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# Chemiluminescent and Other Processes Leading to the Excitation of CN

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## Contents

## I. Introduction

CN was one of the earliest diatomic molecules whose spectra have been exhaustively studied since the days of Kayser (1910). It has also been one of the few diatomic molecules to be detected in carbon type stars and comets. Since these early days CN has been reported in many studies of combustion, flames, electric discharges, chemical reactions in the gas phase, upper atmosphere, astral bodies, and other sources. Investigations of its spectrum both in emission and absorption have led to the observation of seven excited electronic states and have helped to provide some understanding of the chemical reactions taking place in these diverse sources. In addition, perturbations and rather unique disposition of potential energy curves of the various electronic states have made many interesting experiments possible and hence attracted a large number of workers, who have made significant contributions to the knowledge of CN and the processes leading to its formation and excitation. Studies of $N_2$ afterglow and its reactions with organic and inorganic molecules have been surveyed by Wright and Winkler in 1968 where CN excitation in atomic nitrogen flames has been incidently and briefly surveyed. Considerable work on CN excitation in atomic flames has been done after 1968. The material is scattered, and the study of these atomic flames has led to data on CN with conflicting inferences on mechanisms of excitation that need to be sorted out. With this background a review of CN excitation in various sources is expected to lead to a systematization of the available information and to

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TABLE I. Wavelength Region, Sources of Excitation and Observed Transitions

| transitions | wavelength range, Å | sources of excitation | ref |
|---|---|---|---|
| $A^2\Pi \rightarrow X^2\Sigma^+$ (red system)[a] | 16000-4370 | carbon arcs, discharges, flames, furnace, etc., and astral sources | 1-8, 19, 26-29, 32, 45, 59-61, 65-67, 74, 87, 92-95, 98-100, 110, 145-154, 160 |
| $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ (violet system)[a,b] | 4600-3440 | | |
| $B^2\Sigma^+ \rightarrow A^2\Pi$ | 5000-4000 | active nitrogen flames | 11, 87, 100 |
| $D^2\Pi \rightarrow A^2\Pi$ | 3000-2200 | discharge through He + $C_2N_2$ | 9 |
| | | argon metstable atoms + cyanides | 22 |
| $D^2\Pi \rightarrow X^2\Sigma^+$ | 2880-2737 | | |
| $H^2\Pi \rightarrow B^2\Sigma^+$ | 3025-2843 | discharge through He + $C_2N_2$ | 9, 159 |
| $G^2\Pi \rightarrow B^2\Sigma^+$[c] | 2025-1950 | | |
| $F^2\Delta \rightarrow A^2\Pi$ | 2383-2048 | discharge through He + $C_2N_2$ | 9, 14, 159 |
| | | discharge through $CH_3CN$ | 16 |
| | | active nitrogen flame of $C_2F_4$ | 24 |
| | | argon metstable atom + cyanides | 22 |
| $J^2\Delta \rightarrow A^2\Pi$ | 1800-1700 | discharge through He + $C_2N_2$ | 10 |
| $E^2\Sigma^+ \rightarrow A^2\Pi$ | 2250-1875 | discharge through He + $C_2N_2$ | 10, 14 |
| | | active nitrogen flame of $C_2F_4$ | 24 |
| | | Ar metstable atom + cyanides | 22 |
| $E^2\Sigma^+ \rightleftarrows X^2\Sigma^+$ | 2050-1600 | discharge through He + $C_2N_2$ | 10 |
| | | active nitrogen flame of $C_2F_4$ | 24 |
| | | Ar metastable atom + cyanides | 22 |
| | 1820-1490 | flashphotolysis | 13 |

[a] Commonly observed bands. [b] Tail bands are present. [c] Tentative assignment of Lutz in ref 13.

delineate areas for fruitful investigation.

## *II. Molecular Parameters of CN*

In this section basic information on the CN molecule is compiled to provide a background for understanding results on CN chemiluminescence.

### A. Electronic States and Transitions

Eight low-lying bound doublet states have been identified[9,10,13,15] for CN and a ninth one ($G^2\Pi$) has been tentatively proposed.[13] The $^4\Sigma^+$ has been identified through perturbation.[23,137,183] No Rydberg states have been observed. Simple molecular orbital configurations are correlated to the known electronic states as indicated:

(1) $4\sigma^2 5\sigma\ 1\pi^4$ $X^2\Sigma^+$
(2) $4\sigma^2 5\sigma^2\ 1\pi^3$ $A^2\Pi$
(3) $4\sigma 5\sigma^2\ 1\pi^4$ $B^2\Sigma^+$
(4) $4\sigma^2\ 1\pi^4 2\pi$ $D^2\Pi$
(5) $4\sigma^2 5\sigma\ 1\pi^3 2\pi$ $E^4E^+$, $F^2\Delta$, $J^2\Delta$, $\Sigma^+$
(6) $4\sigma^2 5\sigma^2\ 1\pi^2 2\pi$ $H^2\Pi$, $G^2\Pi$

Wavelength region and sources for the observed transitions along with references are collected in Table I. Configurations 5 and 6 produce $^4\Sigma^+$, $^4\Sigma^-$, $^4\Delta$, and $^4\Pi$ and sextet states in addition to doublets. Ab initio configuration interaction calculations by Heil and Schaefer[15,97] for $X^2\Sigma^+$, $B^2\Sigma^+$, $^4\Sigma^+$, $^4\Pi$, $^4\Delta$, $^4\Sigma^-$, $E^2\Sigma^+$ states predict $^4\Sigma^+$, $^4\Pi$, $^4\Delta$, and $^4\Sigma^-$ to be the third, fourth, fifth, and sixth bound excited states of CN molecule. This calculation is based on a CN dissociation energy of 6.178 eV, which is about 30% lower than the experimental $D_e$. Thus these calculations typically account for 70% of $D_e$. This point has been stressed by Washida et al.;[20] they made use of it by increasing $D_e$ values of $^4\Sigma^+$, $^4\Pi$, and other states by 30%. This makes $^4\Pi$ and other states repulsive and allows $^4\Sigma^+$ to possess the right kind of energy to explain the population maximum of $B^2\Sigma^+$ state at $v = 7$. However, other experiments[87] indicate that this is a fortuitous coincidence, and hence raising $D_e$ arbitrarily by 30% for $^4\Sigma^+$ is not quite reasonable (see section IIIC).

Potential energy diagrams given by Heil and Schaefer are based on a $D_e$ value of 6.178 eV and produce lower values of $D_e$ for other states. Furthermore, some states show potential maxima that are not experimentally observed. Washida et al.[20] have compiled potential energy curves by using the data of Fallon et al.[18] based on RKR for $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, $D^2\Pi$, and $J^2\Delta$ states, and the data of Lutz[13] for $E^2\Sigma^+$, $F^2\Delta$ (Morse potential function) and $G^2\Pi$, $H^2\Pi$ (purely schematic) states, and the data of Heil and Schaefer for a quartet and higher multiplicity states after increasing their $D_e$ by 30% and keeping CN, $D_e$ = 7.89 eV. Therefore, these curves (reproduced in Figure 1 for reference in later sections) are the most acceptable at present with the limitations indicated above and represent the most up to date.

The most commonly observed transitions are the $A^2\Pi \rightarrow X^2\Sigma^+$ (red) and the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ (violet) systems. The red bands extend over the wavelength region 12000–4000 Å and over $v'v''$ values up to 24. These bands are all degraded to red. The violet bands extend over wavelength region of 5000–3000 Å and over $v'v''$ values of up to 20. These bands up to $v' = 6$ show degradation to violet and $v'$ values greater than 6 give bands degraded to red; these are known as tail bands.

A large number of these bands have been analyzed and the molecular constants have been compiled by Herzberg,[25] Kikuchi et al.,[72] Rosen,[30] Brocklehurst,[31] Barrow,[136] and Suchard.[172] The last being the latest of the compilations; it gives a brief summary of investigations and bibliography (not exhaustive) on CN up to 1973. However, Rosen's compilations are quite exhaustive prior to 1970.

