

Progress of Laboratory Aeronomy and Airglow Research in India during the Last Fifty Years: Part II—Microwave Discharge of Atmospheric Gases

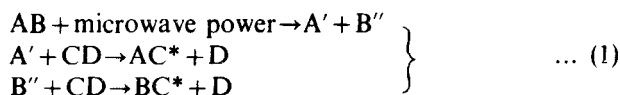
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Microwave discharge of atmospheric gases and collisional processes between dissociated atoms and molecules have been studied. The investigation consists of spectroscopic studies of microwave discharge of molecules and of reaction glow of dissociated atoms and molecules. It also includes investigations on quenching coefficient and quenching mechanism and microphotometric observation and mass spectrometric studies of reaction glow. The spectra excited by microwave discharge have been compared with those excited by spark discharge and proton bombardment.

1 Introduction

In addition to well known methods of excitation of spectra, gases can be excited to emit spectra by microwave discharge. During such a discharge, the molecules are ionized, excited and may be dissociated into atoms. These dissociated atoms being very reactive, while interacting with atoms and molecules, may in many cases produce excited atoms and molecules and thereby create reaction glows. For example,



The excited AC^* and BC^* molecules produce reaction glow. Again, reactions in which one of the reactants is an atom and glows are produced, are important not only for elucidating the basic information of such reactions but also for increasing our knowledge in other field, viz. the upper atmosphere, combustion, etc. To understand the importance of such reaction for the study of the upper atmosphere, one needs only to recall that a large number of molecules in the upper atmosphere are dissociated by solar ultraviolet rays. Since they are created in a tenuous atmosphere, these dissociated atoms do not recombine readily and therefore possess rather long life. They react with other atoms and molecules present in the upper atmosphere, producing, in certain cases, reaction glow. From the spectra and photometry of the glow, one is able to obtain information about the reacting species and other data of the atmosphere. For example, if sodium atoms are sprayed from a rocket in the upper atmosphere which on reaction with atmospheric gases

produce a glow, then from the nature of the glow and its time dependence, information of the upper atmospheric parameters can be obtained.

In Table 1, different methods of producing dissociated atoms are given. It may be remembered that the mechanism of a reaction can be established when information on the following is obtained. (i) reactants, final products and, if possible, atoms, molecules and free radicals produced in the intermediate stages, (ii) order of reaction (bimolecular, trimolecular, etc.), and (iii) rate coefficient.

To identify the nature and state of the reactants (normal, excited or ionized atoms or molecules), the spectrum of the microwave discharge through the gas can be observed. The spectrum of the reaction glow reveals information regarding the products of the reaction. The mass spectrometric analysis of the gas in the reaction chamber may lead to the identification of the final reaction products. Again, in order to determine the order of the reaction producing the glow, the variation of the intensity of the glow with the partial pressure of the reaction may be obtained. The rate coefficient of the reaction can be determined by estimating the concentrations of atomic reactants.

The following investigations were carried out by Ghosh and his associates over a period of many years:

(i) Microwave discharge through N_2 , H_2O , CO_2 , N_2 and O_2 mixture, NO and Ar (Table 2). (ii) Reaction glows obtained by reacting atomic nitrogen produced by microwave discharge of nitrogen molecule with N_2 , CCl_4 , $CHCl_3$, CH_2Cl_2 (Table 3). (iii) Reaction glow between dissociated O atoms and Na .

Spectroscopic, photometric, microphotometric and mass spectroscopic studies (for one reaction) are

presented. The mechanisms of excitation of glows are discussed.

2 Instrumentation

A dynamical flow method can be adopted for the production of glow. Since the reactions between atoms and free radicals with molecules are fast processes, the state of reaction and the non-equilibrium distribution of molecules (when the population of molecules in their

various levels of excitation does not follow the Maxwell-Boltzmann distribution) vary rapidly with time. Therefore, a particular state of the reaction is rather difficult to obtain in a static system. On the other hand, by suitable adjustment of the flow of the reacting species in a dynamic system, the desired state of the reaction can be made steady in certain region of the system.

Table 1—Different methods of producing dissociated atoms

Source	Process
Microwave Discharge	The molecular gases are subjected to microwave discharge from an oscillator giving about 100W power (about 10-20% of the gas is dissociated into atoms). In certain cases e.g. N_2 and CO_2 , molecular ions are first formed which then undergo dissociative recombination to produce atoms. In addition to normal atoms excited atoms and molecules are formed. This method is widely used for the production of dissociated atoms (Hartek P., Reeves R. R. and Mannello C., 1958) <i>J. Chem. Phys.</i> 29, 608; Herron J. T. Franklin and Brandt P. J. 1958 <i>Chem. Phys.</i> 30, 879; Young R. A. and Sharpless 1963, 39, 1071).
AC or DC discharge	The percentage of atoms to be obtained by this process is small (10%). Now-a-days this method is seldom used for the production of dissociated atoms.
Photolysis	The molecules are irradiated by high energy photons from X-rays, γ -rays and ultraviolet rays. The atoms are produced by absorption of photons corresponding to the energy of dissociation. The percentage of dissociated atoms is higher compared to that produced by above methods. Ions, excited atoms and molecules are obtained to a small extent.
Shock waves	The molecules are subjected to shock waves whereby they are ionized and dissociated to a high percentage into atoms in the normal & excited states. In this method gases are ionized to a high degree. (Ionization Phenomena in Gases 1960, p 47).
Thermal decomposition	The molecular gases are heated to cause dissociation. As in the previous case the excited atoms, molecules and ions are formed. Unless the gas is heated to a high temperature the percentage of dissociation is small [Mathews, D. L 1959 <i>Phys. Fluids</i> 2, 170].
Bombardment of gases by energetic particles	Bombardment of gases by high energy particles produces ions and dissociated atoms which may be in excited states.
Chemical reaction	The percentage of dissociation is low. Sometimes atoms are produced by mixing different gases. A well known example is the production of O atoms by the following reaction $NO + N \rightarrow N_2 + O$ which is widely used [Young, R. A., Black, C, 1966) <i>J. Chem. Phys.</i> 44, 3741].

Note: Tables 1-7 in this paper have been reproduced as such from Ghosh, S N, Commemoration Volume, Centenary of India Association for the Cultivation of Science and Golden Jubilee of *Indian J Phys*, Part II (1977) 296.

