3748 © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **56**, *3748—3755 (1983)* [Vol. 56, No. 12

Chemiluminescences in the Carbon Monoxide-Active Nitrogen System

Nobuaki Washida, Hiroshi Bandow, and Gen Inoue
Division of Atmospheric Environment, The National Institute for Environmental Studies,
P. O. Tsukuba-gakuen, Ibaraki 305

(Received June 24, 1983)

Chemiluminescences produced in the reaction of CO with active nitrogen were measured in the region from infrared to vacuum ultraviolet. The infrared emission from vibrationally excited CO was measured by means of a FTIR spectrometer. A vibrationally excited CO up to $v''=18$ was observed. The quenching and relaxation of vibrationally excited CO were measured by the addition of other gasses. The formation of carbon atoms was observed by the absorption of carbon resonance lines, and the recombination reaction of $C+N+M \longrightarrow CN^*+M$ is proposed as the mechanism of the violet and red emission of CN. The reaction of $CO^*(a^3\Pi)+CO^* \longrightarrow C+CO_2$ is proposed as the carbon-atom source. The emission of the fourth positive band of CO was observed in the vacuum UV region. The effect of self-absorption by the vibrationally excited CO was reduced by the addition of CO_2. It is suggested that the apparent abnormal vibrational distribution in $CO(A^1\Pi)$ can be reduced by considering the effect of the quenching of $CO(A^1\Pi)$.

The reactions of active nitrogen with other gases are well known[1-4] to produce a variety of chemiluminescences and are widely used in studies of both the spectroscopy of molecules and chemical reactions. Over 1500 papers related to active nitrogen reactions have been published. Suggested active species in the active nitrogen have included N atoms (usually $N(^4S)$, the ground state, and in some special cases excited states, such as $N(^2D)$ and $N(^2P)$), metastable excited states of N_2, such as $N_2(A^3\Sigma_u^+)$ and $N_2(A^1\Pi_g)$, and the vibrationally excited ground state of N_2. One well-known CN radical chemiluminescent reaction in the active nitrogen–hydrocarbon system is the case of the reaction initiated by the N-atom attack on hydrocarbon.[2,4] On the other hand, the chemiluminescent reaction in the active nitrogen–CO system is the case of energy transfer from electronically excited N_2 to CO, because the bond-dissociation energy of CO is very large (11.09 eV) and CO cannot be decomposed by a direct reaction with N atoms.

In the case of the active nitrogen–CO system, the chemiluminescences reported are infrared emission from the vibrationally excited CO,[5,6] visible emission from CN radicals in both $A^2\Pi$ and $B^2\Sigma^+$ states,[7] and the fourth positive band emission from $CO(A^1\Pi)$[8-10] in the vacuum UV region. Studies of the mechanism of these emission bands are interesting because these emissions are produced by energy transfer in various electronic states of N_2 and CO. In the present study, emissions produced in the active nitrogen–CO system are measured by using the same flow reactor in order to study the correlation of each emission band. Several new results concerning the formation mechanism of chemiluminescences will be reported.

Experimental

The discharge flow-system used is illustrated in Fig. 1. The cylindrical Pyrex flow tube is 21.2 mm i.d., 500 mm in length, and sealed off at one end by a lithium fluoride window. The length of reaction zone can be varied by sliding the inlet tube (6 mm o.d.) in an O-ring seal. CO gas enters the main flow through four radially directed holes at the end of the inlet tube. Active nitrogen is generated by flowing nitrogen or a nitrogen–argon mixture at rates between 8 and 9 m s^{-1} and at pressures between 2 and 6 Torr (1 Torr≈133.322 Pa) through a microwave discharge (2450 MHz). The N-atom densities are measured by the well-known NO-titration technique. Quenching gases, such as CO_2 and N_2O, are added from three inlet

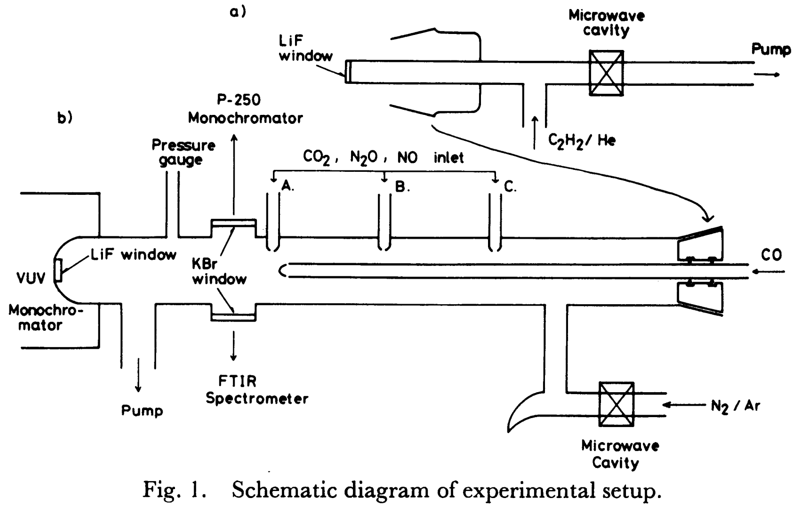

Fig. 1. Schematic diagram of experimental setup.
a) Carbon lamp. b) Discharge flow reactor.

ports, A, B, and C. The interval of each inlet port is 50 mm. In most cases, the C inlet port is used. The infrared emission spectra are measured side-on by means of a Nicolet 7199 FTIR spectrometer through a KBr window. The detector used was a liquid nitrogen cooled Hg–Cd–Te detector, which is sensitive from 800 to 4000 cm^{-1}. In the present study, in order to cut the strong thermal emission appearing below 1500 cm^{-1}, a sapphire filter (transmitting above 1600 cm^{-1}) was set in front of the detector. Therefore, the emission spectra from 1600 to 4000 cm^{-1} could be detected. The visible emission spectra were measured on another side by means of a 0.25 m monochromator (Nikon P-250, 1200 grooves/mm grating blazed at 300 nm) equipped with a photomultiplier (Hamamatsu R-636), a photon-rate meter, and a strip chart recorder. The vacuum UV emission spectra were measured at the end of the flow tube through a LiF window by means of a 0.3 m vacuum-ultraviolet monochromator (McPherson model 218) with a grating blazed at 150 nm (2400 grooves/mm), combined with a solar-blind photomultiplier (Hamamatsu R-976, MgF_2 window), which is sensitive from 115 to 320 nm.