Mention should be made of the Berkeley Atlas on CN (bands with $v' = 0$–8 and $v'' = 0$–12, 15) by Phillips[32] in 1963 for CN red bands and the recent Fourier transform spectral analysis by Cerny et al.[131] of $v' = 0$–4 to $v'' = 0$–4 bands. The first one provides an exhaustive listing of rotational lines and the latter provides molecular constants of improved accuracy. Kotlar et al.[184] have made a complete evaluation of all the available spectroscopic data on CN (A → X) bands and reanalyzed the data of Phillips and of Cerny et al. taking into

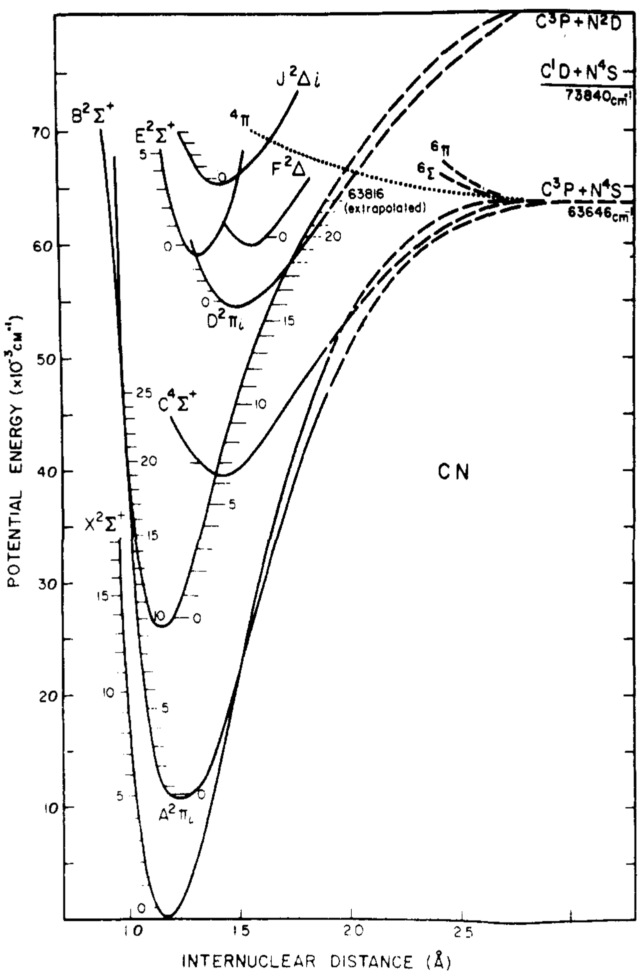

**Figure** 1. Potential energy curves for the CN molecule.

account A → X and B → X perturbations; they report molecular constants for a large number of bands. Schoonveld and Sundaram[192] have analyzed six bands ($v' = 5$–11, $v'' = 7$–12) of the CN, B → X system and revised the molecular constants for these levels only. Rotational spectra of 4–6 and 5–7 bands for high $J$ values has been reported by us[200] in a study of reactions of pink afterglow of nitrogen.

## B. Perturbations

The $B^2\Sigma^+$–$X^2\Sigma^+$ system shows a large number of perturbations. These perturbations are mainly in the B state and are due to mixing of the A state.[10,94] The most investigated perturbation is between $A^2\Pi$ ($v = 10$) and $B^2\Sigma^+$ ($v = 0$) states at $K = 4$, 7, 11, and 15, with weak perturbations at $K = 6$, 8, 14, and 16.[49] In addition to the λ shift the perturbed lines show enhanced intensities and extra lines appear in active nitrogen flames[51,52,57,70] at low pressure. There is a simultaneous decrease in the intensity of corresponding lines of the bands from $A^2\Pi$ ($v = 10$).[52,70] This fact has been ingeniously employed by Broida and his group[43,49,62,71,88,90] in establishing that the CN $B^2\Sigma^+$ ($v = 0$) is mainly formed via $A^2\Pi$ ($v = 10$) in these sources. These intensity anomalies have also been used for the determination of rotational perturbation parameters[88] and for the study of collisional relaxation and lifetime determinations.[43]

The other perturbations reported are (i) in $B^2\Sigma^+$, $v = 5$, by $A^2\Pi$, $v = 17$,[29] and (ii) in $B^2\Sigma^+$, $v = 10$, 11, 12, 13, and 14.[58] The perturbation at $v = 11$ observed recently as enhanced intensity of $K' = 20$ line with no λ shift in a reaction of Ar metastables with hydrocarbons has been attributed to a $^4\Sigma^+$ state.[23] This has been confirmed by Miller et al.[137] by anticrossing spectroscopy. They have observed anticrossings for N ranging from 13 to 30 and have established the state to be $^4\Sigma^+$ with internuclear distance of 1.4213 Å. The $^4\Sigma^+$ state has been detected not only in reactions with Ar metastables but also in reactions with active nitrogen by Cook et al.;[183] the excess population of the $^4\Sigma^+$ state for each system such as Ar/BrCN, N/BrCN, and N/$C_2H_2$ has been measured by using anticrossing spectroscopy. This study has revealed the existence of CN $^4\Sigma^+$ in excess of steady state, and this fact has to be taken into account in formulating mechanisms or path ways for excitation of CN. Also the enhanced intensity of $K' = 20$ line without the λ shift has been skillfully employed as a probe in the study of collision-induced rotational relaxation[91] in CN $B^2\Sigma^+$ by Duewer et al., who have inferred that multiquantum transitions are the rule rather than the exception. The perturbations in $v = 10$, 12, 13, and 14 of the B state are attributed to the $A^2\Pi$ state[58] but are not established with certainty because of the differing character of the perturbations and the response of perturbed lines to change in pressure: bands from $v = 10$ show doubling of lines,[54] bands from $v = 12$ show doubling of lines with enhanced intensity for $K' = 16$ and 18,[58] and bands from $v = 13$ show a line enhancement at $K' = 9$ indicating perturbation.[54] Extra lines and intensity enhancement for 12–12 ($K' = 16$, 18) and 13–13 ($K' = 9$) are reported.[186] Intensity of perturbed line when compared with envelope is found to decrease with increasing pressure for 12–12 whereas for 13–13 it is found to increase;[188] bands with $v' = 14$ show intensity anomalies[91] (reduction of intensity compared to envelope) at $K' = 7$ and 10.

The $X^2\Sigma^+$ ($v = 11$, 12) perturbs $A^2\Pi$ ($v = 7$, $J = 13.5$, 22.5, 24.5 and $v = 8$, $J = 11.5$).[64,68,69,157] Extra lines have been observed in 7–2 and 7–3 bands of the red system for $Q_1$ (12.5) and $Q_2$ (13.5). The intensity ratios of extra and main lines were of the order of 0.2 with no pressure dependence.[49] For other perturbed lines extra lines were not resolved and the perturbed lines were generally of lower intensity compared to envelope with no pressure dependence, indicating possibly a leakage to the X state.

## C. Dissociation Energy

There has been some uncertainty over the dissociation energy of the CN ground state. It has not been determined by accurate spectroscopic methods since no predissociations are known.[13] Gaydon[34] in 1968 reviewed the available data and he favored a value of 7.75 eV. Recently Arnold and Nicholls[46] have reviewed dissociation energy determinations. Significant determinations covered in their review along with later determinations by Lutz[13] and Engleman and Rouse[37] are collected in Table II. Arnold and Nicholls[46] favor 7.89 ± 0.13 eV which is quite reasonable.

Engleman and Rouse[37] in 1975 tried to fix the value of the dissociation energy by using high-temperature CN emission. Their value of 7.66 ± 0.05 eV based on the accepted average value of $f_v$ of 0.033 is lower and is likely to be less dependable in view of the insensitivity of $D_e$ to changes in $f_v$.

TABLE II. Measured CN Dissociation Energies

| ref, date | $D_0$(CN), eV | method |
|---|---|---|
| Engleman and Rouse,[37] 1975 | 7.66 ± 0.05 | heat of formation of CN |
| Arnold and Nicholls,[46] 1973 | 7.89 ± 0.13 | shock-tube measurements |
| Lutz,[13] 1970 | 7.85 | vibrational levels convergence limit |
| Levitt and Parsons,[36] 1969 | 7.8 ± 0.2 | shock-tube measurements |
| Berkowitz et al.,[33] 1969 | 7.65 ± 0.09 | photoionization of HCN |
| Davis and Okabe,[38] 1968 | 7.87 ± 0.04 | photodissociation of $C_2N_2$ and cyanogen halides |
| Setser and Stedman,[41] 1968 | 7.89 | CN excitation with Ar* |
| LeBlanc,[12] 1968 | ⩽8.0 | Birge-Sponer extrapolation |
| Tsang et al.,[194] 1962 | 7.9 ± 0.25 | shock-tube absorption |
| Douglas and Routly,[9] 1955 | $8.2 \pm {}^{+0.2}_{-1.25}$ | vibrational analysis of $X^2\Sigma^+$ |
| Brewer et al.,[75] 1951 | 8.14 ± 0.3 | variation of CN (0-1) emission with temperature |

## D. Transition Probabilities

Franck–Condon factors for *red system* have been calculated by Fraser et al.,[119] Nicholls et al.,[182] Nicholls,[122] Wyller,[120] and Spindler[121] using Morse, Hulburt–Hirschfelder, and RKR potential functions. Brocklehurst et al.[31] have presented Franck–Condon factors and *r*-centroids of Jarmain[125] and of McCallum and Nicholls[154] (Klein–Dunham potential) in tabular form. Similarly, Franck–Condon factors have also been tabulated by Wyller and Spindler and *r*-centroids were tabulated by Wyller and Katti and Sharma.[124] Refinement in these values is much ahead of the accuracy obtainable in experimental determination of intensities.

