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Chemiluminescence in cryogenic matrices

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ABSTRACT. The literature data on chemiluminescence (CL) in cryogenic matrices have been classified and correlated for the first time. The role of studies on phosphorescence and CL at low temperatures in the development of cryochemistry is shown. The features of low-temperature CL in matrices of nitrogen and inert gases (fine structure of spectra, matrix effects) and the data on the mobility and reactivity of atoms and radicals at very low temperatures are examined. The trends in the development of studies on CL in cryogenic matrices, such as the search for systems involving polyatomic molecules and extending the forms of CL reactions, are followed. The reactions of active nitrogen with hydrocarbons that are accompanied by light emission and CL in the oxidation of carbenes at $T \geqslant 77$ K are examined.

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I. Introduction

During the last three decades a separate new branch of chemistry has been formed—cryochemistry. The impressive results obtained in low-temperature chemistry have been correlated in a number of monographs and review articles.[1-10] There are quite a number of theoretical models that examine the mechanisms of low-temperature reactions; but in representing the kinetics of such processes a number of problems still occur, which cannot be resolved without the collection and classification of experimental material. The kinetics and mechanism of low-temperature solid-state reactions have mainly been studied using spectroscopic methods, among which chemiluminescence (CL) plays an important role.

Every year hundreds of reports on new CL reactions, investigations of their mechanisms, and applied aspects of the phenomenon are published. In this stream of information, some studies on low-temperature solid-state CL, comparatively few in number but very interesting, get lost. It is appropriate to recall here that the CL method can be used to measure directly the rate of a chemical process. When the high sensitivity of the CL method, which under favourable conditions permits the monitoring of changes down to only thousands or even hundreds of molecules per second, which are inaccessible to calorimetry, EPR, and absorption spectroscopy, is taken into consideration, it becomes clear that there is future potential in using low-temperature CL to study those solid-state processes which, as a rule, occur at a low rate. It is a favourable circumstance that in cryogenic systems temperature quenching of luminescence is suppressed to a considerable degree, and there is a substantial increase in the number of particles which can exist in electronically excited states during the time required to record them.

Low-temperature CL reactions do not constitute an exotic class; they occur over a wide range of temperatures and in various media—from cryogenic matrices of nitrogen and inert gases to frozen aqueous[11,13-15,17,18] and nonaqueous[12,16,19,20] solutions. Chemiluminescence at low temperatures accompanies radical recombination, atom transfer reactions, and a number of redox reactions such as oxidation of sulphur with ozone,[11] uranium(IV) sulphate complexes with ozone and xenon difluoride and trioxide,[12] luminol with oxygen and hydrogen peroxide,[13,15,18] triethylaluminium with xenon difluoride,[16] and reduction of $[Ru(bipy)_3]^{3+}$ with sodium borohydride,[14] the hydrolytic reduction of XeF_2,[17] and several other reactions.[12,19,20]

In this review we will not examine frozen solutions but will confine ourselves to CL in cryogenic matrices. The CL method is used to study the stabilisation of free radicals in nitrogen and inert gas matrices, to simulate under laboratory conditions the photochemical reactions that occur on the surface of dust particles in interstellar space, and to monitor the course and kinetics of chemical reactions in low-temperature matrices. Up to the present time, however, there have been no reviews in the world literature on studies devoted to low-temperature CL.

The present article serves a double purpose: firstly, to draw the attention of cryochemists to the unique possibilities of the CL method and, secondly, to alert the specialists in the field of gas-phase and liquid-phase CL to a new extensive region for application of efforts—low-temperature solid-state chemical reactions.

II. Early studies of phosphorescence and chemiluminescence at low temperatures

Investigations into the problems relating to the phenomenon of low-temperature CL were undertaken by Becquerel, Dewar, Lewis, and Rayleigh. The progress made by the end of the last century in the preparation and storage of liquid gases made it possible to widen the scope of studies in low-temperature chemistry and physics. Phosphorescence was detected at the temperature of liquid air for a large number of organic compounds, such as alkaloids, hydrocarbons, acids, alcohols, ethers,[1] but the mechanism of the phenomenon remained uncertain up to the 1940's, when as a result of the efforts of Jablonski,[21] Lewis,[22] Terenin,[23] and Kasha[24] it was

established that phosphorescence spectra are due to triplet-singlet electronic transitions from the lowest excited triplet states of molecules.