The carbon atoms produced in the reaction of active nitrogen with CO were monitored photoelectrically through the axis of the flow tube by means of the attenuation of the carbon-atom resonance lines at 156.1 or 165.7 nm. A carbon-resonance lamp was attached at the other end of the flow tube in place of the movable inlet. In this case, CO was added from the side inlet port, B. A microwave-powered carbon-resonance lamp using a mixture of a few percent of acetylene in flowing helium was used.[11,12)]

The spectral sensitivity of the P-250 monochromator with associated photomultiplier was determined by using a calibrated tungsten lamp. The wavelength calibration of the relative sensitivity of the VUV monochromator detecting system was achieved by measuring the intensities of the Lyman bands emitted from a discharge in argon with a trace amounts of H_2O.[13)] The total and partial pressures of the gases were measured with an MKS Baratron gauge. All the measurements were done at room temperature, 298±3 K.

The gases, used without further purification, were N_2 (Nippon Sanso, 99.9995%), Ar (Nippon Sanso, 99.9995%), CO_2 (Nippon Sanso, 99.5%), N_2O (Takachiho, 99.9%), and NO (Matheson, 99.5%). The CO (Takachiho, 99.95%) was used after passing it through a hot quartz tube (800 °C) and a column packed with Molecular Sieve in order to remove any metal carbonyls.

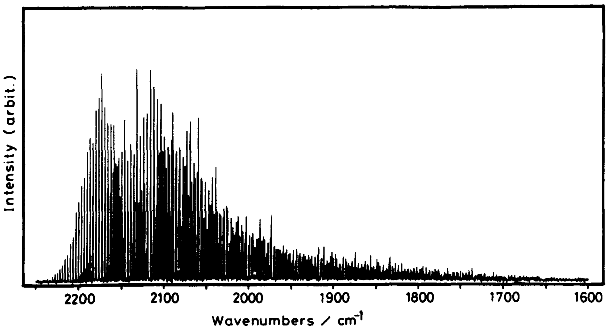

Fig. 2. High resolution (spectral resolution 0.25 cm^{-1}) infrared emission spectrum of vibrationally excited CO in the fundamental region. The spectrum was observed in the reaction of active nitrogen (microwave discharge of N_2, 2 Torr, and Ar, 2 Torr, mixture) with CO, 70 mTorr.

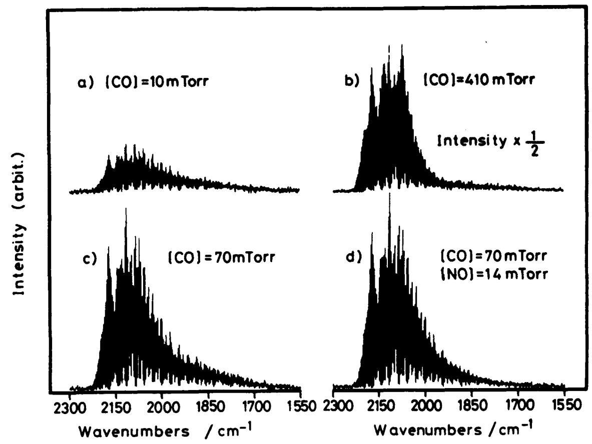

Fig. 3. Changes of the spectral distribution of the infrared emission of vibrationally excited CO by pressures of CO and the addition of NO. Active nitrogen was produced in the microwave discharge of N_2 (2 Torr) and Ar (2 Torr) mixture ([N]=4.2 mTorr). Spectral resolution is 1 cm^{-1}. a) 10 mTorr of CO was added. b) 410 mTorr of CO was added. Spectral intensity should be doubled. c) 70 mTorr of CO added. d) 14 mTorr of NO was added in addition to 70 mTorr of CO.

Results

A. Infrared Emission from the Vibrationally Excited CO. The high-resolution (spectral resolution 0.25 cm^{-1}) infrared emission spectrum of the vibrationally excited CO in the fundamental region is shown in Fig. 2. The spectrum was measured after 70 mTorr of CO had been added to the active nitrogen flow (4.2 Torr of total pressure) at a point 100 mm upstream from the observing point. Emissions from the vibrationally excited CO up to $v''=18$ could be observed.

The effects of the vibrational relaxation by CO and NO were also measured; they are shown in Fig. 3. Figures 3 (a) and (b) show the emission spectra when 10 and 410 mTorr, respectively, of CO were added to the active nitrogen flow. In these cases, the spectral resolution was 1 cm^{-1}. It should be clear that vibrational relaxations occur efficiently at high v'' levels. Figures 3(c) and (d) show the spectra in, respectively, the absence and presence of NO (14 mTorr) in the CO (70 mTorr)-active nitrogen flow. Relaxations can be observed very slightly in the high v'' levels. In these cases, the concentration of N atoms was 4.2 mTorr; *i.e.*, the color of the afterglow was changed from yellow (N_2 first positive-band emission due to N+N recombination) to green (NO_2 afterglow due to NO+O recombination) at the point of 4.2 mTorr NO addition. Therefore, vibrationally excited CO was still present even after all the N-atoms had been converted to O-atoms by the reaction of $N+NO \longrightarrow N_2+O$. This suggests that the formation of the vibrationally excited CO does not originate in the N-atom reaction. The integrated emission-band intensity as a function of the CO concentration is shown in Fig. 4 by solid circles. The total emission intensity increased with an increase in the CO concentration until it reaches a saturation point at about 300 mTorr of CO. The integrated-band intensity when NO was added to 70 mTorr of CO is shown by open circles in

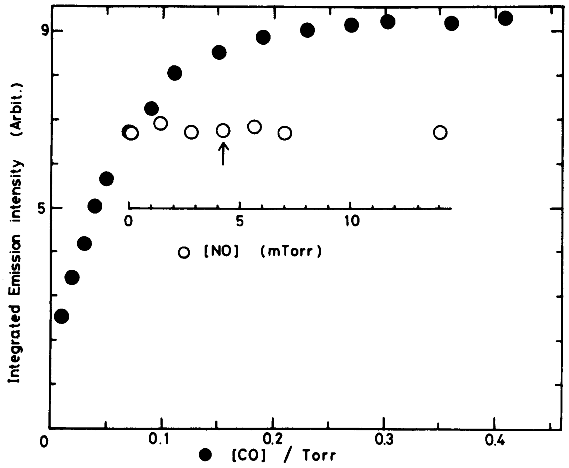

Fig. 4. Integrated intensity of infrared emission of CO as a function of the partial pressure of CO (solid circles). Intensities when NO was added in addition to 70 mTorr of CO are shown by open circles. An arrow indicates the titration point of N atoms. Active nitrogen was produced in the microwave discharge of N_2 (2 Torr) and Ar (2 Torr) mixture ([N] = 4.2 mTorr).