Dixon and Nicholls[56] have measured integrated band intensities and used them along with Franck–Condon factors, calculated on the basis of Morse potentials,[119] to find electronic transition moments as functions of *r*-centroid as

$$R_e(r) = \text{constant}(1.044 + 0.174r) \qquad (1)$$

$$\text{for } 1.04\ \text{Å} \le r \le 1.27\ \text{Å}$$

Jeunehomme[44] measured radiative lifetimes $\tau_v$ for the vibrational levels of the $A^2\Pi$ state and obtained

$$R_e(r) = R_e(\bar r_{00})[1 + \alpha(r - \bar r_{00})] \qquad (2)$$

where $\alpha = 1.9 \pm 0.2$ Å$^{-1}$ and $r_{00}$ is the centroid of the (0,0) band. Lambert[198] has derived relative band oscillator strength from equivalent width measurements of CN lines from solar spectrum for nine bands. He finds $\alpha$ to be 1.6 ± 0.2 Å$^{-1}$ for RKR potentials. Even then the divergence between the two results is high. Jain[73] has reexamined his data and finds

$$R_e(r) = \text{constant}(1 + 0.7318\ r) \qquad (3)$$

$$\text{for } 1.08\ \text{Å} \le r \le 1.21\ \text{Å}$$

He has also used the rescaling procedure described by Nicholls by adopting the intensity data of Dixon and Nicholls and LeBlanc and reports the following relationships

$$R_e(r) = \text{constant}(1 + 0.5717r) \qquad (4)$$

$$\text{for } 1.05\ \text{Å} \le r \le 1.27\ \text{Å}$$

$$R_e(r) = \text{constant}(1 + 3.46r) \qquad (5)$$

$$\text{for } 0.97\ \text{Å} \le r \le 1.10\ \text{Å}$$

He argues that relation 5 is spurious because of the scatter of points in the plot of $(I_{v'v''}/\nu^4_{v'v''}q_{v'v''})^{1/2}$ vs. $\bar r_{v'v''}$. This scatter has been interpreted to mean that $R_e(r)$ does not vary significantly with $r$[31,114,123] and that the relationships 3 and 4 are consistent and satisfactory within experimental errors. Dismissing the relationship 5 as spurious may be not entirely satisfactory in view of the fact that the intensity measurements of LeBlanc extend over many bands in comparison with other measurements. So it is desirable to have better intensity data for a large number of bands before finally accepting any relationship.

Franck–Condon factors for the *violet system* were calculated by Fraser et al.[119] and Tawde[86] using Morse potential function, by Spindler[121] using RKR potential function, and by Liszt and Hesser[39] using radiative lifetime. Values of Franck–Condon factors and *r*-centroids have been tabulated by Kikuchi et al.[72] for the main and tail bands. The variation of $R_e(r)$ has been studied by Nicholls[162] using the band-head measurements of Ornstein and Brinkman.[164] Later Prasad[161] and others[8,163,166] studied this feature using Tawde's[86] and Floyd and King's[167] intensity data, which are also band-head measurements. Parthasarathi et al.[165] used the eye estimate intensities of LeBlanc and Tanaka.[168] These have been inconsistent with one another and have been reviewed by Klemsdal.[169] The inconsistency can be seen from the values given below:

| | $R_e$ function |
|---|---|
| Nicholls | $-1 + 2.579r$ |
| Prasad | $1 - 0.03r$ |
| Parthasarathi et al. | $R_e \simeq$ constant |
| Reis | $R_e(\Delta v = 1)/R_e\ (\Delta v = -1) = 0.9$ |
| Prasad and Prasad | $-1 + 1.7r$ |

The band profiles in these bands differ from band to band, more so at $v \ge 5$, and hence the situation demands the use of integrated intensities.

An effort, though not exactly in this direction, has been made by Danylewych[79] and Nicholls[170] to improve the situation by measuring the intensity of main bands (up to $v' = 6$) of the violet system and comparing them with computer-synthesized spectra. In this process they were able to obtain transition probability data for a large number of bands and also to compare $R(0,0)$ with $R(1,0)$. This should be extended to cover more bands and eventually $R_e(r)$ variation.

Schoonveld[126] has reported calculations of Franck–Condon factors and *r*-centroids for the ($B^2\Sigma^+ \rightarrow A^2\Pi$) bands up to high $v$ values by using Morse potential. No $R_e(r)$ determinations are available for this system.

Rao and Lakshman[17] calculated from the true potential energy curves *r*-centroids and Franck–Condon factors (RKRV potential) for the bands of the $E^2\Sigma^+ \rightarrow$

TABLE III. Measured Oscillator Strengths

| ref, and date | $f_{el}$, λ | wavelength region, Å | method |
|---|---|---|---|
| | B → X Transition | | |
| Engleman and Rouse,[37] 1975 | 0.00685 | 3883 | heat of formation of CN |
| Jackson,[178] 1974 | 0.0342 ± 0.0005 | 3883 | lifetime |
| Luck and Bersohn,[40] 1973 | 0.037 ± 0.001 | 3883 | lifetime |
| Cook and Levy,[47] 1972 | 0.058 ± 0.008 | 3883 | lifetime |
| Arnold and Nicholls,[46] 1973 | 0.033 ± 0.005 | 4170 | shock-tube measurements |
| Levit and Parsons,[36] 1969 | 0.027 | 4215 | shock-tube measurements |
| Reis,[163] 1965 | 0.019 ± 0.004 | 3580 | ballistic |
| Liszt and Hesser,[39] 1970 | 0.039 ± 0.004 | 3880 | lifetime |
| Bennet and Dalby,[177] 1962 | 0.027 ± 0.003 | 3900 | lifetime |
| | A → X Transition | | |
| Duric et al.,[196] 1978 | $(5.9 \pm 0.6) \times 10^{-3}$ | 10970 | lifetime |
| Treffers,[199] 1975 | $(3.3 \pm 1.9) \times 10^{-3}$ | 10970 | king furnace emission spectra |
| Arnold and Nicholls,[197] 1972 | $(4.5 \pm 0.9) \times 10^{-3}$ | 10970 | dissociation energy |
| Jeunehomme,[44] 1965 | $(3.4 \pm 0.3) \times 10^{-3}$ | 10970 | lifetime |

$X^2\Sigma^+$ system for low $v$ values.

## E. Radiative Lifetimes and Oscillator Strength

Radiative lifetime measurements have been made by several workers using different methods for the $A^2\Pi$ and $B^2\Sigma^+$ states, and there is considerable variation in the values reported. By direct measurement of the spontaneous radiative lifetime of the upper electronic state Bennett and Dalby[177] obtained a value of $\tau$ of $(8.5 \pm 0.1) \times 10^{-8}$ s for the $B^2\Sigma^+$ state. Radiative lifetimes for the $v = 0, 1, 2$ of $B^2\Sigma^+$ have been determined by Liszt and Hesser[39] using the phase shift technique and are found to be in the range 59.3 ± 6 ns, which agree fairly well with 65.6 ± 1.0 ns obtained by Jackson[178] from laser fluorescence measurements. By monitoring the emission at 3883 Å of CN (0,0) with a bandwidth of 70 Å as a function of time after the flash lamp was fired, Luk and Bersohn[40] obtained a decay rate, which when extrapolated to zero pressure yielded a lifetime of 59.9 ± 2.1 ns for B state with ICN as the parent gas and of 61.7 ± 0.2 ns with BrCN as the parent gas. Both the values are nearer to the Liszt and Hesser[39] determinations. Tokue and Kuchitsu[42] have reviewed the available data. Among the values reported, the lifetime of 39 ns estimated from line widths[47] sets the lower limit, since the possibility of systematic errors contributing to lowering of lifetimes is high in this method. On the other hand the results of 85–59 ns by measurement of direct decay[177,40] and phase shift[39,48] probably provide an upper limit. Therefore the lifetime of $CN(B^2\Sigma^+)$ seems to be in the range 50–60 ns.

B state lifetimes show a slight increase with pressure for perturbed rotational levels whereas unperturbed levels are unaffected[196] and hence there is no need for extrapolation to zero pressure.

An approximate value of 0.6 μs for the radiative lifetime of the $A^2\Pi$, $v = 10$, state was estimated by Radford and Broida[43] from their measurements of the ratio of lifetimes of certain rotational levels of the $A^2\Pi$ and $B^2\Sigma^+$ states and on the basis of $\tau = (8.5 \pm 1.0) \times 10^{-8}$ s for the lifetime of $B^2\Sigma^+$ state. Jeunehomme[44] measured lifetimes of vibrational levels of the $A^2\Pi$ state from $v = 1$ to 9 in a pulsed electrodeless discharge through acetonitrile; it varies from 6.45 to 7.4 μs.