Table 2—Spectroscopic observations of microwave discharge of molecules

Reference	Gas	Colour of the after-glow	Spectral features	Remark
Ghosh, Sharma and Sharda Nanda 1962 <i>Proc. Phys. Soc.</i> (London) 79, 207-218	N ₂	A bright reddish discharge is observed.	1PG and 2PG systems of N ₂ , 1NG system of N ₂ ⁺ and some unidentified lines (Fig 4 and Figs 31 and 32)	There is indication of Meinel system of N ₂ ⁺ . Its identification is uncertain because in its spectral region strong 1PG band system of N ₂ appears. 1PG systems are important features of aurora and nitrogen afterglow. 2PG bands of N ₂ are observed in the discharge of N ₂ and air and also in arcs at low pressures. Pink afterglow is excited in highly pure N ₂ and also by bombardment of N ₂ by ions. The afterglow excited in N ₂ of ordinary purity contains mainly 1PG and very weak 2PG systems.
Ghosh, Shukla and Srivastava 1970 <i>Ind. Jour. Pure and App. Phys.</i> 8, 806-810.	H ₂ O	Weak whitish yellow	Balmer series of H atom, NaD lines. At 180 × 10 ⁻³ torr NaD line is not excited. At higher pressure, it is excited and its intensity is found to be pressure-dependent. The presence of Balmer lines in the spectrum excited by the microwave discharge indicates that H ₂ O at low pressures is dissociated to H and OH and a fraction of the H atoms is excited. (Fig 5)	NaD line is excited by reacting H and OH obtained from microwave discharge of H ₂ O with Na ₂ O boiled off from the pyrex glass of the experimental tube. (Pyrex glass contains about 3.8% of Na ₂ O and of this 0.1–0.01% is realised by heating it to 100°C.) $\begin{aligned} \text{Na}_2\text{O} + \text{OH} &\rightarrow \text{NaO} + \text{NaH} \\ \text{Na}_2\text{O} + \text{H} &\rightarrow \text{NaH} + \text{NaO} \\ \text{NaO} + \text{H} &\rightarrow \text{NaH} + \text{O} \\ \text{NaH} + \text{H} &\rightarrow \text{Na}^* + \text{H}_2 \\ \text{NaH} + \text{OH} &\rightarrow \text{Na}^* + \text{H}_2\text{O} \\ \text{Na}^* &\rightarrow \text{Na} + h\nu \end{aligned}$
Ghosh and Gupta 1972 <i>Ind. Jour. Phys.</i> 46, 8-17	CO ₂	Purple	CO Angström band (B ¹ Σ ⁺ → A ¹ π) 3PG (b ³ Σ ⁺ → a ³ π), 4PG (A ¹ π → X ¹ Σ ⁺). Some bands of the 1NG and comet tail system of CO ⁺ are also observed. In addition a few weak features of the Fox-Duffendack-Barker and the CO-flame bands of CO ₂ are present. Some unidentified bands are also observed (Figs 6, 33 and 35).	As in the case of microwave discharge of N ₂ , dissociation may occur through ionization followed by dissociative recombination. Assuming the same mechanism for CO ₂ , excited CO molecule will be produced by the reaction $\text{CO}_2 + h\nu \rightarrow \text{CO}^* + \text{O}.$ The excitation of 3PG, 4PG and Angström bands of CO may be explained as follows: $\begin{aligned} \text{CO}_2(\text{B}^2\Sigma_u^+) + h\nu &\rightarrow \text{CO}(\text{B}^2\Sigma^+) + \text{O} + 2.3\text{eV} \\ \text{CO}_2(\text{B}^2\Sigma_u^+) + h\nu &\rightarrow \text{CO}(\text{B}^1\Sigma^+) + \text{O} + 1.9\text{eV} \\ \text{CO}(\text{B}^2\Sigma^+) &\rightarrow \text{CO}(\text{a}^2\pi) + h\nu \text{ (3PG band of CO)} \\ \text{CO}(\text{B}^1\Sigma^+) &\rightarrow \text{CO}(\text{A}^1\pi) + h\nu \text{ (Angstrom band of CO)} \\ \text{CO}(\text{A}^1\pi) &\rightarrow \text{CO}(\text{X}^1\Sigma^+) + h\nu \text{ (4PG and of CO)}. \end{aligned}$

Pressure Effect

Spectra are obtained at CO₂ pressures of 0.05, 0.10, 0.15 and 0.20 torr. It is observed that although the decrease of intensity takes place over the entire spectrum (2000 Å–7000 Å), it is faster in the higher wavelength region. (Fig 7)

Temperature Effect

Spectra were taken at room temp. (300°K) and at 370°K and 475°K. A visual inspection of these plates shows that the spectra of discharge are not affected by temp. CO₂ at pressures of 0.08 and 0.20 torr. (Fig 8).

An electronic discharge through air produces a greenish-white afterglow which is produced by the reaction:

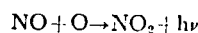


Table 2—Continued

Reference	Gas	Colour of the afterglow	Spectral features	Remark
			where $h\nu$ is a continuum. Stutt 1911 observed it in the spectral range 4200-6700Å in the air afterglow and believed it to originate from reaction between NO and O₂. Spealman and Rodebush 1936 remarked that the continuum is produced by the above reaction between NO and O and not between NO and O₂. Tanaka and Shimazu 1949 confirmed the mechanism and observed that in the reaction between NO and O₂, the intensity distribution is different compared to that for the continuum. Fontijn et al 1964 produced the glow in the range 3900-14000Å by reacting NO and O and observed that the glow attains maximum intensity at 6000Å. Reeves et al 1964 observed that in the range 3.20×10^{-3} torr. The intensity of the continuum is proportional to square of pressure.	
Ghosh, Srivastava and Shukla 1970 <i>Ann. Geophys.</i> 26 , 53-58	N ₂ and O ₂ mixture	Greenish white	Distinct NO ₂ continuum in the range 4000-7000Å was observed. Below 4500Å a few bands of N ₂ 2PG and 1NG band of Na ⁺ were present. (Fig 9).	$N + O + N_2 \rightarrow NO + N_2$ $NO + N \rightarrow N_2 + O$ $NO + O \rightarrow NO_2$ $NO_2^* \rightarrow NO + h\nu$ (NO ₂ continuum)
Ghosh, Srivastava and Shukla (1970) <i>Ind. Jour. Phys.</i> 44 , 162-171			<i>Temperature Effect</i> Considerably quenched with the rise of temperature in the range 25-180°C 2PG & 1NG bands have a small negative temperature coeff.	$N + O + N_2 \rightarrow NO + N_2$ ($A^3\Sigma^+_u$) $O + O + N_2$ ($A^3\Sigma^+_u$) $\rightarrow$ O ₂ + N ₂ ($C^3\pi_u$) N_2 ($C^3\pi_u$) $\rightarrow$ N ₂ ($B^3\pi_u$) + $h\nu$ (2PG System of N ₂)
				For the excitation 2PG system in N₂ afterglow, the presence of O is essential. The quenching of 2PG system by O₂ is much larger compared to that by N₂. In the night airglow, there is a continuum in the spectral range 4000-7000Å (Krassovsky, 1962 <i>Planet. Space Sci.</i> 9, 883-915). It shows maximum intensity at 6000Å. The mechanism is suggested for the emission of continuum in the night airglow (Krassovsky V. I. 1951 <i>Doklady. Acad. Nauk U.S.S.R.</i> 78, 669-672; Bates D. R., <i>Rocket Exploration of the Upper Atmosphere</i> 1954, Pergamon Press, London, p 347; Broida, H. P and Gaydon A. G. 1954 <i>Proc. Roy. Soc. (London)</i> A, 222, 181-195).
Ghosh, Dixit and Prasad (in preparation)	NO	Pale reddish orange excited by 100 MHz high frequency discharge	Gamma band of NO, 1PG and 2PG of N₂ & 1NG of N₂⁺ and certain feature unidentified (Figs 10 and 34). <i>Effect of Pressure</i> The intensity of the glow was found to be maximum at a NO pressure of about 200 mtorr and then decreases continuously as the pressure was increased to about 900 mtorr.	It is to be noted from M.I.T. Wavelength Tables that intensities of Ar II lines excited by spark discharge are very faint. Also by proton bombardment Ar II lines are not detected because of small charge exchange cross-section for excitation by low energy protons. The observed absence of Ar II lines by microwave discharge may be due to low intensity of ionized lines. <i>Temperature Effect</i> From room temperature to 200°C, it was observed that the intensity of the glow is independent of temperature.
Ghosh & Dasgupta (in preparation)	**Ar	Faint purple glow	Only neutral lines of Ar are excited (Figs 11 and 29).	

*Nitric Oxide has been the subject of numerous studies due to its importance in Aeronomy. They are summarised in the papers of Norton and Barth 1970, Reid 1971 and Mitra and Rowe 1974.

