $[CO]/[CO^+] \sim 1$, however, *does* constrain the field of ionizing radiation present in the region of the mantle ejecta where we believe that the CO is formed. Our model suggests that the rate at which CO is ionized by UV photons corresponds, with the temporal scaling discussed above, to a rate of $\sim 0.85\ s^{-1}$ per CO molecule, at day 100.

The $\sim 10^{-4}\ M_\odot$ of CO produced in the supernova in a dynamic equilibrium with respect to dissociation as suggested by the model presented here, constitute only a minor fraction of the $\sim 0.1\ M_\odot$ that could have formed if all the available C were locked up in CO in regions of the ejecta where both coexist. Carbonaceous dust can therefore form even in oxygen-rich regions of the ejecta. This has important implications for the formation site of isotopically anomalous xenon (see Clayton 1988) which has to be preserved in carbon solids since it is detected in meteoritic diamonds (Lewis *et al.* 1987).

Finally, we point out that supernovae are not likely to be an important contributor to the interstellar CO abundance. Even if all galactic SN produced the same amount of CO as is observed in SN 1987A, it will have no effect on its galactic abundance, first because the CO mass is too small ($\sim 10^{-5}\ M_\odot$) to be of any significance, and second, because any CO produced in the ejecta will probably not survive subsequent events, such as reverse shocks propagating through the ejecta, that are likely to occur before it is mixed with the general interstellar medium.

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Note added in proof.—We now believe the 2.28 μm feature in the early spectra of Bouchet *et al.* (1987) to be due to blueshifted emission of neutral argon in the supernova envelope.

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