Wentink et al.[45] have reported a value of 3.5 μs which was subsequently revised to 7 or 8 μs (a private communication to Brocklehurst[31]) in a direct measurement of CN red emission in a pulsed discharge through $CH_3CN$.

Pressure effect on lifetime determinations of the A and B states of CN have been studied by Duric et al.;[196] they find an increase in lifetimes with pressure. This has been interpreted as due to collisional transfer from the X state to the A state of CN. Using these data they have determined lifetimes at zero pressure, which are about 4.5 μs for $v = 2$–9 levels. However, this is much lower than the value of lifetime (extrapolated to zero pressure) for the $v = 0$ level determined by Conley et al.[187] when they produced CN(A) in the flash photolysis of $C_2N_2$. The population of this CN(A) is monitored by observing fluorescence of B → X on excitation from A → B with dye laser at different pressures of $C_2N_2$ and at different intensities. The technique yields lifetimes extrapolated to zero pressure. These values are the first for $v = 0$ of $A^2\Pi$, are in good agreement with Jeunehomme's values, and suggest that Duric values are less reliable.

From antilevel crossing spectroscopy, Cook and Levy[47] have determined the lifetimes for B ($v = 0$) and A ($v = 10$) levels. These values are 39.4 ± 9.3 and 137 ± 45 ns, respectively. Though the value for the B state is comparable with other determinations, the value for the A state is too low and is nearer the determination of Radford and Broida[43] and that of microwave measurements.[90,191] It may be pointed out that the measurements of Cook and Levy and those of Radford and Broida do not involve direct time measurement; they concentrate only on perturbed levels and as such tend to yield low values. Since other determinations[44,187] are for unperturbed levels and the variation is not significant over $v$ values 1 to 9, an average value of 7 μs for the A state appears reasonable.

Oscillator strengths ($f_{el}$) are determined either by using lifetime determinations or by shock-tube and thermal methods; the latter involve dissociation energy determinations that are still uncertain though within narrow limits. So it is expected that $f_{el}$ determinations derived from lifetimes should be more dependable. Unfortunately there is some variation in these also.

Oscillator strength $f_{el}(\lambda)$ determinations for CN(B → X) transitions have been reviewed by Arnold and Nicholls.[46] Some representative and reliable experimental determinations of $f_{el}(\lambda)$ by various workers are collected in Table III. The best average value for $f_{el}(\lambda)$ is ~0.033 ± 0.005. Engleman and Rouse[37] have reported 0.00684 for oscillator strength from measurements of line absorption in a high temperature furnace. The authors have not been able to explain this low value.

Schadee,[76] using the basic formula and the experimentally measured[162] $R_e$ ($\bar{r}_{v'v''}$) for CN(B → X), has calculated $f_{el}$. His value of 0.019 for $f_{\Delta v=\pm 1}$ agrees with that of Reis.[163] However, it is difficult to rely much on these values because of approximations in the calculation of Franck–Condon factors and the uncertainties in the determination of vibrational intensities.

Schadee has also calculated $f_{el}$ for the CN(A → X) transition by using the $R_e$ ($\bar{r}_{v'v''}$) values of Dixon and Nicholls.[56] His value for $f_{0,0}$ ($3.4 \times 10^{-3}$) is in close agreement with that of Jeunehomme,[44] whose determination is based on measured lifetime of the A state for $v = 1$ to 9. Treffers[199] has determined $f_{0,0}$ by using emission data from Kings furnace.

Relative oscillator strengths $f_{v'v''}/f_{0,0}$ have been determined[198] for nine bands ($v' = 0$–7) in the solar spectrum by determining equivalent width for the absorption lines. They could be converted to absolute oscillator strength by laboratory determination of $f_{0,0}$.

Recently Conley et al.[187] have reported the lifetime of $A^2\Pi$ ($v = 0$) (section IIE), which is about the same as average lifetime value of Jeunehomme.[44] From these, the value of $3.4 \times 10^{-3}$ for $f_{0,0}$ appears reasonable. Selected data on oscillator strength are collected in Table III.

Duric et al.[196] have measured lifetimes of the A and B states in electron beam dissociative excitation of CN at different pressures. Their observed increase in lifetime for the A state has been interpreted to be due to collisional transfer from the X to the A state. They have extrapolated the results to zero pressure to eliminate the effect of pressure. Using these values and taking into account electronic transition moment variation they have calculated $f_{0,0}$ of A → X. This value is $(5.9 \pm 0.6) \times 10^{-3}$ and is significantly larger compared to other determinations. Thus the authors argue for the need to take into account collisional transfer. However, an increased pressure effect on vibrational levels 7 and 8, if observed, would have supported this argument.

$R_e(r)$, lifetimes, $f_{0,0}$, and dissociation energies are interlinked and hence any determination of one involving the other would inherit all the uncertainties of the other. Thus, greater emphasis should be placed on the data for each obtained independently or cross-checked by methods following different routes.

## *III. Atomic Nitrogen Flames*

Flames with atomic nitrogen have been known[2] to produce CN bands. The unusual intensity distribution in vibrational and rotational structure and their sensitive dependence on parameters such as pressure, kind of discharge used to produce atomic nitrogen, and fuel have led to a variety of experiments that have contributed considerably to the understanding of the chemiluminescence of CN in these sources. Still, there are areas not yet clearly understood. Another interesting feature of these flames is that only CN red and violet bands are emitted, except in very rare circumstances.[22] This rather unusual chemiluminescence of CN and the ease with which experiments can be set up have made this area rich and interesting.

### A. Behavior under Different Experimental Conditions

The common type of experimental setup consists of a discharge tube made of Pyrex glass, connected into a vacuum system with facilities for metering and mixing of discharge products of gas and fuel. The discharge products (afterglow) are drawn into a reaction tube to be mixed with fuel entering the same reaction tube through another port. The size and shape of the reaction chamber vary from experiment to experiment. Reaction flame of glow is seen at the mixing point of the afterglow and the fuel, and this often extends to 20 to 30 cm beyond the mixing point. The emission is observed (or photographed) by viewing the flame end-on or side-on with suitably placed windows.

Different kinds of discharges have been used to produce active nitrogen. However, microwave discharge and condensed discharge have been popular. Also, carrier gases such as helium and argon have been used. Different types of experimental setup have been developed, but the basic principle remains the same.

In some cases, special types of burners have been used that facilitate examination of different zones of the flame. One such burner used by Brown and Broida[54] consisted of a Pyrex cylinder 12 cm in diameter and 15 cm long with a flat quartz window sealed on each end. Fuel was introduced into the side of the burner at its midpoint through a 2-mm inner diameter glass tube directly opposite the active nitrogen inlet. Setser and Thrush[55] and Meyer and Setser[179] have modified the experimental setup to study the effect of temperature on the kinetics of reactions in active nitrogen–oxygen flames.

### B. Intensity Distributions in CN

The color and brightness of the atomic nitrogen flames are known to be strongly dependent on fuel and pressure. Commonly observed general features are as follows. For orange flames, at low pressures a large number of CN red bands are observed and are intense but the emission in the violet bands is mainly from $v' = 0$. As pressure increases the violet bands gain intensity, and bands from high $v$ appear and quite often become more intense than the red bands at high enough pressures. Further, vibrational intensity distributions in both red and violet bands are affected by the changes in pressure. Flames rapidly become weak as total pressure is decreased below 0.1 torr.[49,96] Blue flames are observed at medium and high pressures with trace fuel, and the reaction spreads out even beyond the reaction chamber. Such flames emit strongly violet bands with fairly intense tail bands; bands from $v' = 15$ to 18 have been reported. LeBlanc[12] has reported up to $v' = 25$ in red bands and $v' = 16$ in violet bands. Regular flame (pink and orange) conditions have been widely investigated, but blue flame conditions have not been examined in that detail and also the mechanisms operating there are not clearly understood.

Most of the atomic flames emitting CN have been obtained with yellow (Lewis Rayleigh) afterglow. There are a few reports of the reaction where pink afterglow (known to be rich in high-energy species) is used.[5,11,82,127] We have studied the emissions resulting from the reaction of pink afterglow with $C_2H_2$ and BrCN.[186] We find CN(B → A) bands that are rarely observed in addition to CN(A → X) and CN(B → X) bands; the overall intensity of (A → X) and (B → X) bands is high compared to emission from the flame with Lewis Rayleigh glow. (B → X) bands are intense, with well-developed tail bands going up to $v' = 15$. In addition, excitation of high $J$ rotational lines leading to high and anomalous rotational temperature is also observed.