The (NO) γ -bands are prominent in the near ultra-violet spectrum of the airglow. Barth 1966 first reported observations on nitric oxide spectrum in the day airglow and observed that the airglow spectrum in the region of 2000-3000Å is dominated by nitric oxide spectrum. Ghosh 1968 calculated its distribution and afterwards verified it from rocket observations. Oliver 1974 reported its number densities to be 2×10^7 cm⁻³ and 1.6×10^8 cm⁻³ at 130 km and 280 km respectively.

**Afterglows of inert gases (He and Ar) have been studied in detail.

Table 3—Spectroscopic studies of reaction glow of dissociated atoms and molecules

Reference	Dissociated atoms of	Reacting molecules	Colour of the glow	Spectral feature	Reaction	Remark
Ghosh, Jain and Gupta 1972, <i>Ind. Jour. Chem.</i> 10 , 182-186	N ₂	***CCl ₄		CN violet and red bands (Fig 12)	$N + CCl_4 \rightarrow CN^* + 2Cl_2$	A comparison of the intensity of CN bands in the reaction glow with CCl ₄ , CHCl ₃ , and CH ₃ Cl ₃ shows that the intensity decreases as Cl ₂ content of the compound increases. It appears that Cl ₂ molecules in reaction with CCl ₄ and CHCl ₃ quenches CN*. To confirm it Cl ₂ was introduced separately and it was observed that for each of the three compounds CN band intensity decreases considerably.
Ghosh, Jain and Gupta 1972, <i>Ind. Jour. Chem.</i> 10 , 182-186	N ₂	***CHCl ₃		CN violet and red bands (Fig 12)	$N + CHCl_3 \rightarrow CN^* + HCl + Cl_2$	Mass spectrometric studies of reaction of the gaseous mixture drawn from the reaction chamber shows that HCl is formed.
Ghosh, Sharma and Sharda Nand 1962 <i>Proc. Phys. Soc.</i> 79 , 207-218	N ₂	***CH ₂ Cl ₂	A faint orange glow	CH(4312.5 and 4315 Å) and CN violet and red bands (Fig 13)	$N + CH_2Cl_2 \rightarrow CN^* + 2HCl$	
Ghosh, Srivastava and Shukla 1969 <i>Ind. J. Phys.</i> 43 , 631-645	O ₂	†Na	Yellow	5893, 3302 } Na (Fig 30) 5679 } and H α and Na line at 6157.5 Å — weak 1 PG of N ₂ and NO- β bands	$Na + O \rightarrow NaO$ $NaO^* \rightarrow NaO + h\nu$ $NaO + O \rightarrow Na + O_2$ $Na^* \rightarrow Na + h\nu$ (5893, 3303 Å) $N + O_2 \rightarrow NO + O$ $N + NO \rightarrow N_2 + O$ $O + O + wall \rightarrow O_2 + wall$	Sodium glow does not appear with N ₂ free from O ₂ . The glow is produced by NaO reaction. The amount of oxygen required to produce the glow is small (about 5%). The intensity of NaD line in the atmosphere at night has maximum intensity around 100 km and has value 30R in summer and 200R in winter. The intensity decreases fast with increasing temp.

***Reactions between organic compounds and active nitrogen were first studied by Stutt. He introduced organic compounds into active nitrogen and observed CN bands. Detailed studies of such reactions have been carried out by many investigators (5-10). Ghosh et al investigated reactions between active nitrogen and methylene chloride. These studies have been extended to include reactions between active nitrogen and chloroform and carbon tetrachloride.

†Tanaka 1951 and Tanaka & Ogawa 1954 produced sodium glow in the laboratory by reaction between ozone and sodium vapour and concluded the following:

- (1) Compared to atomic sodium, molecular sodium plays a more important role in the reaction.
- (2) The sodium glow is produced mainly by reaction between molecular sodium and ozone and not between molecular sodium and oxygen. It was shown by Ghosh, Srivastava & Shukla 1969 that oxygen quenches the sodium glow to a great extent. Hence the glow produced by reaction between sodium and oxygen may be subsequently quenched. It was also shown by them that the amount of oxygen required to produce the glow is small (about 0.5 per cent) and that compared to N₂ and Ar, O₂ quenches sodium glow strongly.

Table 4—Photometric studies of reaction glow

Emitted Radiation	Range of pressure variation	Gas whose press is varied	Intensity variation
N_2 2PG bands at 3371Å and 3577Å (Ghosh, Srivastava and Sukla 1970 <i>Ind. Jour. Phys.</i> 44, 162-171)	100-650 torr for 3371Å and 3577Å	N_2 varied keeping O_2 const.	Intensity of these bands at first rises linearly with N_2 pressure so that $I=k_1 p$ and after attaining a maximum in the pressure range (300-400 mitorr) begins to fall linearly so that $I=k_2 p$. (Fig 14)
	85-200 torr for 3371Å and 3577Å	O_2 varied keeping N_2 const.	Quenching by O_2 is considerable even at small concentration. The fall of intensities are given by $I p^2 = K_3$, for 3577 and for 3371Å $I p^2 = k_4$. (Fig 15)
	25-325°C		The fall of intensity with temp. is small and can be represented by (Fig 16). $I = \alpha T + I_0$ where $\alpha = -1.84 \times 10^{-3}$ micro A/°C for 3371Å. and $\alpha = -2.92 \times 10^{-3}$ micro A/°C and with pressure (Fig 17).
H_2 in the afterglow of H_2O (Ghosh, Shukla and Srivastava 1970 <i>Ind. Jour. Pure and App. Physics</i> , 8, 806-810)	190-1000 mitorr 330-1000 mitorr	H_2O at fixed flow rate of H_2O	The nature of fall of intensities with pressure for the three cases are similar.
NO_2 Continuum (Ghosh, Srivastava and Shukla 1970 <i>Ann. Geophys.</i> 26, 53-58)	290-1000 mitorr 120-600 mitorr	O_2 at fixed flow rate of H_2O As the O_2 pressure is increased keeping flow of N_2 fixed, the intensity at 5300Å increases as $I=k_2 p$ attains max at 200×10^2 torr and then decreases as $I=k_3 p^{-1}$. (Fig 18).	Four sets of observations were made, namely the variation of the intensity of the continuum with (1) wavelength (2) with N_2 pressure (3) O_2 pressure (4) the effect of the ratio N_2/O_2 of the intensity maximum.
	340-600 mitorr 90-400 mitorr 120-500 mitorr	The effect of N_2/O_2 ratio in the intensity of continuum at 5300Å shows that the intensity maximum shifts towards lower pressure as the N_2 concentration is increased. (Fig 19).	The intensity is maximum at about 210×10^{-2} torr. At first the intensity increases with wavelength, attains maximum at 6000Å and then decreases. (Fig 20).
CN band at 3883Å (Ghosh, Jain and Gupta 1972, <i>Ind. Jour. Chem.</i> 10, 182-186)	0-0.70 torr (for CCl_4 & $CHCl_3$) 0-0.15 (CH_2Cl_2)	Keeping N_2 constant and varying CCl_4 , $CHCl_3$ and CH_2Cl_2 vapour partial pressure (Fig 22)	For observing the variation of intensity with N_2 pressure, the continuum at 5300Å was selected. With fixed flow rate of O_2 the intensity rises with press as $I=k_1 p^3$, attains max at 240×10^{-2} torr and then decreases as $I=k_2 p^{-1}$. (Fig 21).
			Intensity at first increases rapidly with pressure and after attaining max it is quenched following a rectangular hyperbolic curve with pressure and finally at a total press of 5-6 torr the glow is completely quenched. For CH_2Cl_2 , within the experiment error, it is found that while the glow is being produced, the intensity varies as $5/2$ power of pressure of CH_2Cl_2 . The initial increase in the rate of production of excited CN is due to the increased number of these organic molecules which react with the active nitrogen. When the number of these organic molecules increases further, the unreacted organic molecules start quenching the excited CN molecules.