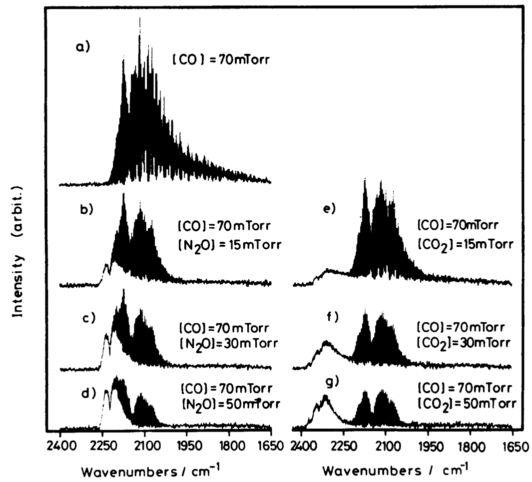

Fig. 5. Relaxation and quenching of the vibrationally excited CO by the addition of N_2O and CO_2. Spectral resolution is 1 cm^{-1}. Emissions appeared in (b)—(d) in the 2250—2100 cm^{-1} region are emissions from the vibrationally excited N_2O. Emissions appeared in (e)—(g) in the 2400—2200 cm^{-1} region are emission from the vibrationally excited CO_2. Active nitrogen was produced in the microwave discharge of N_2 (2 Torr) and Ar (2 Torr) mixture ([N] = 4.2 mTorr).

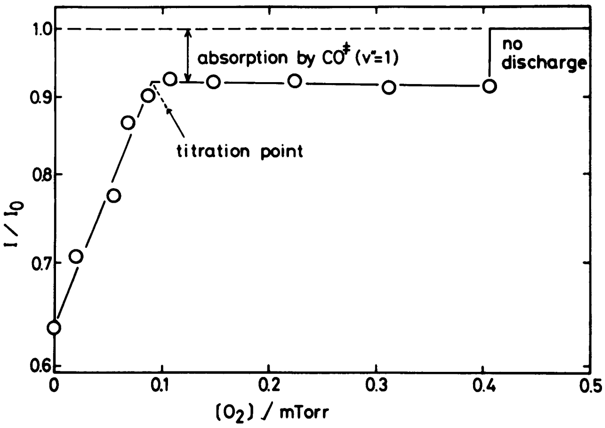

Fig. 6. Relative carbon atom absorption *versus* O_2 partial pressure (scale of ordinate is logarithmic). The 165.7 nm carbon atomic line was used to measure the resonance absorption of carbon atoms when 6 mTorr of CO was reacted with active nitrogen. "NO discharge" is the case when microwave discharge of the N_2 (2 Torr)–Ar (2 Torr) mixture was turned off.

Fig. 4. The total band intensity was not changed by the addition of NO. The arrow in Fig. 4 indicates the titration point of the nitrogen atoms.

The relaxation and quenching of the vibrationally excited CO occurred much more effectively upon the addition of N_2O and CO_2. Variations in the band profiles are shown in Fig. 5. The infrared emission bands of N_2O and CO_2 in the fundamental region appear with a decrease in the CO emission band. Further, highly vibrationally excited CO is quenched much more effectively. In both cases, when more than 150 mTorr of N_2O and CO_2 were added, the emission of CO was quenched completely, only emissions of N_2O and CO_2 remaining.

B. Visible Emission and Carbon Atoms in the CO–Active Nitrogen Mixture. When CO was added to the straw yellow Lewis–Rayleigh afterglow of active nitrogen, the color changed slightly to deep blue. This chemiluminescence resembles the so-called "blue flame" observed in the reactions of active nitrogen with hydrocarbons[14] or C_2N_2.[15] That is, emissions of CN violet ($B^2\Sigma^+ \longrightarrow X^2\Sigma^+$) and CN red ($A^2\Pi \longrightarrow X^2\Sigma^+$) bands were observed, and strong tail bands appeared in the B→X bands, with a maximum at $v'=7$ and extending up to $v'=15$, just as in the cases of hydrocarbons[14] and C_2N_2.[15]

The existence of carbon atoms was observed by means of the resonance absorption of the carbon resonance lines. As will be described below, the chemiluminescence of the fourth positive band of CO ($A^1\Pi \longrightarrow X^1\Sigma^+$) was observed. The resonance lines of the carbon lamp, 156.1 and 165.7 nm, partially coincide with the 0-2 and 1-1 bands of the fourth positive emission respectively. However, under less than 10 mTorr of CO, the emission intensity of the fourth positive band is quite weak in comparison with that of resonance lines from the carbon lamp. Vibrationally excited CO was produced in the system, as has been mentioned before. The 0-2 and 1-1 bands in the A←X transition of CO absorb the resonance lines from the carbon lamp. In order to obtain the resonance absorption only by carbon atoms, a small amount of O_2 (less than 1 mTorr) was added to the system.[12,16] The carbon atoms in the system were consumed by the reaction of $C+O_2 \rightarrow CO+O$. On the other hand, the vibrationally excited CO was not quenched by less than 1 mTorr of O_2. A typical titration of carbon atoms by O_2 at 165.7 nm is shown in Fig. 6. The absolute steady-state concentrations of carbon atoms (0.02—0.1 mTorr, depending on the CO partial pressure) were determined by means of this O_2 titration method.[12,16] The intensity of the CN violet-band emission was proportional to the carbon-atom

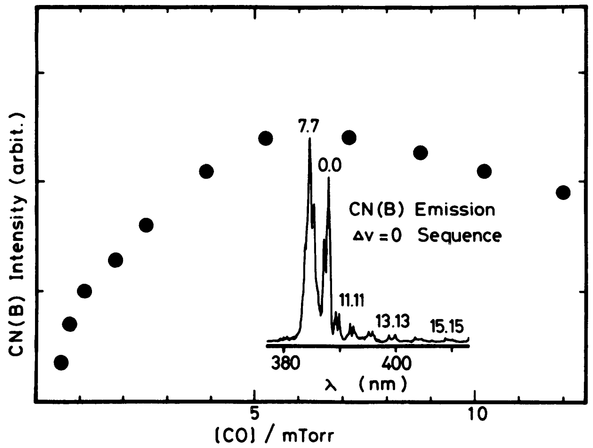

Fig. 7. Intensity of the CN violet emission band of $\Delta v=0$ sequence as a function of the pressure of CO. Spectrum shown is the CN violet emission of $\Delta v=0$ sequence. Concentration of nitrogen is constant ([N] = 4.2 mTorr).