It was Dewar[25] who first observed the phosphorescence of a number of compounds at the boiling point of hydrogen. Back in 1903 in conjunction with Moissan he carried out a study of the reaction of liquid hydrogen with solid fluorine at 20.5 K.[26] Dewar was the first to use low-temperature traps cooled with liquid air for the preservation of unstable compounds.[27,28] Moreover, in conjunction with Jones he was the first to observe flashes of light accompanying the low-temperature explosive polymerisation of carbon monosulphide, whose spectrum contained cyanogen lines and sulphur and hydrocarbon bands.[27,28] Even earlier, in 1894, Dewar had detected the accumulation of ozone in liquid oxygen when exposed to electric discharge and he observed the luminescence of molecular and atomic oxygen produced by electron bombardment.[29] In the luminescence spectrum of oxygen he recorded, in particular, a green line (557.7 nm), which caused many disputes 34 years later in attempts to determine the nature of the aurora borealis and the luminescence of the night sky.

In 1924 Vegard[30] put forward the suggestion that the aurora borealis is caused by the luminescence of crystals of nitrogen present in the upper atmospheric layers when exposed to intense cosmic radiation. In attempting to confirm experimentally his hypothesis about the mechanism of this natural phenomenon, Vegard detected and studied in detail the luminescence of solid nitrogen condensed on a surface cooled to 20.5–4.2 K and then subjected to bombardment with electrons or positive ions. He considered that the green line that he observed with wavelength 557.738 nm was due to radiation from an excited nitrogen molecule. Vegard's hypothesis proved to be incorrect. McLennan and co-workers[31] measured the wavelength of the green line of oxygen with a Fabry–Perot interferometer and obtained a value of 557.7341 ± 0.0004 nm, which was in excellent agreement with the value of 557.7350 ± 0.0005 nm determined from astronomical measurements by Babcock.[32] Thus, it was demonstrated that the green line at 557.7 nm was due to the radiative $^1S \rightarrow {}^1D$ transition of an oxygen atom formed in the upper atmosphere as a result of solar radiation on molecular oxygen.[33]

Vegard was responsible for a remarkable observation which to a large degree assisted an extensive study of free radicals started three decades later. He found that after bombardment of solid nitrogen has ceased, a bright luminescence occurs for several minutes. On increasing the temperature of the sample the luminescence appears again, and its intensity and spectroscopic composition undergo changes during warming. The luminescence is not phosphorescent in nature, as was clear even after the first experiments of Vegard, who observed the emission of light from the sample when it was warmed several hours after electron bombardment had ceased. Consequently, it was shown that the luminescence produced by warming an irradiated nitrogen matrix is CL caused by the recombination of nitrogen atoms. Thus, Vegard was the first to observe CL in cryogenic matrices and to undertake a spectroscopic study of it under experimental conditions with good reproducibility.

Also to Vegard's credit is that he was in fact the first to use the method of matrix isolation in low-temperature spectroscopy. A pioneer in the concept of matrix isolation was Schmidt.[34] By assuming that the phosphorescence of compounds in liquid solution is considerably reduced as a result of the loss of excitation energy through molecular collision, he attempted to reduce the deactivation effect of excited particles by diluting them with inert molecules, placing the compound being studied in a rigid matrix or crystal (gelatine, sugar, papaverine). It was the experiments of Schmidt that served as an impetus for studying the effect of temperature and viscosity of the solvent on phosphorescence.

At the end of the 1920's many spectroscopists who had tried to obtain radicals by electrical discharge observed an unusual luminescence in the low-temperature traps protecting vacuum pumps. In some cases condensed ozone, hydrogen peroxide, and other compounds were detected.[1] At that time radical chain reactions were of considerable interest to research workers, so evidently they made considerable efforts to elucidate the role of radicals in the luminescence observed in traps and in detonation of frozen products. Thus, Lavin and Bates[35] reported a blue-green luminescence in a trap at 93 K to which was admitted ammonia that had previously passed through a discharge zone. It was concluded that the luminescence was due to the formation of NH and NH_2 particles. Lunt and Mills[36] reproduced these experiments and observed CL by interacting the decomposition products of gaseous ammonia in an electrical discharge on a solid surface of NH_3 at 93 K, having thus confirmed the results of Lavin and Bates.[35] The authors[36] considered that the reaction of metastable NH particles with hydrogen molecules in the ground state was the most probable source of CL

$$2\ {}^1\Delta\,NH + {}^1\Sigma H_2 = N_2^*H_4 \rightarrow 2\overset{*}{N}H_2.$$

The reaction product—an excited hydrazine molecule—dissociates to give two electronically excited NH_2 particles, which emit the CL.