Continued

Table 4—Continued

Emitted Radiation	Range of pressure variation	Gas whose press is varied	Intensity variation
5893Å and 3302Å of Na Ghosh, Srivastava and Shukla 1969, <i>Ind. Jour. Phys.</i> 43, 631-645	In the range 18-150 mtorr	Keeping CCl ₄ , CHCl ₃ and CH ₂ Cl ₂ at constant pressures and varying N ₂ pressure (Fig 23).	It is seen that CN band intensities are lower for reactions between active nitrogen and CHCl ₃ and CCl ₄ by a factor of about 10 and 15 respectively. It was observed that the CN band intensity in- creases rather slowly with the N ₂ partial pressure in the range 0.0-4 torr. This may be due to slow increase in the number density of atomic nitrogen with the partial press of N ₂ in that range. At high pressure (above about 0.4 torr) the intensity variation is linear with the N ₂ partial pressure. The reactions are first order in nitrogen atoms and the reacting organic compounds.
3134Å (0, 2) 3PG 4393Å (1, 1) Angström band of CO (Ghosh and Gupta 1972 <i>Ind. Jour. Phys.</i> 46, 8-17)	20-250 mtorr	Varying the intensity with pres- sure of (a) tank N ₂ , (b) tank O ₂ , (c) tank N ₂ at a fixed flow rate of argon and (d) tank argon at fixed flow rate of tank N ₂ , (e) with purified N ₂ , (f) with purified N ₂ and fixed flow rate of tank argon (g) with tank argon fixed flow rate of purified N ₂ Varying CO ₂ pressure	The increase of intensities of 5893Å and 3302Å with pressure before reaching the maximum values can be represented by $I=cp^2$. These lines are quenched in decreasing order by tank O ₂ , tank Ar, tank N ₂ and a mixture of tank N ₂ and argon. The quenching of these lines (when the glow was produced by N ₂ nearly free from O ₂) by tank argon is large compared to the quenching by pure N ₂ and mixture of pure N ₂ and tank argon. It is observed that starting with the maximum intensity of CO ₂ pressure of about 0.04 torr, the minimum at which the discharge can sustain, intensities of both these bands go on decreasing with increasing CO ₂ pressure. The variation of 3134Å' can be represented by $I=$ k/p where k is a constant. The intensity variation of the (1, 1) Angström band at 4393Å decreases linearly with increasing CO ₂ pressure from 40 to 240 mtorr and may be re- presented as

$$I=I_0-kp$$

where I_0 is the intensity corresponding to the rate
of production of CO* at 40 mtorr. This may be
due to the fact that CO($B^1\Sigma^+$) is deactivated by
certain non-linear reactions in addition to the first
order deactivation by CO₂ molecules.

Life time= 1.05×10^{-8} sec. of vibrational level
 $v=2$ of $A^1\Pi$ of CO. Since $B^1\Sigma^+$ and $b^3\Sigma^+$ states
also undergo electric dipole transitions their life
times may be comparable.

Continued

Table 4—Continued

Emitted Radiation	Range of pressure variation	Gas whose press is varied	Intensity variation
Ghosh and Dasgupta (communicated)	A	40-250 mtorr	The intensity increases as the pressure is increased, attains a maximum at about 70 mtorr after which the glow is quenched at first slowly and then rapidly. It is observed that for the building part of the glow, the variation of intensity is parabolic with pressure. The quenching curve can be divided into two parts: (i) For the pressure ranging from 85 to 147 mtorr where the variation of intensity ratio is linear with particle concentration: The mechanism for excitation in this pressure range is $\begin{aligned} \text{Ar} + h\nu &\rightarrow \text{Ar}^* \\ \text{Ar}^* + \text{Ar} &\rightarrow \text{Ar}' + \text{Ar}'' \\ \text{Ar}^* &\rightarrow \text{Ar} + h\nu \end{aligned}$ (ii) when the pressure lies between 147 and 175 mtorr the variation of intensity is parabolic. The following mechanism has been proposed for this pressure range. $\begin{aligned} \text{Ar} + h\nu &\rightarrow \text{Ar} \\ \text{Ar} + \text{Ar}^* &\rightarrow \text{Ar}' + \text{Ar}'' \\ \text{Ar}^* + \text{Ar} + \text{Ar} &\rightarrow \text{Ar}_3^* + \text{Ar} \\ \text{Ar}_3^* &\rightarrow \text{Ar} + h\nu. \end{aligned}$ The intensity increases linearly with N_2 pressure $N + N + N_2 \rightarrow N_2(^4\Sigma_g^+) + N_2 \rightarrow N_2(B^3\Pi_g) + N_2$. Observation may be explained by assuming that for large conc. of O_2, N atoms are consumed by O_2 in a 3-body reaction. $N + N + O_2 \rightarrow N_2 + O_2'$ The intensity first increases parabolically with pressure becoming maximum at 200 mtorr and then it decreases. The intensities are maximum at 30 mtorr. Thereafter 2PG of N_2 and 1NG of N_2 decreases exponentially and 1PG of N_2 hyperbolically with pressure.
N_2 1PG band at 5804Å (Ghosh and Gupta) 1972 <i>Ind. Jour. Phys.</i> 46, 18-27	220-430 mtorr	N_2 varied O_2 varied (N_2 fixed)	
2370 2478	25-1000	NO	
3371 3577 6000 3914	25-250	NO	

Table 5— Quenching coefficient and quenching mechanism of reaction glow

Reference	Wavelength of emitted radiation (Å)	Quenching Species	Quenching Coeff. (cm ³ mol ⁻¹ sec ⁻¹)	Quenching Mechanism
Ghosh, Srivastava and Shukla 1970a <i>Ind. Jour. Phys.</i> 44 , 162-171	3371	O ₂	1.1 × 10 ⁻⁸	N ₂ (C ² π _u) + N ₂ → N ₂ ' + N ₂ ' N ₂ (C ² π _u) + O ₂ → N ₂ ' + O ₂ ' N ₂ (C ² π _u) + O → N ₂ ' + O' where N ₂ ', O ₂ ' and O' are energetic species.
	3371	N ₂	1.9 × 10 ⁻⁸	
	3577 of N ₂ , 2PG	O ₂	1.3 × 10 ⁻⁸	
	3577	N ₂	1.0 × 10 ⁻⁸	
Krasorsky and Shefov 1962 <i>Planet. Space Sci.</i> 9 , 883	N ₂ (A ³ Σ ⁺ _u)	N	10 ⁻¹⁰	N + CCl ₄ → CN* + 2Cl ₂ N + CHCl ₃ → CN* + HCl + Cl ₂ N + CH ₂ Cl ₂ → CN* + 2HCl
Ghosh, Jain and Gupta 1972 <i>Ind. Jour. Chem.</i> 10 , 182-186 Ghosh, Sharma and Sarda Nanda (1962), <i>Proc. Phys. Soc.</i> 79 , 207-218	3883Å band of CN	CCl ₄	1.4 × 10 ⁻⁸ at 300°K	
	" "	CHCl ₃	2.0 × 10 ⁻⁸ at 300°K	
	" "	CH ₂ Cl ₂	1.0 × 10 ⁻⁸ at 300°K	
Ghosh, Srivastava and Shukla 1970 <i>Ann de Geophys.</i> 26 , 53-58	NO ₂ continuum at 5300Å°	O ₂	$\frac{K}{A}(\text{O}_2) = 2.1 \times 10^{-16} \text{ cm}^3 \text{ mol}^{-1}$	NO ₂ * + O ₂ → NO ₂ + O ₂ *
		N ₂	$\frac{K}{A}(\text{N}_2) = 1.1 \times 10^{-16} \text{ cm}^3 \text{ mol}^{-1}$ A is the transition probability for emission of the continuum.	NO ₂ * + N ₂ → NO ₂ + N ₂ *
Ghosh, Shukla and Srivastava 1970 <i>Ind. Jour. Pure, App. Phys.</i> 8 , 806-810	H ₂ produced from microwave discharge of H ₂ O	H ₂ O O ₂ N ₂	1.80 × 10 ⁻⁸ 3.32 × 10 ⁻⁸ 1.98 × 10 ⁻⁸	H(2P) + M → H(n=2) + M' The quenching coeffs. for H ₂ O, N ₂ and O ₂ are similar to those of excited N atom by CH ₂ Cl ₂ (Ghosh, Sharma and Sharda-nand 1962 <i>Proc. Phys. Soc.</i> 79 , 207-218.