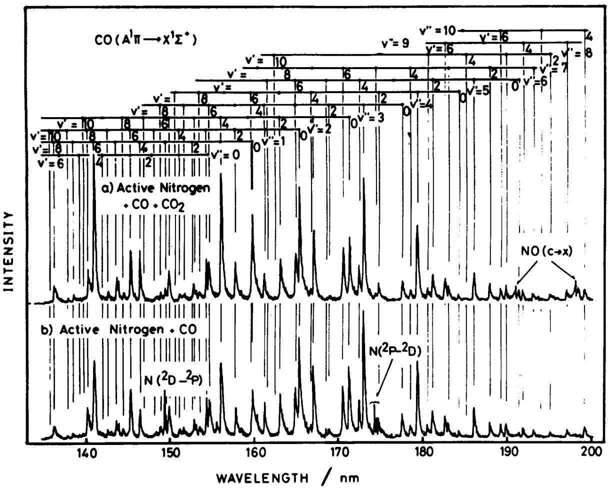

Fig. 8. Fourth positive band emission of CO observed in the reaction of active nitrogen with CO. Spectral resolution is 2 nm. Active nitrogen was produced in the microwave discharge of N_2 (3.5 Torr) and Ar (2.0 Torr) mixture ([N] = 5.7 Torr). a) [CO] = 410 mTorr and [CO_2] = 110 mTorr, b) [CO] = 410 mTorr and CO_2 is absent.

concentration; *i.e.*, the intensity of the violet emission decreased with a decrease in the carbon atoms upon the addition of O_2. These results suggest that the formation mechanism of the CN emission bands is quite similar to that proposed in the case of the "blue-flame conditions" of the active nitrogen–hydrocarbon reactions.[15,16] As will be described later, the formation mechanism of the CN emission bands proposed in the blue-flame condition is the recombination mechanism of C+N+M.

Figure 7 shows the intensity of the CN violet emission band of the $\Delta v=0$ sequence as a function of the partial pressure of CO. The intensity approaches a maximum at about 6 mTorr of CO. At 6 mTorr of CO, the intensity of the first positive-band emission of N_2 was not reduced. Therefore, it is probable that the precursor of the CN violet emission is not a nitrogen atom, but a metastable excited N_2 atom. The dependences of the CN red emission intensity and the concentration of the C atoms on the partial pressure of CO are similar to the case of the CN violet emission (Fig. 7).

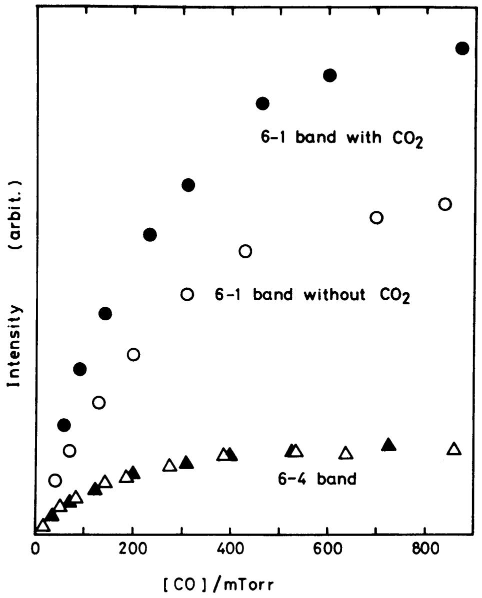

Fig. 9. $CO(A^1\Pi \rightarrow X^1\Sigma^+)$ intensities *vs.* partial pressure of CO. ●; 6-1 band in the presence of CO_2 (90 mTorr), ○; 6-1 band in the absence of CO_2, △; 6-4 band in the presence of CO_2 (90 mTorr), ▲; 6-4 band in the absence of CO_2. The condition of active nitrogen is as same as the case in Fig. 8.

C. Vacuum Ultraviolet Emission of CO. The fourth positive-band emission of CO was observed in the vacuum UV region as has been reported by Fontijn *et al.*[9] and by Golde *et al.*[10] The spectra measured are shown in Fig. 8. Figure 8(b) shows the $CO(A^1\Pi \longrightarrow X^1\Sigma^+)$ emission spectrum observed in the CO–active nitrogen system. Emission bands up to $v'=8$ were observed clearly, as was suggested by Golde *et al.*[10] In addition, very weak bands from $v'=9$ and 10 were observed in the present study. When 100 mTorr of CO_2 was added to the system, the intensities of several bands increased, as is shown in Fig. 8 (a). The increment occurred mostly in the $v''=1$ and 2 sequences. A similar result was obtained when N_2O was added to the system. Those results can be explained by the self-absorption by the vibrationally excited ground-state CO produced in the reaction of active nitrogen with CO. As is shown in Fig. 5, vibrationally excited CO was quenched by the addition of CO_2 and N_2O. The absence of any emission band in the $v''=0$ sequence is a result of the self-absorption by CO in the ground state.

The emission-intensity dependencies of the 6-1 and 6-4 bands on the partial pressure of CO are shown in Fig. 9. The open symbols in Fig. 9 show the emission intensity when CO was reacted with active nitrogen, while the solid symbols show the results when 90 mTorr of CO_2 was added to the system. It should be clear that the apparent intensity of the 6-1-band emission increased upon the addition of CO_2, while the intensity of the 6-4 band did not change when CO_2 was added. This can be explained by the fact that there was a large amount of CO in the ground electronic state populated at $v''=1$ and a lesser amount at $v''=4$. The intensity of the emission bands increased up to about 1 Torr of CO. This suggests that a precursor to produce the fourth positive emission would be different from that in the case of CN-emission bands.