III. Chemiluminescence in solid nitrogen

In 1954 Broida and Pellam[37] detected considerable luminescence accompanying the condensation of active nitrogen on a surface cooled to 4.2 K. It was suggested that the solid inert gases and nitrogen could be used as media for matrix isolation.[38,39] Their selection was determined not only by their considerable inertness but also by their transparency over a wide range of wavelengths (from the far infrared region of the spectrum to the vacuum ultraviolet) and by their adequate rigidity at 4.2–20 K. The reader can find detailed information about the method of matrix isolation, the properties of the matrices, condensation of solid deposits, and generation of highly active particles in several studies.[2,6–9,40–47]

After the report of Broida and Pellam,[37] extensive studies were carried out on luminescence spectra recorded not only by depositing the products of microwave discharge in gaseous nitrogen[48–56] but also by stimulation of luminescence through a high-voltage discharge using a Tesla transformer,[57] electron bombardment,[58,59] and the action of X-ray emission.[60]

Problems concerning the stabilisation of nitrogen atoms were studied by Fontana.[61,62] He came to the conclusion that if the condensing gas contains more than 1–2 mol % of nitrogen atoms virtually all of them recombine when the solid condensate is formed. It transpired that not more than 0.01–0.04 mol % of nitrogen atoms were stabilised in the nitrogen matrix.

Subsequently, Edwards[2] attempted to interpret the main characteristics of CL in solid nitrogen. He suggested that when the condensate is warmed up, diffusion of nitrogen atoms is initiated, and they migrate and undergo recombination to form nitrogen molecules in the ground ($X^1\Sigma_g^+$) and electronically excited ($A^3\Sigma_u^+$) states:

$$N(^4S) + N(^4S) \rightarrow N_2; \quad N(^4S) + N(^4S) \rightarrow \overset{*}{N}_2.$$

It was later suggested that the heat evolved from these reactions causes an increase in temperature of the sample and thus stimulates subsequent chemical processes. It was therefore assumed[2] that the β-lines in the CL spectrum are due to oxygen atoms formed in an excited state by the reaction:

$$N+NO\rightarrow N_2+O^*;\ O^*\rightarrow O+h\nu.$$

The transfer of energy from an excited N_2^* molecule to an oxygen atom is also allowed

$$O+N_2^*\rightarrow O^*+N_2^{\neq};\ O^*\rightarrow O+h\nu\ (\beta\text{-line});$$
$$O^*(N_2^{\neq})\rightarrow O+N_2+h(\nu_{el}\pm\nu_{vib})(\beta\text{-, }\beta'\text{- and }\beta''\text{-lines}),$$

where $N_2^{\neq}$ is a vibrationally excited nitrogen molcule, $O^*(N_2^{\neq})$ is an intermediate state which decomposes with emission of β-lines. The appearance of α-lines was accounted for by the occurrence of similar processes, except that, instead of an oxygen atom, a nitrogen atom was assumed to take part in the reactions:

$$N+N_2^*\rightarrow N^*+N_2^{\neq};\ N^*\rightarrow N+h\nu\quad(\alpha\text{-line});$$
$$N^*(N_2^{\neq})\rightarrow N+N_2+h(\nu_{el}\pm\nu_{vib})(\alpha\text{-, }\alpha'\text{- and }\alpha''\text{-lines}).$$

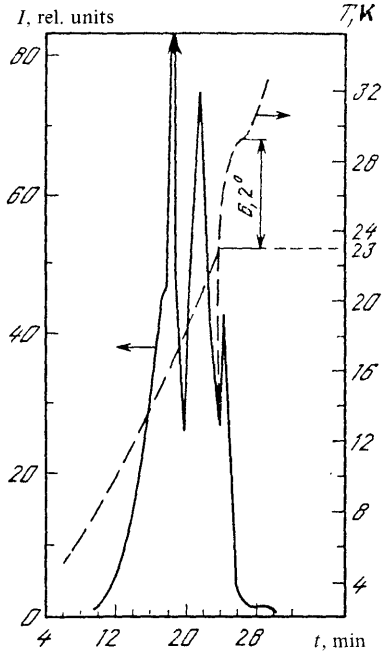


Figure 1. Dependences of the intensity of the α-band in the chemiluminescence spectrum (solid line) and the temperature of the sample (broken line) on time during the warming of a solid condensate of the products of ultra-high frequency discharge in gaseous nitrogen.[63]