(Continued)

Table 5—Continued

Reference	Wavelength of emitted radiation (Å)	Quenching Species	Quenching Coeff. (cm ³ mol ⁻¹ sec ⁻¹)	Quenching Mechanism
Ghosh, Srivastava and Shukla 1969 <i>Ind. Jour. Phys.</i> 43, 631-645	NaD line	O ₂ Ar N ₂	1.9 × 10 ⁻⁷ at 300°K 1.1 × 10 ⁻⁸ at 300°K 3.8 × 10 ⁻¹⁰ at 300°K	Na* + O ₂ → Na + O ₂ Na* + Ar → Na + Ar Na* + N ₂ → Na + N ₂ O ₂ , N ₂ are vibrationally or electronically excited. Compared to N ₂ and Ar, O ₂ quenches the sodium glow very strongly.
Carrington 1959 <i>J. Chem. Phys.</i> 30, 1087	OH electronically excited	H ₂ O	3.5 × 10 ⁻¹⁴ cm ³	
Young and Black 1966 <i>J. Chem. Phys.</i> 44, 3741	O(¹ So)	O ₂		
Ghosh and Gupta 1972 <i>Ind. Jour. Phys.</i> 46, 8-17	3134 Å CO (3PG) 4393 Å CO (ANG)	CO ₂ CO ₂	3.5 × 10 ⁻⁸ 1.7 × 10 ⁻⁸	
Ghosh & Dasgupta (communicated)	4158 Å	Ar	K ₁ = 1.8 × 10 ⁻⁹ cm ³ /sec K ₂ = 3.2 × 10 ⁻¹⁰ cm ³ /sec	Ar* + e → Ar* Ar* + e + Ar → Ar* + Ar* The three-body process is operative throughout the whole pressure range (40-250 mtorr)
Ghosh, Prasad and Dixit (preparation)	2370 2478 3914 3371 3577 6000	NO	1.2 × 10 ⁻⁹ 6.5 × 10 ⁻¹⁰ 4.1 × 10 ⁻⁹ 4.4 × 10 ⁻⁹ 3.5 × 10 ⁻⁹ 1 × 10 ⁻¹⁰	NO* + NO → NO* + NO* Also NO is quenched by the wall.
Ghosh and Gupta, 1972 <i>Ind. J. Phys.</i> 1972, 46, 18-27	5804	O ₂	2.9 × 10 ⁻¹⁴	N + N + O ₂ → N ₂ + O ₂

Table 6—Ar lines excited by different processes

Emitted line (Å)	Excited by Spark discharge	Excited by proton bombardment	Excited by microwave discharge
3567, 3554	faint	faint	fairly strong
3947	strong	not excited	not excited
4044	strong	strong	faint
4198, 4510	strong	strong	not excited
4596, 4522	fairly strong	very faint	very faint

Table 7—Detailed information of Ar lines excited by different processes

Wavelength from M.I.T. tables (Å)	Element	Intensity by Spark discharge	Wavelength by Proton bombardment (Å)	Wavelength by Microwave discharge (Å)	Intensity by Proton bombardment (Visual)	Intensity by Microwave discharge (Visual)
1	2	3	4	5	6	7
4596.10	ArI	1000	4595.81	4596.90	VF	VF
4545.08	ArI	200	4544.54		VF	VF
4522.32	ArI	800	4522.01	4523.01	VF	VF
4510.73	ArI	1000	4510.71		M	
4426.01	ArI	300				
4348.11	ArI	500				
4345.17	ArI	1000	4347.18	4347.82	M	M
4335.34	ArI	800				
4333.56	ArI	1000	4333.35	4334.08	M	S
4331.25	ArI	200				
4300.10	ArI	1200	4300.15	4300.80	S	S
4272.17	ArI	1200	4272.13	4272.80	S	S
4266.29	ArI	1200	4266.09	4266.69	S	M
4259.36	ArI	1200	4259.74	4259.70	S	S
4251.19	ArI	800	4251.41	4252.00	S	M
4200.68	ArI	1200	4201.13	4200.40	S	S
4198.32	ArI	1200	4198.73		M	
4191.03	ArI	1200	4191.54	4191.10	M	M
4190.71	ArI	600				
4181.88	ArI	1000	4182.40	4182.60	M	M
4164.18	ArI	1000	4164.32	4164.00	M	M
4158.59	ArI	1200	4158.63	4158.52	S	S
4103.91	ArI	200		4102.19		F
4044.42	ArI	1200	4044.03	4045.00	S	F
4013.87	ArI	200				
3968.36	ArI	200				
3948.98	ArI	2000	3947.71	3948.00	S	S
3947.50	ArI	1000				
3894.66	ArI	300	3894.10		VF	
3850.57	ArI	400				
3834.68	ArI	800	3833.86	3834.51	M	M
3781.36	ArI	300				
3770.37	ArI	400	3771.43	3769.80	VF	VF
3729.29	ArI	200				
3690.90	ArI	300		3690.30		VF
3675.22	ArI	300		3674.80		VF
3670.64	ArI	300	3670.57	3670.24	VF	VF
3659.50	ArI	100		3659.13		VF
3649.83	ArI	800	3649.33	3649.21	F	VF
3643.09	ArI	100		3642.89		VF
3634.46	ArI	300	3634.54	3634.23	VF	VF
3632.68	ArI	300	3632.94	3632.01	VF	VF
3606.52	ArI	1000	3606.97	3606.45	M	M
3588.44	ArI	300				
3576.62	ArI	300	3576.35		F	
3572.29	ArI	300	3569.46		VF	
3567.66	ArI	300	3565.24	3567.88	VF	M
3563.26	ArI	100		3562.79		VF
3551.31	ArI	300	3554.78	3554.69	F	M

The reaction system is made of pyrex glass (Fig. 1). It was thoroughly cleaned by rinsing with dilute hydrofluoric acid and then with distilled water, thereby removing the effects of surface conditions on the reaction kinetics. Gases introduced into the tube through needle valve n_1 were dissociated directly by microwave discharge. Several molecules, e.g., N_2 and CO_2 were first ionized by microwave discharge and then were followed by dissociative recombination. A microwave reflector was placed in front of the tube. A Raytheon microtherm (magnetron oscillator) of Type CMD-4 and having maximum output power of 100 W was used for the generation of microwaves at a frequency of 2450 MHz. The products of microwave discharge and the gases to be reacted were introduced into the reaction chamber. The flow of reaction gases was regulated by the needle valve n_2 .