### 1. *Vibrational Populations and Various Distributions*

Bayes[63] has identified the intensity distribution in CN red bands as due to a sum of two population distributions in $A^2\Pi$ state: (a) $P_1$—population distribution that decreases monotonically from $v = 0$ to $v = 3$; (b) $P_2$—population distribution that extends from $v = 3$ to $v = 10$ with a maximum at $v = 7$. Iwai et al.[49] have added one more distribution from a study of CN red bands under blue flame conditions, i.e., (c) $P_3$—population distribution that goes up to high $v$ (e.g., $v = 24$).

Following Bayes's identification of $P_1$ and $P_2$ distributions in the $A^2\Pi$ state, Setser and Thrush[55] noticed concurrent changes in the violet system and identified $P_1'$ and $P_2'$ distributions in $B^2\Sigma^+$ state as follows: (a′) $P_1'$—population maximum between $v = 5$ and $v = 9$; (b′) $P_2'$—mainly $v = 0$ is populated, accompanied by $P_2$ distribution in $A^2\Pi$, whereas Iwai et al.[49] have identified three distinct vibrational population distributions $P_1'$, $P_2'$, and $P_3'$ in $B^2\Sigma^+$, which are accompanied by $P_1$, $P_2$, and $P_3$ distributions in the $A^2\Pi$ state. Their identifications are as follows: (a′) $P_1'$—populations in $v = 3$, 4, 5 decrease with pressure (note: this is different from Setser); (b′) $P_2'$—mainly $v = 0$ is populated; (c′) $P_3'$—population distribution peaks near $v = 7$ and high $v$ levels are populated.

On the basis of further work Boden and Thrush[78] classified the vibrational populations in the $B^2\Sigma^+$ state into three groups: (i) $v = 0$ to 2, (ii) $v = 5$ to 12, and (iii) $v = 13$ to 15. The population distributions in each group of levels showed similar behavior for the changes in experimental conditions such as pressure, quenching, and carrier, indicating the possibility of three different mechanisms operating for the excitation of CN. However, it may be noted that these distributions are qualitative and overlapping and should not be taken too rigidly.

### 2. *Temperatures*

Wherever peaking has been observed, vibrational temperatures have been defined by using the low values of $v$ prior to peaking. These temperatures are generally high and depend significantly on fuel and pressure. Iwai et al.[49] obtained the following values in the case of red system: for BrCN, 8000 K; for $CH_3CN$, 3200 K; for $C_2N_2$, 2600 K; and for $CH_2Cl_2$, 3500 K. We have obtained for $C_2H_2$ 13 370 K, 6500 K, and 4140 K, at 25, 5, and 0.5 torr, respectively, for the violet system under blue flame condition.[87]

Rotational temperatures have been determined, and they too are found to depend on fuel and pressure. Iwai et al.[49] found that the rotational distribution for the $A^2\Pi$ state was a sum of two Maxwell–Boltzmann distributions with rotational temperatures around $T_2 = 340$ K and $T_1 = 2100$ K, the difference between the two decreasing with increasing pressure. This process of thermalization has been analyzed and found to yield a value of about 15 Å for collisional cross section for rotational relaxation in CN.

However, the rotational temperature of the ground state ($v = 0$) was 300 ± 40 K and 350 ± 30 K for 0.5 and 1.3 torr, respectively, as determined by absorption (X → B) measurements.[85]

Rotational temperatures for the B state have been found to be 315 ± 15 K by Kiess and Broida.[53] However, our measurements[188] show that rotational temperature depends on fuel and pressure, and rotational distribution is a sum of two distributions for high $v$ values with $T_1 = 1200$–$3000$ K and $T_2 = 400$ K. $T_2$ is not much affected by pressure changes whereas $T_1$ decreases with pressure, indicating rotational relaxation. However, low $v$ bands show temperature around 320 K with no dependence on pressure.

### 3. *Effect of Fuel and Pressure*

Different fuels produce flames of different colors and intensity. Large numbers of such fuels have been studied by Broida and his group.[49,53,54] Their effect on the red and violet systems has also been investigated. In general, three groups are recognizable: halogenated hydrocarbons, hydrocarbons, and cyanogen derivatives. Compounds with high hydrogen content generally produce weak flames.[53,63,77] At blue flame conditions, where trace amount of fuels are needed, there is no difference in the spectra observed for different fuels. Otherwise cyanogen-containing flames generally produce a $P_1$, $P_1'$ distribution and other compounds produce a $P_2$, $P_2'$ distribution. Fuels like BrCN have been found to produce highly intense flames at low pressures[49,96] when compared to other fuels which give high intensity at high pressures. Increased fuel reduces the brightness of the flame and localizes it at the fuel inlet. At a total pressure of 0.1 torr the population in $A^2\Pi$ maximum shifts from $v' = 8$ to $v' = 6$ when the fuel/nitrogen ratio changes from 0.1 to 0.5, indicating vibrational quenching by the fuel.[49] But at high pressures no such changes have been noticed by earlier workers, which may be due to lack of systematic data on this aspect.

The population distribution in the B state has been determined by many workers, but the effect of pressure on population has not been examined by all. Iwai et al.[49] report no pressure effect on the population distribution. However, our results[87] significantly demonstrate the effect of pressure: the population distribution peaks at $v' = 10$ at 0.5 torr and the peak shifts to $v' = 7$ at 25 torr, indicating vibrational relaxation;[190] in addition the population of high $v$ becomes higher than $v = 0$ at high pressures. The results of Provencher and McKenney[132] on population distribution and pressure effect are also similar. The earlier result of Iwai et al. is due possibly to the use of peak intensities in population determination. However, $CH_3CN$ gave a weak flame and did not show much change in intensity or intensity distribution on changing pressure. The population maximum occurred around $v = 8$ and the population of $v = 8$ was about the same as that of $v = 0$.

### 4. *Quenching Measurements*

Setser and Thrush[55,179] and Boden and Thrush[78] have studied the reaction kinetics of the flames of active nitrogen and oxygen as a function of quenchers. They find differential quenching for various vibrational states and have identified three groups: (a) $v = 0$ to 2; (b) $v = 5$ to 12; (c) $v = 13$ to 15. They report $NH_3$ to be effective in quenching group b. However, our results[188] of quenching by $NH_3$ do not lend to such simple grouping. We find that the population of the $v = 0$ level is quenched least (60%), $v = 2$–5 are quenched 85–90%, $v = 8$–11 about 80%, $v = 12$, 13 about 90%, and $v = 14$, 15 about 98%. Two broad observations can be made: (i) the $v = 0$ level behaves differently from other levels and is quenched least and (ii) the highest levels are quenched most, with a slightly reduced quenching around $v = 10$. These results suggest that the energy levels of the precursor for the excitation of CN may be of importance. $NH_3$ may remove a chain carrier responsible for CN emission[63] or may quench a precursor like $N_2^\dagger$ but not $A^3\Sigma^+_u$ (see below). Safrany,[80] Ghosh and his group,[81] Jackson and Faris,[83] and Tereschenko[84] have determined the reaction rates and quenching cross sections; quenching efficiencies are indicated to be in following order $NH_3 > NO > O_2 > H_2 > SO_2 > CO > N_2O > SF_6$. Iwai et al.,[85] Setser and Thrush, Meyer and Setser,[179] and Bayes[63] have used the results of the quenching measurements to identify the possible precursor for the CN emission.

Hg when admitted to afterglow of nitrogen is excited and this excitation is accepted to be due to energy transfer from $N_2(A^3\Sigma_u^+)$.[142] However, Hg is known not to quench $N_2^\dagger(X^1\Sigma_g^+)$. This is used in discriminative quenching of energy carriers so that the mechanisms can be distinguished. Provencher and McKenney[128] found no change in the intensity of CN bands on addition of Hg and inferred a minor role, if any, for $N_2(A)$ in the excitation of CN (vide section C). It may be noted here that in a study of quenching of Hg emission by $NH_3$ added to active nitrogen containing Hg, it was found[102] that the cross section for quenching of $A^3\Sigma_u^+$ by $NH_3$ is at least one-fifth of that of Hg.

### *5. Repeated Afterglow on Addition of Excess Fuel*

Safrany and Jaster[80] have reported that reactions of $C_2N_2$, $C_2H_2$, and HCN with active nitrogen produced flames, but the $N_2$ afterglow was observed beyond the flame even when the reactant was added in large excess. This indicates that reactive species survived the reaction zone, in contrast to the reactions of alkenes and alkanes in which the reactions go to complete consumption of the reactive species.[80] This survival of reactive species has not been reported by others. We[189] have also observed faint glow beyond the reaction zone when excess $C_2H_2$ was added and referred to this as repeated afterglow (RA). The spectra of RA consisting of CN violet bands and $N_2$ first and second positive bands suggest that some percentage of nitrogen atoms are surviving or are possibly regenerated down the way to the pump. Existence of reactive species is confirmed by our observation of enhanced glow on addition of fuel at about 100 cm from the main reaction zone.