The increases in the 6-1-band intensity upon the addition of CO and CO_2 are shown in Fig. 10. In this case, CO_2 was added to the 700 mTorr of CO. The emission intensity increases up to a maximum at the addition of about 90 mTorr CO_2, and after that it decreases rapidly. Probably the decrease results from the quenching of $CO(A^1\Pi)$ or a precursor by CO_2.

The atomic lines of the nitrogen atoms appearing in Fig. 8(b) might be produced by the energy transfer from N_2 in the excited state to nitrogen atoms. The emission bands of NO shown in Fig. 8(a) are produced by the reaction of CO_2 with active nitrogen.[17]

Discussion

A. Infrared Emission from the Vibrationally Excited CO. The formation of vibrationally excited ground-state N_2 in the active nitrogen produced in the discharge of nitrogen was first inferred by Evans and Winkler[18] from chemical studies. The physical evidences were reported by Kaufman and Kelso[19] by means of temperature measurements and by Dressler[20] using the vacuum-UV-absorption of N_2. Tanaka *et al.*[21] extended the vacuum-UV-absorption measurements and observed transitions originating from levels up to $v''=29$ of the ground electronic state. Vibrational-energy transfer from vibrationally excited N_2 to CO was first suggested by Legay,[5] who measures the IR emission from CO. In the present study, the finding that the intensity of the IR emission of CO did not depend on the concentration of nitrogen atoms (Figs. 3 and 4) is consistent with the energy-transfer mechanism. As is shown in Fig. 4, since vibrationally excited N_2 is not quenched by the addition of NO, the system can be used as the source of the vibrationally excited N_2 under N-atom-free conditions.

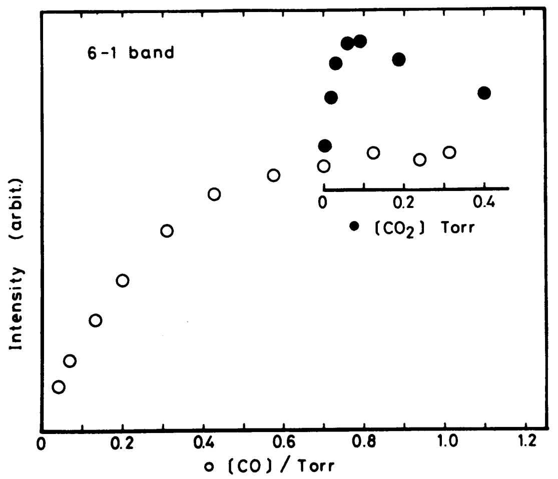

Fig. 10. ○; Increase of the 6-1 band intensity by the addition of CO and CO_2. ●; CO_2 was added to the 700 mTorr of CO. The conditions of active nitrogen are the same as the case in Fig. 8.

The rotational and vibrational temperatures of CO in the active nitrogen have been reported[5,6] to be 300—400 and 4000—8000 K respectively. It has also been reported that the rotational population[6] shows a Boltzmann distribution, while the vibrational population shows a non-Boltzmann distribution,[6,22] which coincides with a Treanor-type distribution.[23] In the present study, vibrationally excited CO up to $v''=18$ was observed.

An infrared emission due to the energy transfer from the vibrationally excited N_2 to CO_2[24] and N_2O[25] has also been reported. In the present study, emissions from CO_2 and N_2O were measured when CO_2 or N_2O was added to active nitrogen directly. Increases in the emission intensities as functions of CO_2 or N_2O were faster than in the case of CO, although the rate of self-quenching was also faster. Therefore, the decrease in the CO emission upon the addition of CO_2 or N_2O (shown in Fig. 5) results from both vibrational-energy transfer from N_2 to CO_2 or N_2O in competition with CO and the quenching of vibrationally excited CO by CO_2 or N_2O; the former process is preferable because of the excellent energy matching.

The amounts of the vibrationally excited N_2 or CO at $v''=1$ have been estimated[10,20] to be 5—10% of those at $v''=0$. In the present study, the emission intensity of the CO in the active nitrogen was compared with the infrared emission intensity of the CO produced in the $C+O_2 \rightarrow CO+O$ system[26] (O_2 was added to the active nitrogen–C_2H_2 system). From the intensity ratio of the CO–active nitrogen to the C_2H_2, O_2–active nitrogen system, the amount of the vibrationally excited CO in the CO–active nitrogen system was estimated to be 10% or more of the CO at $v''=0$. In this estimation, it was assumed that the concentration of the vibrationally excited CO was equal to the concentration of carbon atoms in the C_2H_2, O_2–active nitrogen system. The value of 10% is interesting because the yield of the singlet oxygen, $O_2^*(a^1\Delta_g)$, produced in the discharge of O_2 is also about 10% of the O_2 in the ground electronic state.

A very large amount of vibrationally excited N_2 can be produced in the discharge of N_2, and a part of it is very highly excited. The vibrational energy transfer from N_2 to other molecules occurred very efficiently. Therefore, these vibrationally excited species can play a role in the chemiluminescent reactions of active nitrogen flames, although there have been no reports that the vibrationally excited N_2 is a precursor of the chemiluminescence in the active nitrogen flames.

B. Visible Emission of $CN(A^2\Pi$ and $B^2\Sigma^+)$. The spectral distribution of the CN violet band ($B^2\Sigma^+ \longrightarrow X^2\Sigma^+$) is quite similar to that observed under blue-flame conditions in the active nitrogen–hydrocarbon system. Under the blue-flame conditions, the formation mechanism of the CN chemiluminescences has been suggested[15] to be a recombination reaction of $C+N+M$:

$$C(^3P) + N(^4S) + M \longrightarrow CN^*(C^4\Sigma^+) + M, \tag{1}$$

$$CN^*(C^4\Sigma^+) + M \longrightarrow CN^*(B^2\Sigma^+) + M, \tag{2}$$

$$CN^*(B^2\Sigma^+) \longrightarrow CN(X^2\Sigma^+) + h\nu(\text{violet band}), \tag{3}$$

$$CN^*(B^2\Sigma^+)\ M \longrightarrow CN^*(A^2\Pi) + M, \tag{4}$$

$$CN^*(A^2\Pi) \longrightarrow CN(X^2\Sigma^+)\ h\nu(\text{red band}). \tag{5}$$

The unusual intensity distribution in the vibrational structure of CN cmission bands could be explained[4,15] by the crossing of potential energy curves between $C^4\Sigma^+$ and $B^2\Sigma^+$ states.