In the mechanism examined a direct connection between CL and heat processes accompanying the recombination of atoms was assumed. Hemstreet and Hamilton[63] did not agree with such a treatment. They interpreted the dependence of the intensity of CL on time when the sample was warmed up (Fig. 1) by assuming the possible stabilisation of nitrogen atoms occurring not in the ground state but in an electronically excited state in the N_2 matrix.[63] This type of hypothetical stabilisation of excited particles, the life-time of which is several tenths of a second (we should remember that the radiative life-time of nitrogen atoms in the ^2D-state in a vacuum amounts to ~20 h, and in the ^2P-state to about 4 s), occurred, according to Hemstreet and Hamilton, via the formation of a weak complex between an electronically excited nitrogen atom and an N_2 molecule in the ground state. It was suggested that this complex inhibited the spontaneous deactivation of nitrogen atoms until it was destroyed on warming the matrix.

The presence of two maxima on the intensity curve (Fig. 1) was accounted for by Hemstreet and Hamilton[63] on the basis that there were two types of trap in ordered and disordered parts of the matrix respectively. It transpired that the maxima for CL and heat liberation did not necessarily coincide in time. Hemstreet and Hamilton saw that there was a discrepancy in the model of Edwards mainly because according to their data the luminescence peak occurred earlier than the heat liberation processes resulting from the recombination of nitrogen atoms in the ground state were recorded.

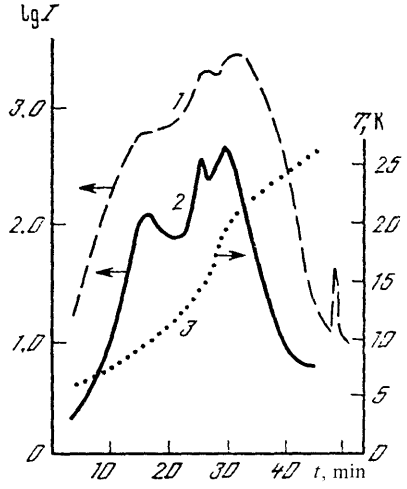


Figure 2. Dependence of the logarithm of the intensity of chemiluminescence on time (curves *1* and *2*) during warming and a thermogram of the sample in the case of irradiation with annealing (curve *3*). *1*, irradiation without annealing; *2*, irradiation with initial annealing.[64]

However, the results of Brocklehurst and Pimentel[64] based on quantitative thermometric and spectroscopic studies of solid nitrogen subjected to electron bombardment at 4.2 K contradicted the theory of Hemstreet and Hamilton. When the sample was warmed up the authors[64] observed three broad CL peaks and light emission at 35 K—the phase transition temperature (curve *1*, Fig. 2). When there was initial annealing of the sample, curve *2* was obtained with good reproducibility. The peaks were better resolved in the case of the annealed sample of solid nitrogen, which made it possible to exclude any of the observed CL maxima from being attributed to a process involving the ordering of imperfections in the crystal lattice

that develop when the condensate is formed. Thus, it remained to Brocklehurst and Pimentel to propose a mechanism for CL which would account for the presence of not two, as found by Hemstreet and Hamilton,[63] but three luminescence peaks.

In order to try and explain the presence of three luminescence peaks using the model of Hemstreet and Hamilton, it would be necessary to admit the existence of three complexes of excited atoms with molecules of the matrix, each of which would decompose irreversibly at a given temperature. Therefore, Brocklehurst and Pimentel returned to the model of Edwards, having modified it slightly. They proposed that each CL peak was due to the same active particles—this followed directly from the lack of change in the luminescence spectrum of a sample when its temperature was varied from 4–20 K. Subsequently, the authors,[64] by assuming that the given luminescence maxima were initiated by diffusion, postulated that the $N(^4S)$ nitrogen atoms were stabilised in the nitrogen matrix in three different positions (relative to the matrix environment), each of which was characterised by one of three values for its enthalpy of activation of diffusion. This model satisfactorily explained a number of features of CL in a nitrogen matrix, since the recombination reaction of $N(^4S)$ nitrogen atoms provides sufficient energy (225 kcal mol^{-1}) to excite the nitrogen atoms to the ^2D (54.7 kcal mol^{-1}) or ^2P (86.4 kcal mol^{-1}) states by exciton transfer.