## C. Mechanisms for Excitation of CN

The various features of CN emission appear to depend on the experimental parameters in a complicated way and seem to demand specially tailored mechanisms. But the quenching experiments have added significant data that are helpful in the choice of mechanisms.

Broida and his group[43,53,62,71] on the basis of observed anomalous population of $B^2\Sigma^+$ ($v = 0$, $K = 4$, 7, 11, and 15) were the first to propose the formation of CN $B^2\Sigma^+$ ($v = 0$) via CN $A^2\Pi$ ($v = 10$) and also to suggest that CN is formed at least 20 times more in the A state than in the B state. This mechanism has since been accepted. This applies to $P_2'$ distribution.

Bayes[63] observed quenching of CN emission on addition of $NH_3$, which is known not to react with N atoms. So, he suspected the possible role of $N_2(A^3\Sigma_u^+)$ in the excitation of CN and proposed the following mechanisms which explained his other observations as well:

$$N_2(A^3\Sigma_u^+) + XCN \rightarrow N_2(X^1\Sigma_g^+) + XCN^* \quad (6)$$

$$XCN^* \rightarrow X + CN \quad (7)$$

$$N + CN \rightarrow CN_2 \quad (8)$$

$$CN_2 + N \rightarrow CN^* + N_2 \quad (9)$$

He suggested the possibility of involvement of $N_2(X^1\Sigma_g^+)$ in high vibrational states in place of $N_2(A^3\Sigma_u^+)$. The following deserve to be mentioned: (i) Campbell and Thrush[180] have proposed excitation of $CN(B^2\Sigma^+)$ as an energy transfer reaction involving $N_2(A^3\Sigma_u^+)$.

$$N_2(A^3\Sigma_u^+) + CN \rightarrow CN(B^2\Sigma^+) + N_2(X^1\Sigma_g^+) \quad (10)$$

(ii) Setser and Thrush[55] have proposed

$$N_2(A^3\Sigma_u^+) \text{ or } N_2(^5\Sigma^+) + CN \rightarrow CN(B^2\Sigma^+ \text{ or } A^+\Pi) + N_2(X^1\Sigma_g^+) \quad (11)$$

or

$$N + N + CN \rightarrow CN(A \text{ or } B) + N_2(X) \quad (12)$$

for $P_1$ and $P_1'$ distributions; and a chemical reaction leading to formation of CN in the $P_2$ distribution and then through perturbation to $P_2'$ distribution, consistent with the proposal of Broida.

Absolute intensity measurements and quenching studies indicate that the active species appear to be $N_2(A^3\Sigma_u^+)$ in low vibrational levels and $N_2(X^1\Sigma_g^+)$ in high vibrational levels (Boden and Thrush[78]).

Iwai et al.[49] confirm the above mechanisms for $P_1$, $P_1'$ and $P_2$, $P_2'$ distributions and suggest reactions 11 and 12 as possible mechanisms for $P_3$, $P_3'$ distributions. Their later[85] results on absorption measurements are also consistent with this suggestion. Further, they[49] have revised the earlier report of Broida and suggest that CN is formed at least 30 times more in the A state than in the B state. Brown and Broida[54] have suggested collisional transfer from a highly excited A state as in eq 13. However, it is to be noted that reaction 12 for

$$CN(A^2\Pi, v \geq 12) + M \rightarrow CN(B^2\Sigma^+, v < 15) + M \quad (13)$$

$P_3'$ seems to produce distributions $P_1$, $P_1'$ and $P_3$, $P_3'$ as well. The observed $P_1$, $P_1'$ without $P_3$, $P_3'$ in some experiments may be due to quenching by fuel itself of the $P_3$, $P_3'$ distribution or their degradation to the $P_1$, $P_1'$ distribution.

LeBlanc[12] has reported high "$v$" excitations in active nitrogen flames of methane and has observed that the violet bands with $v' = 5$, 7, and 9 appear enhanced while the corresponding energy red bands with $v' = 17$, 20, and 23 appear to be reduced in intensity. From this he has inferred that these levels of the $B^2\Sigma^+$ state are populated by collision-induced transfer from the A state, thus supporting suggestion of Brown and Broida.[54]

Provencher and McKenney[128,132] have used Hg to quench $\mathrm{N_2(A^3\Sigma_u^+)}$ and study its effect on CN violet emission up to $v' = 15$. Since emission intensity was essentially unaffected, they conclude that $\mathrm{N_2(A^3\Sigma_u^+)}$ is not involved in CN excitation and probably $\mathrm{N_2^\dagger(X^1\Sigma_g^+)}$ is involved. This view has also been supported by Meyer and Setser.[179] However, $\mathrm{N_2(A^3\Sigma_u^+)}$ might be a source for production of $\mathrm{N_2^\dagger(X^1\Sigma_g^+)}$[132] and may be responsible for the complicated pressure dependence; i.e., they suggest

$$\mathrm{N + N_2(A^3\Sigma_u^+) \rightarrow N_2^\dagger(X^1\Sigma_g^+) + N} \tag{14}$$

$$\mathrm{N_2^\dagger + CN \rightarrow CN^*(B^2\Sigma^+) + N_2(X)} \tag{15}$$

Young and Morrow[129] have studied CN emission from an active nitrogen flame of CO. Their results appear to indicate the noninvolvement of $\mathrm{N_2(A^3\Sigma_u^+)}$ and do not substantiate reaction 18 in the formation or excitation of CN. They favor the following reactions:

$$\mathrm{N_2^*(W^3\Delta_u) + CO \rightarrow CN + NO} \tag{16}$$

$$\mathrm{N_2^{**}(^5\Sigma) + CN \rightarrow N_2 + CN^*} \tag{17}$$

similar to eq 11. However, it is possible that these suggestions are valid in a limited way for their system alone. Also, these reactions do not find support in the work of Meyer and Setser[179] and Broida and Heath.[112]

On the other hand, Savadatti and Broida[50] suggest eq 18 for their CN observations in carbon vapor atomic flames. Winkler and Haggart[130] have proposed chain

$$\mathrm{C + N + M \rightarrow CN^* + M} \tag{18}$$

reactions for $\mathrm{C_2N_2}$:

$$\mathrm{N + C_2N_2 \rightarrow CN + CN_2} \tag{19}$$

$$\mathrm{CN + N \rightarrow CN_2} \tag{8}$$

$$\mathrm{CN_2 + N \rightarrow N_2 + CN^*}\text{(regenerates CN)} \tag{9}$$

Reactions 8 and 9 have also been proposed by Bayes.

Safrany and Jaster[80] have examined reactions of atomic N + atomic H with $\mathrm{C_2N_2}$ and later have extensively studied reaction of active nitrogen with $\mathrm{C_2N_2}$ and other hydrocarbons in the presence of other gases such as $\mathrm{N_2O}$, CO, $\mathrm{CO_2}$, $\mathrm{SF_6}$, and $\mathrm{O_2}$. Their system contained too many parameters[80] to yield a clear cut picture of what was happening. Still, their work is highly interesting and throws light on the many plausible reactions taking place involving C, CN, and $\mathrm{CN_2}$. They suggested the following reactions to be operating in their system:

$$\mathrm{N_2^* + C_2N_2 \rightarrow N_2 + 2CN} \tag{20}$$

$$\mathrm{CN + N \rightarrow N_2 + C}\text{ (supported by Becker)} \tag{21}$$

$$\mathrm{C + C_2N_2 \rightarrow C_2N + CN} \tag{22}$$

$$\mathrm{C_2N + N \rightarrow 2CN}\text{ (regenerates CN)} \tag{23}$$

C atoms have been observed in these sources by atomic absorptions at 1657 and 1560 Å (Kley et al.[20,21]), justifying the involvement of carbon atoms in these reactions.

Johnson and Fontijn[24,158] have reported observation of $\mathrm{CN(E^2\Sigma \rightarrow A^2\Pi)}$, $\mathrm{CN(F^2\Delta \rightarrow A^2\Pi)}$, and C (156.1, 165.5, and 193.0 nm) chemiluminescence in the active nitrogen flame of $\mathrm{C_2F_4}$. This is the only observation reporting E and F states in atomic nitrogen flames and C chemiluminescence from $^3$P and $^1$D states. They have explained their data on the basis of reactions 24 and 25. They feel that there is adequate abundance of C and N to support the above reactions.

$$\mathrm{C(^3P) + N(^4S) + M \rightarrow CN(E,F) + M}\text{ (same as (18))} \tag{24}$$

$$\mathrm{N_2^* + CN(X) \rightarrow CN(E,F) + N_2}\text{ (7.7 eV are to be available)} \tag{25}$$

The experiments of Johnson and Fontijn are difficult to reconcile in two respects:

(i) They observe atomic carbon emission and emission from CN, E, and F states; these are explained only on the basis of C and N, both of which appear[20,21] to be common ingredients of all N atomic flames. Why, then, are these emissions absent in other flames? Or does the fuel $\mathrm{C_2F_4}$ have a role to play?