Young and Morrow[7] have measured the CN-emission bands in the CO–active nitrogen system and proposed the following mechanism:

$$N_2^*(B^2\Pi \text{ or } W^3\Delta_u) + CO \longrightarrow CN + NO, \qquad (6)$$

$$N_2^*({}^5\Sigma_g^+) + CN \longrightarrow N_2 + CN^*(B^2\Sigma^+). \qquad (7)$$

The mechanism of Young and Morrow can, however, be refuted by the following results in the present study: 1) If NO is produced by Reaction 6, emission bands of NO (γ, β, δ) can be observed in the active nitrogen system. However, no emission band from NO was observed here; 2) the formation of carbon atoms was observed, and the intensity of the CN violet emission was proportional to the steady-state concentration of the carbon atoms, just as in the case of the blue-flame conditions of the hydrocarbon system; 3) when a small amount of O_2 was added to the system and carbon atoms were consumed by the reaction of $C+O_2 \rightarrow CO+O$, the CN emission bands disappeared; 4) as is shown in Fig. 7, the intensity of the CN violet band approaches its maximum at 6 mTorr of CO. Under 6 mTorr of CO, the first positive band emission of N_2 is little reduced, *i.e.*, N_2^*-$(B^3\Pi)$ is little quenched. Therefore, if the CN violet emission is produced by Reaction 7 subsequent to Reaction 6, the intensity maximum of CN emission should appear at a much larger amount of CO; 5) the potential energy curve of $N_2^*({}^5\Sigma_g^+)$[27] is nearly repulsive. It is, then, very unlikely that the $N_2^*({}^5\Sigma_g^+)$ is a precursor of the CN emission; 6) the unusual spectral distribution of the CN violet band can not be explained by the energy-transfer mechanism.

It was found that the purification of CO is very important in the present study. Usually, the CO gas in the cylinder contains a large amount of metal carbonyls. In the present study, as has been mentioned in the Experimental section, the CO was purified carefully. When CO was used without purification, the pink orange flame[15] appeared stronger than the blue flame, and the 0-0 band was much stronger than the 7-7 band in the CN violet system. These phenomena probably resulted from the reaction of metal carbonyls with active nitrogen. In the previous work by Young and Morrow, the procedure of the purification was not described.

The formation mechanism of carbon atoms in the CO–active nitrogen system can not be determined directly. The most probable mechanism is, however, the energy-transfer process from the metastable $N_2^*(A^3\Sigma_u^+)$, which can be produced by the recombination of nitrogen atoms:

$$N + N + M \longrightarrow N_2^*(A^3\Sigma_u^+), \qquad (8)$$

$$N_2^*(A^3\Sigma_u^+) + CO \longrightarrow CO^*(a^3\Pi) + N_2, \qquad (9)$$

$$CO^*(a^3\Pi) + CO \longrightarrow C(^3P) + CO_2. \qquad (10)$$

Carbon atoms are reproduced by Reaction 11 subsequent to Reactions 3 and 5:

$$CN + N \longrightarrow C + N_2. \qquad (11)$$

The energy-transfer process in Reaction 9 is known[28] to occur very efficiently. The quenching of $CO^*(a^3\Pi)$ by $CO(X^1\Sigma^+)$ has been suggested[29,30] to occur by means of Reaction 10, which is exoergic by $\simeq 8$ kcal/mol (1 cal $=4.814$ J). However, no direct experimental verification of Reaction 10. has been made. If the carbon atoms are produced by Reaction 10, the intensity of the CN emission should be proportional to $[CO]^2$. However, as is shown in Fig. 7, the CN emission intensity is not proportional to $[CO]^2$. Another possible process is that the $CO^*(a^3\Pi)$ reacts with the highly vibrationally excited CO more rapidly:

$$CO^*(a^3\Pi) + CO^*(\text{high } v'') \longrightarrow C + CO_2. \qquad (12)$$

The concentration of high v'' states might approach their maximum concentration under a low CO concentration, and after that, $[CO^*(\text{high } v'')]$ might be in its steady-state concentration because of the competition with the quenching processes. Therefore, if Reaction 12 occurs only in the very high v'' states, the carbon atoms formed (the intensity of CN emission) is proportional to the concentration of CO. Also, if there is a deactivation process such as Reaction 13, the dependence of the CN emission intensity on the CO concentration shown in Fig. 7 can be understood:

$$CO^*(a^3\Pi) + CO \longrightarrow CO + CO \qquad (13)$$

When several mTorr of CO_2 were added to the system, the CN emission was reduced efficiently. Since the rate of the reaction of carbon atoms with CO_2 has been reported[31] to be very slow, slower than 10^{-15} cm^3 molecule^{-1} s^{-1}, the reduction of the CN emission does not result from the consumption of carbon atoms. The rate of the quenching of $N_2^*(A^3\Sigma_u^+)$ by CO_2 has been reported[28] to be slow, about 5500 times slower than CO. The quenching rate of $CO^*(a^3\Pi)$ by CO_2[32] is 20 times slower than CO. Probably, then, the reduction of CN emission is caused by the quenching of highly excited CO by the addition of CO_2; Reaction 12 is proposed as the source of the carbon atoms.

C. Vacuum Ultraviolet Emission of CO. Since the absolute transition probability of each transition in the fourth positive band of CO has been reported,[33] the

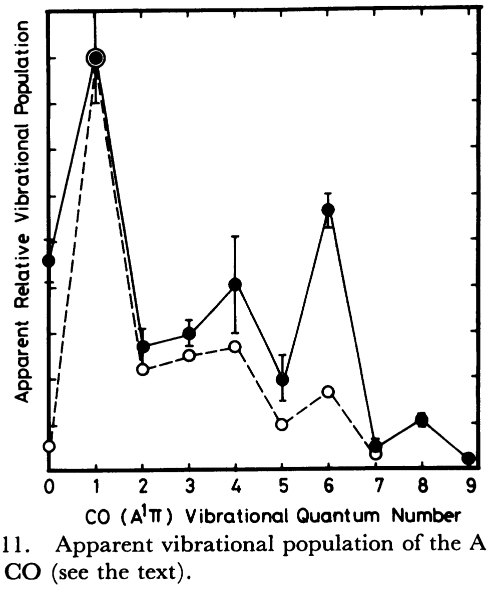

Fig. 11. Apparent vibrational population of the A¹ state of CO (see the text).