The partial pressures of the dissociated atoms and the reacting gases were measured by an alphanatron gauge (Type 0510, National Research Corporation, USA) calibrated against an oil manometer and connected to the tube in the vicinity of the reaction chamber. The mouth of the outer tube of the reaction chamber was closed with a quartz window. In order to ensure quick removal of the reaction products, a high speed Cenco Hyvac I4 rotary pump was employed. Through an additional tube having a needle valve n_3 , a third gas was sometime introduced to observe quenching of the glow.

The following procedure was adopted for obtaining the reaction glow. The reaction system was evacuated and the gas to be dissociated was slowly introduced into the discharge tube through the needle valve n_1 . A microwave discharge through the gas in the tube was then initiated.

The reacting gas was then introduced into the reaction chamber through the other needle valve n_2 . The reaction glow then appeared in the reaction chamber. The brightness of the glow was increased to maximum by adjusting the flow of the two gases. It was

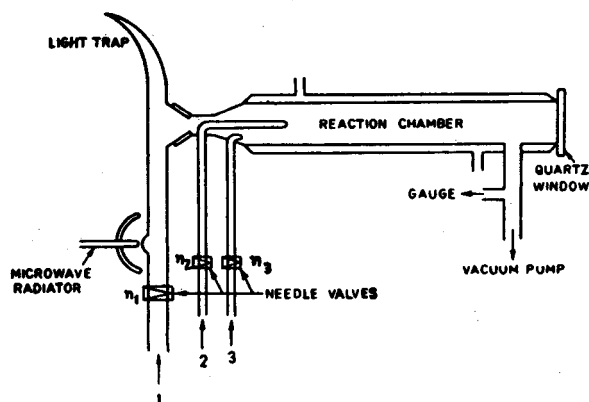


Fig. 1—Experimental arrangement for the dynamical flow system

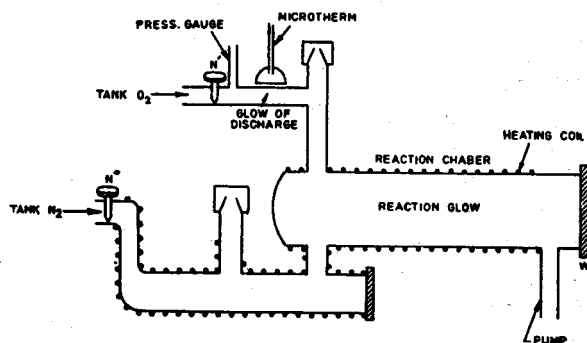


Fig. 2—Experimental arrangement for the study of afterglow

observed that in certain cases, for example, the reaction between dissociated N atoms and CH_2Cl_2 , the intensity of the reaction glow diminished considerably with time and within half an hour the intensity became so faint that it was invisible. In order to maintain the glow with constant intensity, in this case, the reaction chamber was cooled by circulating cold water through the jacket. It was then observed that the intensity of the glow did not change appreciably even after an hour.

For reaction between sodium and oxygen, the apparatus shown in Fig. 2 was used. Sodium vapour was produced in a chamber below the reaction chamber by heating solid sodium in an atmosphere of N_2 or argon (these gases prevent burning of sodium in the residual oxygen present in the system). The vapour was carried to the reaction chamber by a current of N_2 or argon gas. The wall of the reaction chamber was heated to prevent condensation of sodium vapour on it. The O_2 gas (tank O_2 or O_2 containing about 0.5% of tank N_2 as impurity) was dissociated by microwave discharge and was introduced into the reaction chamber opposite to the inlet of the sodium vapour. The discharge was maintained by a Raytheon microtherm.

The spectroscopic, photometric and microphotometric studies were carried out with the help of equipment detailed in the following:

3 Observational Methods

3.1 Spectroscopic Studies

The spectra of the glow were taken with a Hilger E₁ Quartz spectrograph using Kodak I03a, F and O plates. The spectra were taken in the region 2000–7000 Å. As mentioned in Sec. 1, the spectra of microwave discharge and of reaction glow revealed information on the nature and state of the reactants and of reaction products respectively.

3.2 Photometric Studies

For photometric studies, certain strong bands or lines of the spectrum were picked up with a Bausch and

Lomb monochromator of type 33-86-40 using a grating of 250 mm focal length, 600 lines per mm and a dispersion of $66 \text{ \AA mm}^{-1}$. The intensities were measured by a photomultiplier (RCA IP28) to which an ultrasensitive dc microammeter (RCA W.V-84B) was connected. The voltages to the different dynodes of the photomultiplier tube were applied from a superstable high voltage power supply (3I2A, Baird Atomic Inc.) which can give a maximum voltage of 1500V. Keeping the flow of one of the reactant gases constant, the variation in the intensity of the glow with the partial pressure of the other reactant (recorded by an alphasatron gauge, which was previously calibrated with respect to an oil manometer) was plotted. From the nature of the curve, the order of the reaction producing the glow and its quenching was obtained.

3.3 Microphotometric Studies

To obtain the intensity of the lines and bands of discharge and of reaction glow, the photodensitometric records of their spectra were taken by a Kipp and Zonen Molt microphotometer (Type A).

In certain cases, the intensities were recorded by a Hilger and Watts (London) microphotometer (No. L459.301/57) utilizing RCA931A photomultiplier tube coupled to a Minneapolis Honeywell recorder (Model I53X 17V-X-3R). The photomultiplier tube was supplied with a voltage of 800V by a series of dry batteries. To account for the drift in the coupling and dc amplifiers, the dark current signal was recorded at regular intervals. The plates were scanned from 2800 to 7000 $\text{\AA}$ with the help of a servomotor rated for a speed of 0.75 mm/min.

3.4 Mass Spectrometric Studies

With the help of mass spectrometric analysis of the gases near the reaction glow, the products of the reaction were identified.

3.5 Method of Determining Reaction Order and Quenching Coefficient

Let us consider reaction (1). With the increase of partial pressure of CD molecules, the intensity of the glow rises till it attains a maximum, after which the glow decreases and finally it is completely quenched (Fig. 3). The ultrasensitive dc microammeter then reads only the dark current of the photomultiplier tube. For higher flow of molecules, it will be observed that the nature of the curve is the same except that the value of maximum intensity increases and is attained at a lower CD pressure. The curves relating to the intensity with CD molecular pressure for the building and also for the quenching portion are then determined. From the nature of these curves, the order of the reaction and the quenching coefficient can be determined. In certain

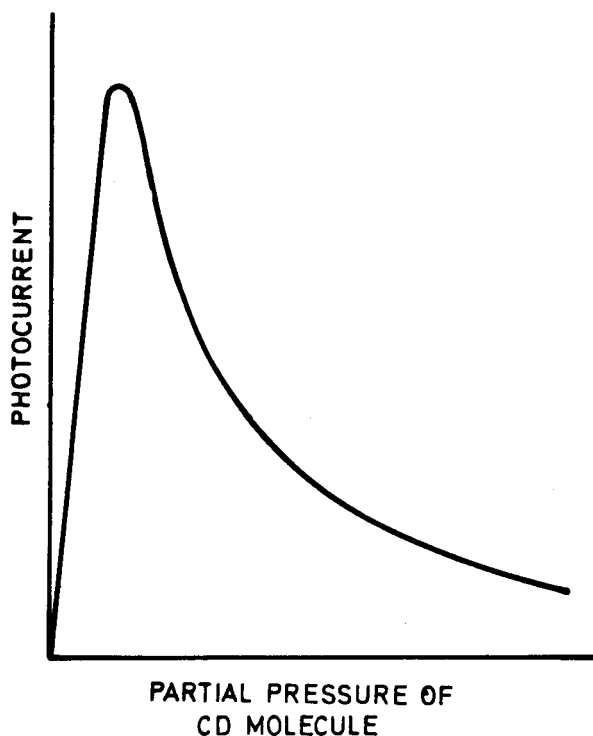


Fig. 3—Intensity variation of glow with increase of partial pressure of CD molecules

reactions, the intensity of the glow for the rising part increases very quickly with pressure, so that sufficient number of observations cannot be taken. To compensate for this, several curves relating the variation of the intensity of the glow with the partial pressure of CD (for the same flow of AB) are drawn and the mean of these curves is then plotted.