(ii) Kley et al.[20,21] have observed the presence of C atoms in N + $\mathrm{C_2H_2}$ flames through absorption experiments. Johnson and Fontijn when repeating their experiments failed to detect any C atoms, although in their N + $\mathrm{C_2F_4}$ flame they observed C atom emission. Perhaps it would have been of some help if they had given data on the red and violet bands of CN for their source.

Kley et al.[20,21] have observed that the C atom concentration was maximum at the blue flame condition where CN violet was more intense than CN red, and hence suggested that

$$\mathrm{C + N + M \rightarrow CN^*(A,B) + M} \tag{18}$$

is an important reaction in blue flame conditions.[20] On the basis of their observations on the various parameters involved, they did not favor the reactions proposed by Safrany, Fontijn, Young and Morrow, Meyer and Setser, and Iwai et al. for the excitation of CN. They claim $\mathrm{CN(^4\Sigma^+)}$ to be the precursor for excitation of $\mathrm{CN(B^2\Sigma^+)}$ with high $v'$ in view of the perturbation of $\mathrm{CN(B^2\Sigma^+}, v' = 11)$ by $\mathrm{CN(^4\Sigma^+)}$. Their mechanisms can be summed up as follows:

$$\mathrm{CN(^4\Sigma^+) + M \rightarrow CN(B^2\Sigma^+}, v = 7, 8\ ...) + \mathrm{M}$$

$$\mathrm{CN(B^2\Sigma^+}, v = 7, 8\ ...) + \mathrm{M} \rightleftarrows \mathrm{CN(A^2\Pi}, v \geq 20) + \mathrm{M}$$

$$\mathrm{CN(A^2\Pi}, v \geq 20) + \mathrm{M} \rightarrow \mathrm{CN(A^2\Pi}, v \leq 20) + \mathrm{M}$$

$$\mathrm{CN(A^2\Pi}, v < 20) + \mathrm{M} \rightleftarrows \mathrm{CN(B^2\Sigma^+}, v < 7) + \mathrm{M} \tag{26}$$

The pink afterglow gives very intense reaction flames with organic molecules ($\mathrm{C_2H_2}$, BrCN) emitting CN red and violet bands. This in itself is indicative of high concentration of reactive species $\mathrm{N_2^{\dagger *}}$ in the pink afterglow,[82] leading to increased reaction rate and consequent increased concentration of excited CN. The excitation mechanism operating in this case is more likely

$$\mathrm{N_2^{\dagger *} + CN \rightarrow CN^*(B) + N_2}$$

but not the direct formation of CN in excited state in chemical reaction. This would also be consistent with observed abnormal high rotational temperature.[186]

The present situation can be summed up as follows:

(1) The CN(B), $v = 0$, is populated definitely via CN(A), $v = 10$, level with 20–30 times higher population in the A state. Furthermore, there is evidence to show that some other levels of the B state ($v$ = 5, 7, 9, 12, and

14) are also populated via corresponding vibrational levels of the A state ($v$ = 17, 20, 23, 27, 30).

(2) Formation of CN, A and B, states through

$$C + N + M \rightarrow CN^* + M$$

is widely acceptable compared to other proposed mechanisms. M should play a significant role in the excitation of E and F states of CN in the study of Johnson and Fontijn.[24] The population of the B state via the $^4\Sigma^+$ state ($^4\Sigma^+$ perturbs $v$ = 11 of B state), as suggested by Washida et al.,[20] is attractive and is supported by the work of Cook et al.,[183] who have reported 150–300 times excess steady-state population for $^4\Sigma^+$ state compared to the B state. However, it is puzzling why intensity enhancement of the line from $N$ = 20, $v$ = 11, in the B state is not observed in spite of such excess population (refer to section IVC).

(3) Washida et al. while explaining their observation of population maximum at $v'$ = 7 have drawn support from the above mechanism via $^4\Sigma^+$ whose potential minimum occurs at 41 000 $cm^{-1}$, very close to $v$ = 7 of B state. However, other results[87] where greater care has been excercised in intensity measurements show that the population maximum at low pressures occurs at $v'$ = 10 and the population distribution is sensitive to pressure and the maximum shifts to $v'$ = 7 at high pressure. For these results to be consistent the potential minimum of the $^4\Sigma^+$ state should be ca. 45 000–46 000 $cm^{-1}$.

## *IV. Other Sources of CN Excitation*

### A. Atomic Oxygen Flames of CN-Containing Compounds

Atomic oxygen flames of CN-containing compounds are known to emit CN red and violet bands. A systematic study of these emissions and their kinetics has been reported by Setser and his group.[55,179] They have investigated O atom reaction with $C_2N_2$ and $C_4N_2$. The flame is bright purple with intensity distributions in CN corresponding to $P_1$ and $P_1'$ distributions. Perturbed lines of the $B^2\Sigma^+$ ($v$ = 0) seem to be less pronounced and the rotational temperatures higher when compared with those of atomic N flames. Further they found that the response of all the bands from $v'$ = 0 to 15 of CN-($B^2\Sigma^+$) to changes in pressure and quenchents is about the same, and hence suggested a single excitation mechanism for all these levels. They observed emission of CO($A^1\Pi$–$X^1\Sigma$) bands as well, indicating the availability of high energy (~9 eV) for excitation. They have discussed the various possible mechanisms for the chemiluminescence of CN but have been unable to arrive at a definite conclusion. However, they favor a single mechanism for the excitation of both the A and B states.

### B. Atomic Carbon Flames

Atomic carbon flames with atomic nitrogen[50] and nitrous oxide[208] have been spectrally investigated. Atomic carbon plus atomic nitrogen reactions produce flames similar to blue flame conditions and have been referred to under atomic nitrogen flames. The nitrous oxide flames of the carbon atom (obtained from the reaction of H + $CHCl_3$) is red and gives only CN red bands with population inversion having a maximum at $v'$ = 1 and extending up to $v'$ = 7. The distribution fits a chemical reaction

$$C + N_2O \rightarrow CN(A^2\Pi) + NO(X^2\Pi) \qquad \Delta H = 1.47 \text{ eV}$$

(see section IVE).

### C. Metastable Rare Gas Atoms Reacting with Cyanides

Metastable rare gas atoms generated in an electric discharge have been found to have enough energy to react dissociatively with cyanides[22,23,91,117,118] and generate CN chemiluminescence that is predominantly CN red and violet bands. The experimental setup is similar to that of active nitrogen flames, with rare gas replacing nitrogen. The dissociative reactions were visualized as a two-step process:[22]

$$Ar^*, Xe^* + R\text{–}CN \rightarrow R\text{–}CN^* + Ar, Xe$$

$$R\text{–}CN^* \rightarrow R + CN^*(A,B)$$

Kolts et al.,[195] from a study of reactive quenching of Xe(6s,$^3P_2$) by chlorine-containing molecules, have modified the above two-step process as follows:

$$Xe(^3P_2) + CNX \rightarrow XeCN^* + X$$

$$XeCN^* \rightarrow Xe + CN(A \text{ and } B)$$

These reactions find support from similar studies of Gundel et al.[206] and Kolts et al.[207] using Ar*.

Coxon et al.[22] report emissions from the E, F, and D states of CN in addition to red and violet systems. Their[23] significant observation is the enhancement of $K$ = 20 of $v$ = 11 in the B state, to such an extent that at low pressures the entire intensity of 11–11 band is in this line only. This has been attributed to a perturbation of $v$ = 11 of $B^2\Sigma^+$ at K = 20 by a $^4\Sigma^+$ state. Such perturbation has been observed recently by Miller and Freund by the technique of level crossing spectroscopy.[137] Interesting population anomalies in vibrational and rotational levels hitherto unknown have also been reported[22,117,118,202,203] for the $B^2\Sigma^+$ state, particularly in reactions with BrCN and ICN. In these reactions alone (HCN and ClCN included) the perturbation in $v$ = 11 is observed. Further, the population of $v'$> 10 in the B state is much higher than those of $v'$< 10, and the population distribution for $v'$> 10 show peaking at $v'$ = 12, 14, and 18;[203] the origin of these enhancements is not understood. Kuchitsu et al., when extrapolating intensity values of $v'$ = 11, $K$ = 20 to zero pressure, infer that the population of this state is partly (though small) not via the $^4\Sigma^+$ state. However, their identification of perturbation in $v'$ = 13 as due to the $^4\Sigma^+$ state remains doubtful since it is based on their observation of pressure independence of the intensity of the perturbed line, which has been observed to show[96,188] variation with pressure in active nitrogen flames of BrCN.