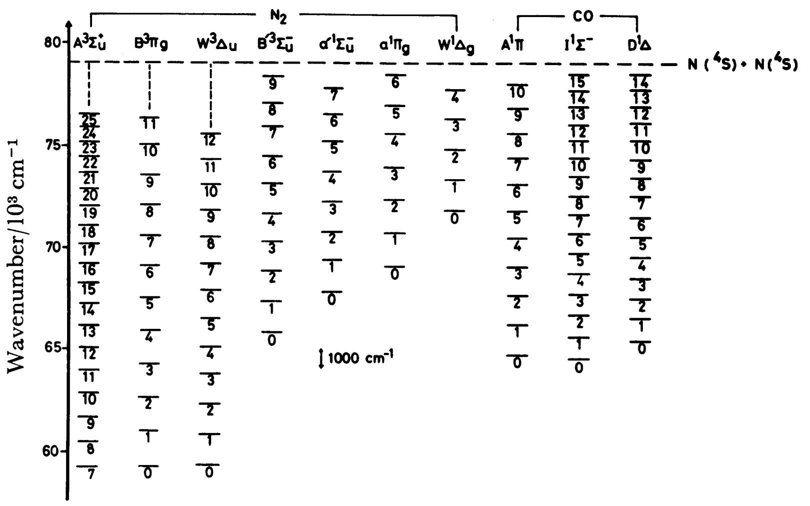

Fig. 12. Energy level diagram for electronically excited N_2 and CO. The energy of $N(^4S)+N(^4S)$ is 79030.4 cm^{-1}.

apparent vibrational population of the $A^1\Pi$ state of CO was calculated from the emission intensity of each band shown in Fig. 8(a). The results are shown in Fig. 11 by solid circles, which are the averages of several transitions. The error bars show the scattering of values. The results show that the widely separated $v'=1$ and $v'=6$ are formed most rapidly, as has previously been reported by Golde and Thrush.[10] In order to explain this mode of formation, they suggested an indirect energy transfer involving the collisional crossing from another excited state of CO, such as:

$$N + N + M \longrightarrow N_2^*(a^1\Pi_g) + M, \qquad (14)$$

$$N_2^*(a^1\Pi_g) + CO \longrightarrow CO^*(I^1\Sigma^-) + N^2, \qquad (15)$$

$$CO^*(I^1\Sigma^-) + M \longrightarrow CO^*(A^1\Pi) + M, \qquad (16)$$

in addition to the direct energy-transfer process:

$$N_2^*(a^1\Pi_g) + CO \longrightarrow CO^*(A^1\Pi) + N_2. \qquad (17)$$

Since the levels $CO^*(I^1\Sigma^-)$, $v'=2$, and $v'=9$, are perturbed by $CO^*(A^1\Pi)$, $v'=1$, and $v'=6$ respectively,[34] Golde and Thrush proposed the $CO(I^1\Sigma^-)$ rather than $CO(D^1\Delta)$ as a dominant precursor. Further, for the population of low levels of $CO(A^1\Pi)$, they suggested energy transfer from $N_2^*(a'^1\Sigma_u^-)$ to CO:

$$N_2^*(a'^1\Sigma^-) + CO \longrightarrow CO^*(A^1\Pi) + N_2. \qquad (18)$$

An energy-level diagram for electronically excited N_2 and CO in which energy transfer can occur is shown in Fig. 12. The diagram is based on the molecular constants for N_2[27] and CO[35,36] previously reported. Since the energy of $N(^4S)+N(^4S)$ is 225.958 kcal/mol, *i.e.*, 79030.4 cm^{-1},[37] $CO^*(A^1\Pi)$ can populate energetically up to $v'=10$ if it is formed by the energy transfer from N_2^*.

The population shown in Fig. 11 by solid circles does not include the effects of quenching and relaxation processes in the $CO^*(A^1\Pi)$ state. The quenching cross-sections of $CO(A^1\Pi)$ by several gases previously reported[38,39] are very large (3.3 and 44 Å^2 for Ar and N_2 respectively at low v' levels, and 200, 80, and 120 Å^2 for CO, N_2, and CO_2 respectively at $v'=13$). Under the present experimental conditions (with a total pressure of about 6 Torr), the quenching process is competitive enough with the emission processes, although the radiative lifetime of the $A^1\Pi \rightarrow X^1\Sigma^+$ transition of CO is very short ($\approx$10 ns).[40] The quenching cross-sections of $CO^*(A^1\Pi)$ in individual vibrational levles ($v'=0$—8) have been reported[41] only in cases of rare gases. The quenching cross-section by rare gas is largest at $v'=1$ and smallest at $v'=0$ and 6. Since there have been no reports on quenching cross-sections by N_2, CO, and CO_2 in individual vibrational levels, the populations shown in Fig. 11 by solid circles were multiplied by the relative quenching cross-section by Ar at the individual vibrational levels and normalized at $v'=1$. The results are shown by open circles in Fig. 11. The population at $v'=6$ decreased, and the population became centered at $v'=1$. Of course, the above treatment is not correct. Correction should be done using the values of N_2, CO, and CO_2; in addition, the effect of vibrational relaxation should be considered. However, the results suggest that the formation of $CO(A^1\Pi)$ might be explained by direct-energy transfer from the excited state of N_2, Reactions 17 and 18, without a precursor of $CO^*(I^1\Sigma^-)$. The high population at $v'=1$ in $CO^*(A^1\Pi)$ may be explained by the energy transfer from $N_2^*(a'^1\Sigma_u^-)$ at $v'=0$, Reaction 18. Concerning the $a'^1\Sigma_u^-$ state of N_2 in the active nitrogen, it has been reported[42] that no emission band except that from the $v'=0$ level was observed in the $N_2(a'^1\Sigma_u^- \longrightarrow X^1\Sigma_g^+)$ system, although emissions from the $v'=0$—6 levels were observed in the $a^1\Pi_g \rightarrow X^1\Sigma_g^+$ system.[42,43]

References

1) A. N. Wright and C. A. Winkler, "Active Nitrogen," Academic Press, New York (1968).