Equating the rates of production and destruction of AC^* or BC^* molecules, we obtain

$$\beta n(A' \text{ or } B'')^a n(CD)^b = n(AC^* \text{ or } BC^*) [A + K_1 n(CD)]$$

where β is the rate coefficient of the reaction, $n(A')$ the concentration of A' atoms, $n(CD)$ the concentration of CD molecules, a and b are constants, A the transition probability for the excited AC^* or BC^* molecules and K_1 , the rate coefficient of the quenching process.

Therefore, the rate of emission of photons per $\text{cm}^3(R)$ from the excited AC^* or BC^* molecules is given by

$$R = A \frac{\beta n(A' \text{ or } B'')^a n(CD)^b}{A + K_1 n(CD)}$$

The photomultiplier current (I), which is proportional to R , is given by

$$I = \alpha A \frac{\beta n(A' \text{ or } B'')^a n(CD)^b}{A + K_1 n(CD)}$$

where the constant α depends upon the geometry of the reaction chamber and the sensitivity of the photometric system.

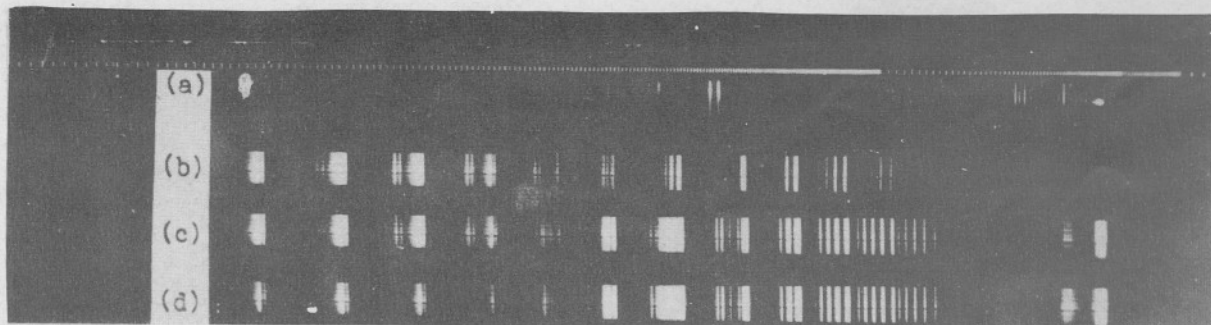


Fig. 4—Spectra of NO gas excited by 100 MHz frequency discharge [(a) copper arc spectrum; (b) NO spectrum at 400 m Torr pressure; (c) NO spectrum at 200 m Torr pressure; and (d) NO spectrum at 300 m Torr pressure]

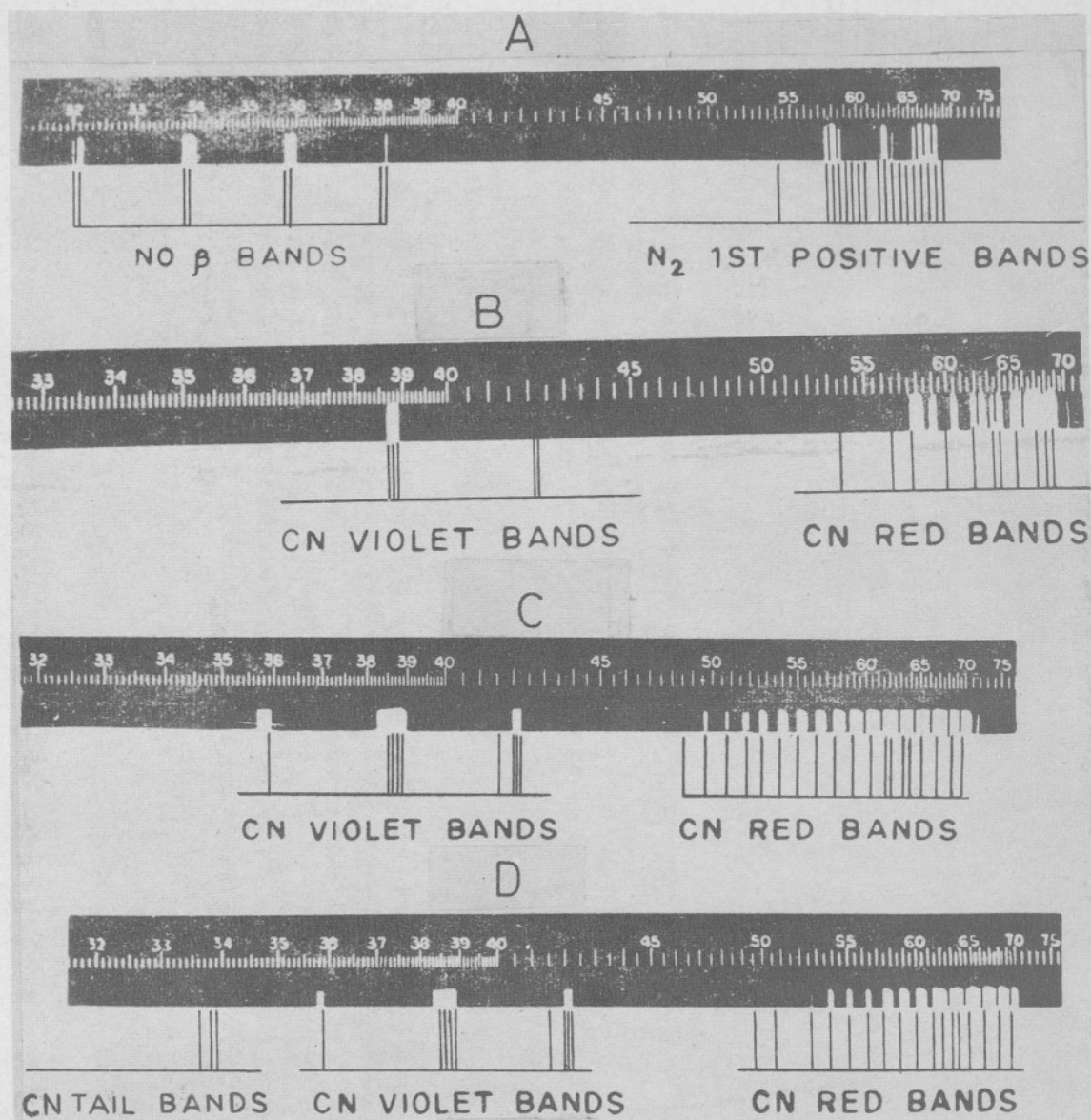


Fig. 5—Spectra of (A) nitrogen afterglow (exposure time, 16 hr); (B) active nitrogen-CCl₄ reaction glow (exposure time, 12 hr); (C) active nitrogen-CHCl₃ reaction glow (exposure time, 8 hr); and (D) active nitrogen-CH₂Cl₂ reaction glow (exposure time, 3 hr)