However, despite the progress achieved by the beginning of the 1960's in understanding the nature of the CL of solid nitrogen, there were still considerable difficulties in attempts to interpret the fine structure of emission spectra. Complications arose because in order to obtain sharp and intense nitrogen luminescence spectra a very pure gas without contamination with oxygen was necessary since the latter quenches the luminescence of nitrogen and gives a series of broad emission bands in the exact spectroscopic region for observing nitrogen lines. In the study of Brocklehurst and Pimentel,[64] where the most complete theoretical analysis of the spectroscopic characteristics of the luminescence of solid nitrogen was carried out, gas of 99.995% purity was used.

In solid nitrogen that is free of impurities, the most intense band in the visible region of the spectra is the α-band. This component of luminescence is attenuated very slowly, and is caused by a very striking green afterglow with $\lambda = 523$ nm, due to the $^2D \rightarrow {}^4S$ transition of the nitrogen atom. The α′-band, as designated by Bass and Broida,[49] is much weaker than the α-band. It was established[52,54] that the difference in frequencies $\Delta\nu = \nu(\alpha)-\nu(\alpha') = 2300$ cm^{-1} is close to the vibration frequency of an N_2 molecule in the ground electronic state. On the basis of this, the α′-band was interpreted as the combination of a $^2D \rightarrow {}^4S$ electron transition of a nitrogen atom and a concurrent vibrational transition $\nu = 0 \rightarrow \nu = 1$ in a neighbouring N_2 molecule.

In the near IR region of the spectrum, the most intense emission comes from the so-called δ-band at 1044 nm, as detected by Peyron and co-workers,[55] and which they attributed to the $^2P \rightarrow {}^2D$ transition of an N atom.

Earlier, the fine structure of the α-band had been studied using spectrograms obtained photographically.[49,55,58] The difficulties which arose in the interpretation of this structure were overcome by Dressler and co-workers,[65] who for the first time obtained a photoelectric record of the α-band in the emission spectrum of solid nitrogen bombarded by electrons at 4.2 K (Fig. 3). It was shown that the spectrum of the α-band may be made up by a series of modified Lorentzian curves. The intensity ratio of lines *1–5* remains constant for different conditions of excitation and condensation of the samples. The overall pattern of these lines was interpreted as a dynamically induced electron-phonon band containing asymmetric molecular vibrations in the ground state, and the O_A and O_B lines were attributed to an unsymmetrically broadened, induced phonon-free band. This assignment was confirmed by a frequency analysis of the satellite vibration lines α′, α″, and α‴.

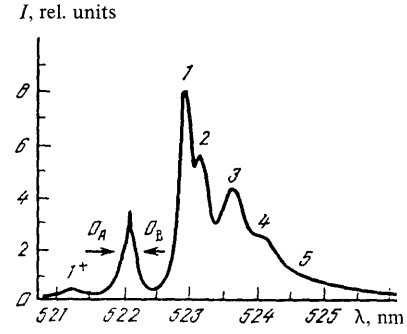


Figure 3. Structure of α-bands caused by the $^2D \rightarrow {}^4S$ transition in the low-temperature (4.2 K) luminescence spectrum of the nitrogen atom.[65]

Information about the structure of the traps containing active particles is of considerable importance for the correct interpretation of CL processes that occur when cryogenic matrices are warmed up. Such information was obtained even in the early studies on the EPR spectra of N atoms in a nitrogen matrix.[66,67] There is an interesting study,[68] in which in order to obtain data on the possible molecular environment of nitrogen atoms, an investigation was made as to how the EPR spectra were affected by the temperature of condensation of the products formed in an ultra-high frequency discharge in gaseous nitrogen. The occurrence of a single group of lines (spectrum *A*) at 7 K and three groups of lines (spectra *A*, *B*, and *C*) in the EPR spectrum of solid nitrogen at 14 K was related by Delannoy and co-workers[68] to the existence of one and three types of trap respectively in the matrix of molecular nitrogen. In an N_2 matrix the nitrogen atoms can occur in different stabilisation sites as a result of three processes (the position is characterised by the distance *R* between the centre of the structural defect occupied by the N atom and one of the adjacent nitrogen molecules):

1) substitution ($R_\alpha = 0.4$ nm);
2) insertion with an octahedral matrix environment ($R_\beta = 0.282$ nm)
3) insertion with a tetrahedral matrix environment ($R_\gamma = 0.244$ nm)

The capture centres of the $N(^4S)$ nitrogen atoms in an N_2 matrix were investigated in the study of Adrian.[69] With the theory he proposed it is possible to establish an interrelationship between the value of the hyperfine splitting constant and the number of neighbouring molecules and also the distance from the latter to the centre of the stabilised atom.