In the reaction of Ar* with $CH_3CN$ anomalously high rotational temperatures are reported[202] but not high vibrational levels compared to halogenated cyanides. However, in all these cases perturbations due to the A state produce enhanced perturbed line intensities, thus indicating direct formation of the A and B states. The formation rate of the A state is about four times that of the B state, which is much less compared to the high rate of formation of the A state (≃30–40 times) in active nitrogen flames.[49]

Simons and others have reported[204] CN, B → X, emission in a crossed molecular beam study of the chemiluminescent reaction. The absence of fluorescence polarization in CN, B → X, radiation has been explained by a two-stage harpooning mechanism:

$$Xe(^3P_{2,0}) + BrCN \rightarrow (Xe^+CN^-)^* + Br$$

$$(Xe^+CN^-)^* \rightarrow Xe(^1S_0) + CN(A,B)$$

Further experimental data are necessary to support this type of mechanism.

## D. Electron Impact Dissociation of Cyanides

Electron impact dissociation of cyanides has been found to produce CN red and violet emissions.[42,89,116,181,201] Studies of these emissions have been used for the determination of cross section for CN formation or for the determination of excitation function.[89,116,201] Though no systematic studies for the intensity distribution in the red and violet systems seem to be available, the study of Tokue, Urisu, and Kuchitsu using HCN, $CH_3CN$, $C_2N_2$, ClCN, and BrCN is fairly extensive. After examining the various molecules, they found that the CN bands showed none of the anomalous features that are common in CN emission from N atomic flames or metastable argon excitation. Violet bands have been found to be more intense than red bands. Vibrational distributions were reasonably Maxwell–Boltzmann. However, rotational distributions showed a superposition of two Maxwell–Boltzmann distributions for $v$ = 0, 11, 12, 13 levels of the $B^2\Sigma^+$ state.

Korol and Kishko[140,141] have reported emission of CN bands by slow electrons impinging on $C_2N_2$. They suggested the following process as the most probable one for excitation of CN.

$$C_2N_2 + e \rightarrow CN^* + CN^+ + 2e$$

They have evaluated absolute excitation cross sections for the $D^2\Pi$, $B^2\Sigma^+$, and $A^2\Pi$ states from the $X^2\Sigma^+$ state of CN.

Recently[201] excitation of CN $B^2\Sigma^+$ from HCN at threshold electron energies has been reported. This brings out the similarity in the results of photon and electron excitation, and the dissimilarity at high electron energies is explained as due to the uncertain quantum of excess energy transfer to fragments. The branching ratio for the CN A state is much smaller than in the Ar metastable excitation, as evidenced by the lack of enhanced perturbation.

## E. Ion Impact Excitation of CN

Jamieson et al.[134] have calculated the cross sections for rotation excitation of CN molecules by proton impact and compared them with other calculations.

$C^+$ ions produced in a plasma source and accelerated to 1 kV have been used with proper decelerations to impinge upon NO gas.[133] Resulting emission was found to be CN violet with $\Delta v$ = 0, 1, −1 with strong C ($^1P \rightarrow {}^1D$) emission. Other features were (i) CN intensity depended on the square of NO pressure and (ii) peaking in vibrational population at $v'$ = 4 with almost no intensity in bands with $v'$ = 0 and 1. From the pressure dependence of band intensity Jamieson et al. suggested $C + NO \rightarrow CN^* + O$ to be responsible for observed CN excitation. Fast reaction of CN with NO would also be relevant in this connection. This reaction, if valid, must have a role to play in systems containing oxygen and atomic nitrogen.

## F. Photodissociation, Flash Photolysis, Shock-Tube Technique, and Flames

CN luminescence on photodissociation of cyanides, using rare gas resonance lines, has been studied by Mele and Okabe,[113] Tereschenko and Dodonova,[84] and Jackson and Faris[83] to determine excess energy distribution in CN excited state and the deactivation processes for excited CN molecules.

Flash photolysis techniques have been used for the production of CN and for the study of their spectra and excess energy distribution. For example, Engleman[29] has made a straightforward study of absorption spectra at high resolution that has led to identification of a perturbation in $v$ = 5 of $B^2\Sigma^+$ by $v$ = 17 of $A^2\Pi$. Basco et al.[115] obtained, in the flash photolysis of $C_2N_2$, BrCN, and CNI, vibrationally excited ground-state ($v \leq 6$) CN, whereas Engleman[111] observed vibrational inversion but failed to obtain lasing, although Pollack[193] had reported (4 → 3) lasing earlier.

Recently West and Berry[144] studied the mechanisms of RCN photodissociation and predissociation in flash photolysis leading to a CN chemical laser involving the electronic transition $A^2\Pi_{3/2}(v = 0) \rightarrow X^2\Sigma^+(v = 0\text{–}2)$ and the vibrational transition in $X^2\Sigma^+$: 5 → 4, 4 → 3, 3 → 2, and 2 → 1. They also proposed collisional nonradiative transfer from $A^2\Pi(v = 0) \rightarrow X^2\Sigma^+(v = 4)$ for understanding the population inversion.

The CN, B → X, fluorescence spectrum in the photodissociation of BrCN with vacuum ultraviolet radiation[205] reveals parallel formation of vibrationally excited CN in both the $A^2\Pi$ and $B^2\Sigma^+$ states. The intensities of the perturbed lines are found to be sensitive to pressure and exciting wavelength. There is a population inversion in vibrational levels of the B state in the absence of collisions. These results establish that higher vibrational levels of the A state are populated than was believed earlier.

A number of shock-tube experiments have been done to determine CN dissociation energy, oscillator strength, radiative lifetime, etc. (Arnold and Nicholls[46]).

CN bands have been reported in atmospheric and low pressure flames for fuels containing CN; details of this are given in books by Gaydon.[108,135] They have been studied as an aid to understanding of flame processes.[109]

## G. CN in Astral Sources

The CN radical emitting the red and violet bands has been identified in many astral sources like sun,[27,99,152] stars,[28,75,101,102,105–107,138,139,143] comet heads,[28,151,171] solar and stellar atmospheres,[25,104,148,149,153] and interstellar clouds[26,107] from which vibrational and rotational temperatures[99,103] and relative abundances of isotopes[74,104,105,143] of $^{12}C$ and $^{13}C$, etc., have been determined. From these observations, the mechanisms of formation and excitation of CN in these sources have been inferred. For example, Solomon and Klemperer[26] propose

$$CH^+ + N \rightarrow CN + H^+$$

for interstellar cloud.

## H. Laser-Induced CN Fluorescence

With the advent of lasers, photofragment spectroscopy has become a powerful tool in the precollision distribution of energy in CN in addition to the straightforward detection of CN on excitation by laser radiation.

Earliest experiments on these lines were due to Jackson,[173,178] who detected CN(X) molecules by studying the fluorescence of (0,1) violet bands on scanning by a dye laser in the (0,0) region of the B → X transition. Significant experiments have been recently done by him and others[155,174] that provide evidence for the population inversion at $v = 4$ in the X state and also suggest a $A^2\Pi(v = 0) \rightarrow X^2\Sigma^+(v = 4)$ collisional transition in the photolysis of $C_2N_2$ and ICN. Sabety-Dzvonck and Cody[174] have also given a brief summary of investigations on ICN photodissociations through 1976. Another significant experiment[187] has been to monitor CN (0,0) emission on laser excitation of $A^2\Pi(v = 0)$ to $B^2\Sigma^+(v = 0)$. This is expected to yield[185] direct information about the A → X collisional transition. Mention should be made of another interesting experiment where Rich and Bergman[35] report excitation of CN violet bands in a system of $CO + N_2 + Ar$ irradiated with a CO laser. This provides an excellent example of a ladder effect leading to very high vibrational excitation and then vibrational transfer. Quantitative data on CN excitation in this case are not available. Lurie and El-Sayed[156] report production of CN ($B^2\Sigma^+$, $v = 0, 1, 2$) from 266-nm laser photolysis of benzoyl cyanide. No emission from the CN A state is observed. A multiphotonic process is invoked to explain the observed results.

## I. Isotopic Studies

Laboratory investigation of isotopic CN are few, although there are some reports of isotopic CN from astral sources.[74,104,105,143] Lagerqvist and his group have analyzed the ${}^{13}C^{14}N$ red system.[175,176] We have also studied the reaction of ${}^{13}CO$ with atomic nitrogen. The resulting spectrum of ${}^{13}C^{14}N$ shows tail bands in the violet system in addition to the usual red and violet bands. The perturbations commonly observed in the spectra of ${}^{12}C^{14}N$ are not evident here.

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