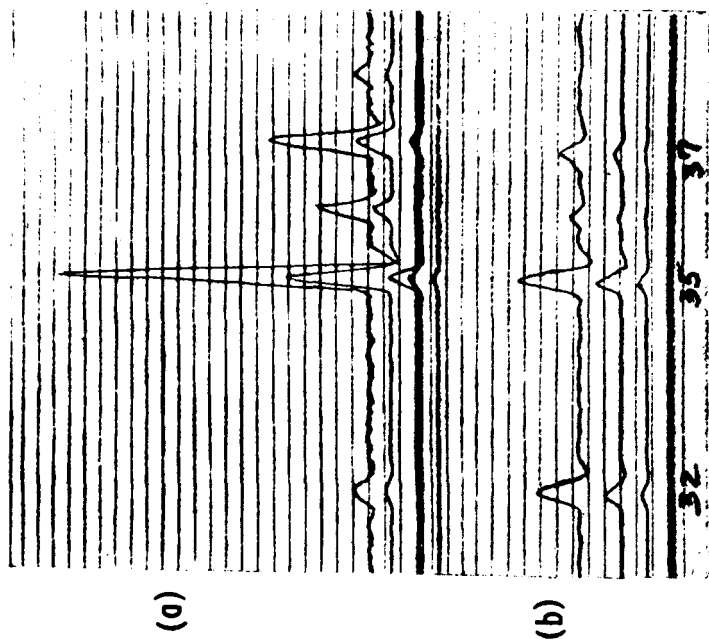


Fig. 8—Mass spectrometric record of the gas collected (a) during discharge and (b) when the discharge is off for the reaction between active nitrogen and CH_2Cl_2 . Note that the spectrum of the gas collected during discharge shows the presence of HCl line.

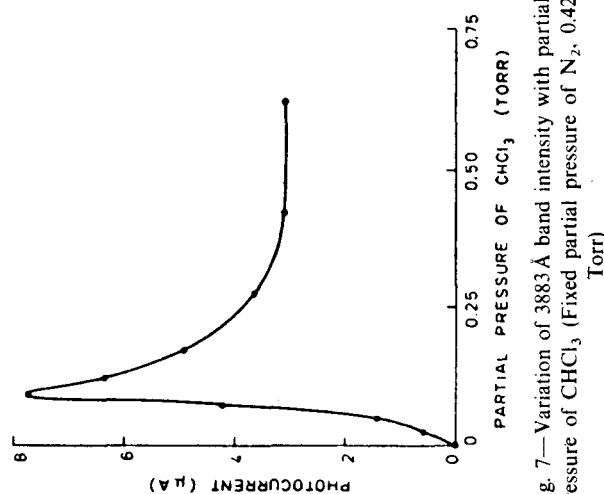


Fig. 7—Variation of 3883 Å band intensity with partial pressure of CHCl_3 (Fixed partial pressure of N_2 , 0.42 Torr)

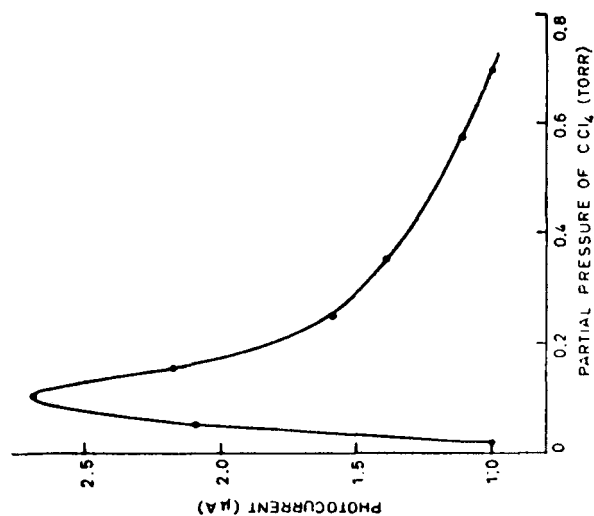


Fig. 6—Variation of 3883 Å band intensity with partial pressure of CCl_4 (Fixed partial pressure of N_2 , 1.00 Torr)

Assuming that the rate of production of excited AC* or BC* molecules becomes constant after attaining the maximum, we have

$$\beta n(A' \text{ or } B'')^a n_M(\text{CD})^b = S$$

where $n_M(\text{CD})$ is the concentration of CD when the rate of production of excited molecules is maximum, and S the rate of production of AC* or BC* molecules when the glow intensity is maximum.

Therefore, the maximum photomultiplier current (I_M) is given by

$$I_M = \frac{\alpha S A}{A + K_1 n_M(\text{CD})}$$

If at a higher concentration of CD molecules, $[n'(\text{CD})]$, the photomultiplier current is half that of the maximum, we have

$$\frac{A + K_1 n'(\text{CD})}{A + K_1 n_M(\text{CD})} = 2$$

or

$$K_1 = \frac{A}{n'(\text{CD}) - 2 n_M(\text{CD})} \quad \dots (2)$$

$n'(\text{CD})$ and $n_M(\text{CD})$ are obtained from the corresponding partial pressure of CD from Fig. 3 and the temperature of the chamber. From the known value of A , one finds K_1 from Eq. 2. When K_1 is known, the quenching cross-section, σ^2 , can be computed from the expression

$$\sigma^2 = K_1 \left[8 \pi k T \left(\frac{1}{m_{AC} \text{ or } m_{BC}} + \frac{1}{m_{CD}} \right) \right]^{-1/2} \quad \dots (3)$$

where k is Boltzmann constant, T the absolute temperature of the reaction chamber, and m_{AC} , m_{BC} and m_{CD} the molecular masses of AC, BC and CD molecules respectively.

4 Experimental Results

4.1 Spectroscopic Studies

Experimental results of (i) spectroscopic studies of microwave and R.F. discharges of N_2 , H_2O , CO_2 , N_2 and O_2 mixture, NO and Ar (Table 2 and Fig. 4), (ii) reactions between dissociated atomic nitrogen and CCl_4 , CHCl_3 , CH_2Cl_2 (Table 3 and Fig. 5), (iii) reactions between atomic oxygen and sodium (Table 3) are summarized. Results of photometric studies of reaction glow are presented in Table 4 and Figs 6 and 7. Quenching coefficients and details of quenching mechanisms of the glow are given in Table 5.

4.2 Microphotometric and Mass Spectrometric Studies of Reaction Glow

Microphotometric traces of lines and continuum in the range 4000-7000 Å were obtained.

A mass spectrometric study was carried out only for one reaction, namely, between active nitrogen and CH_2Cl_2 (Fig. 8). The gas was collected both during discharge and when the discharge was off. The analysis was carried out by a beam-type mass spectrometer. The spectrum of the gas collected during discharge showed the HCl line.

5 Comparison of Excited Spectra

Table 6 shows the intensities of Ar lines excited by spark discharge, proton (1.6 keV) bombardment and microwave discharge. In general, they are more or less similar. However, certain marked differences are observed as given in Table 7.

It is to be noted from MIT Wavelength Tables that intensities of Ar II lines excited by spark discharge are very faint. Also, by proton bombardment, Ar II lines are not detected because of small charge exchange cross-section for excitation by low energy protons. The observed absence of ionized lines in microwave discharge may be due to their low intensity.