2) D. R. Safrany, *Prog. React. Kinet.*, **6**, 1 (1971).

3) M. F. Golde and B. A. Thrush, *Rep. Prog. Phys.*, **36**, 1285 (1973).

4) M. R. Gorbal and M. I. Savadatti, *Chem. Rev.*, **82**, 527 (1982).

5) a) F. Legay, *J. Phys.* (*Paris*), **25**, 999 (1964); b) F. Legay, *J. Chem. Phys.*, **64**, 9 (1967); c) J. P. Kennealy, A. T. Stair, Jr., and M. H. Bruce, *ibid.*, **64**, 43 (1967); d) A. T. Stair, Jr., J. P. Kennealy, and R. E. Murphy, *ibid.*, **64**, 52 (1967).

6) N. Legay-Sommaire and F. Legay, *Can. J. Phys.*, **48**, 1966 (1970).

7) R. A. Young and W. Morrow, *J. Chem. Phys.*, **60**, 1005 (1974).

8) H. P. Knauss, *Phys. Rev.*, **32**, 417 (1928).

9) A. Fontijn and R. Ellison, *J. Chem. Phys.*, **54**, 3649 (1971).

10) M. F. Golde and B. A. Thrush, *Proc. R. Soc. London, Ser. A*, **330**, 97, 109 (1972).

11) a) D. D. Davis and W. Braun, *Appl. Opt.*, **7**, 2074 (1968); b) N. Washida, H. Akimoto, and I. Tanaka, *ibid.*, **9**, 1711 (1970).

12) D. Kley, N. Washida, K. H. Becker, and W. Groth, *Z. Phys. Chem. Neue Folge*, **82**, 109 (1972).

13) K. H. Becker, E. H. Fink, and A. C. Allison, *J. Opt. Soc. Am.*, **61**, 495 (1971).

14) T. Iwai, M. I. Savadatti, and H. P. Broida, *J. Chem. Phys.*, **38**, 644 (1963).

15) N. Washida, D. Kley, K. H. Becker, and W. Groth, *J. Chem. Phys.*, **63**, 4230 (1975).

16) D. Kley, N. Washida, K. H. Becker, and W. Groth, *Chem. Phys. Lett.*, **15**, 45 (1972).

17) I. M. Campbell and B. A. Thrush, *Trans. Faraday Soc.*, **62**, 3366 (1966).

18) H. G. V. Evans and C. A. Winkler, *Can. J. Chem.*, **34**, 1217 (1956).

19) F. Kaufman and J. R. Kelso, *J. Chem. Phys.*, **28**, 510 (1958).

20) K. Dressler, *J. Chem. Phys.*, **30**, 1621 (1959).

21) Y. Tanaka, F. R. Innes, A. S. Jursa, and M. Nakamura, *J. Chem. Phys.*, **42**, 1183 (1965).

22) a) C. A. Brau, G. E. Caledonia, and R. E. Center, *J. Chem. Phys.*, **52**, 4306 (1970); b) K. R. Horn and P. E. Oettinger, *ibid.*, **54**, 3040 (1971).

23) a) G. E. Caledonia and R. E. Center, *J. Chem. Phys.*, **55**, 552 (1971); b) J. Anketell and B. Brocklehurst, *J. Phys. B: Atom. Molec. Phys.*, **7**, 1937 (1974).

24) a) C. K. N. Patel, *Phys. Rev. Lett.*, **13**, 617 (1964); b) E. L. Milne, M. Steinberg, and H. P. Broida, *J. Chem. Phys.*, **42**, 2615 (1965); c) T. K. McCubbin, Jr., and Y. H. Hahn, *J. Opt. Soc. Am.*, **57**, 1373 (1967).

25) C. Alamichel and A. Piard-Bersellini, *Chem. Phys.*, **35**, 381 (1978).

26) E. A. Ogryzlo, J. P. Reilly, and B. A. Thrush, *Chem. Phys. Lett.*, **23**, 37 (1973).

27) A. Lofthus and P. H. Krupenie, *J. Phys. Chem. Ref. Data*, **6**, 113 (1977).

28) J. W. Dreyer, D. Perner, and C. R. Roy, *J. Chem. Phys.*, **61**, 3164 (1974).

29) G. Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand, New York (1950), Vol. I, p. 478.

30) T. G. Slanger and G. Black, *J. Chem. Phys.*, **55**, 2164 (1971).

31) D. Husain and A. N. Young, *J. Chem. Soc., Faraday Trans. 2*, **71**, 525 (1975).

32) G. W. Taylor and D. W. Setser, *J. Chem. Phys.*, **58**, 4840 (1973).

33) J. M. Mumma, E. J. Stone, and E. C. Zipf, *J. Chem. Phys.*, **54**, 2627 (1971).

34) a) G. Herzberg, J. D. Simmons, A. M. Bass, and S. G. Tilford, *Can. J. Phys.*, **44**, 3039 (1966); b) J. D. Simmons and S. G. Tilford, *J. Res. Natl. Bur. Stand., Sect. A*, **75**, No. 5, 455 (1971).

35) P. H. Krupenie, "The Band Spectrum of Carbon Monoxide," Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U. S.), 5 (1966).

36) S. G. Tilford and J. D. Simmons, *J. Phys. Chem. Ref. Data*, **1**, 147 (1972).

37) D. R. Stull and H. Prophet, Project Directors, "JANAF Thermochemical Tables," 2nd ed, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U. S.), 37 (1971).

38) F. J. Comes and E. H. Fink, *Chem. Phys. Lett.*, **14**, 433 (1972).

39) A. C. Vikis, *J. Chem. Phys.*, **69**, 703 (1978).

40) R. E. Imhof and F. H. Read, *Chem. Phys. Lett.*, **11**, 326 (1971).

41) E. H. Fink and F. J. Comes, *Chem. Phys. Lett.*, **25**, 190 (1974).

42) M. F. Golde and B. A. Thrush, *Proc. R. Soc. London, Ser. A*, **330**, 79 (1972).

43) a) K. H. Becker, E. H. Fink, W. Groth, W. Jud, and D. Kley, *Faraday Discuss. Chem. Soc.*, **53**, 35 (1972); b) M. F. Golde and B. A. Thrush, *ibid.*, **53**, 52 (1972).