The next stage in studying the phenomenon of CL observed when condenstates of active nitrogen are warmed up was undertaken by Faure and co-workers.[70] Having used a combination of EPR and optical spectroscopy, they studied the effect of temperature on the capture of nitrogen atoms in traps of various types. When the condensate was warmed up from 5 to 40 K they observed three CL

peaks from the main component of the α-band for the $^2D \rightarrow {}^4S$ atomic transition (at 15.9, 20.3, and 23.5 K), which was consistent with earlier results.[63]

By analysing the changing features of the fine structure of the emitting α-band on varying the temperature, which revealed a different behaviour of the two components of luminescence in the region of the phonon-free band—O_A and O_B (Fig. 4)—Faure and co-workers[70] were able to conclude that N atoms were captured in two different types of trap. In fact, it is very clear from Fig. 4 that there is a relative decrease in intensity of the O_A lines (λ = 522.13 nm) when the temperature of the sample is increased. When a temperature of 18–20 K is reached, line O_A disappears. The observed changes in the spectra correspond, according to Dressler and co-workers,[65] to a change in the background structure due to an exchange of the types of trap in which the nitrogen atoms are stabilised.

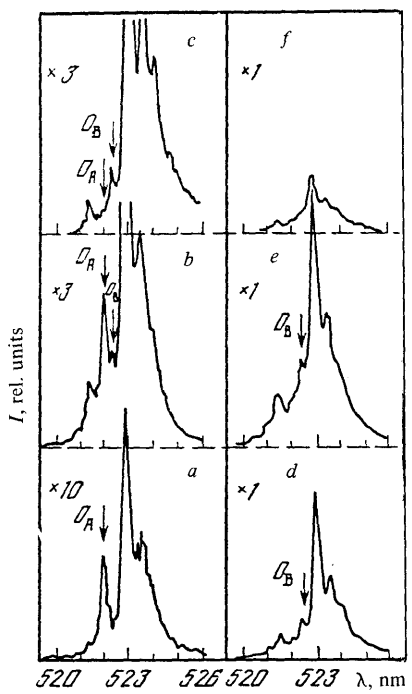


Figure 4. Fine structure of the $^2D \rightarrow {}^4S$ α-band emission obtained at different decomposition temperatures during warming (0.7 deg/min) of the condensate of products of gaseous nitrogen when exposed to ultra-high frequency discharge.[70] The rate of scanning the spectrum was 32 Å/min.
Temperature, K: *a*, 10–11.5; *b*, 14–15.5; *c*, 16–17.5; *d*, 20–21.5; *e*, 24–25.5; *f*, 26–27.5.

The studies started by Faure and co-workers[70] were continued by Tribbollet and Valadier,[71] who analysed the changes that occur in the fine structure of the α-band in the luminescence spectrum recorded during condensation of nitrogen at different fixed temperatures. The observed changes in the relative intensity of lines O_A, O_B, and O_C were interpreted on the basis of the existence of the three types of trap identified previously.[65]

The temperature dependencies of the intensity of the individual lines *1*, O_{AB} and O_C, as shown in Fig. 5, indicate that there can be several possible energy of activation values for each type of trap. Tribollet and Valadier[71] proposed that low-temperature CL is due to two different processes for excitation of nitrogen atoms: firstly, the recombination of atoms situated near each other (this process is responsible for the formation of the first maximum on the temperature curve of CL intensity and occurs in a similar manner to the recombination of electron–hole pairs by a tunnel mechanism); and secondly, the recombination of atoms with a diffusion mobility that is provided by thermal activation (the formation of the second CL peak is due to this mechanism, which has a bimolecular nature).

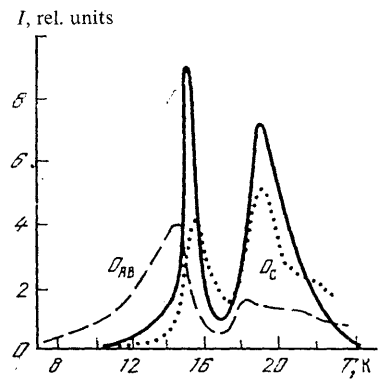


Figure 5. Temperature dependences of the intensity of three lines: *1*, O_{AB} and O_C, present in the luminescence spectrum of the nitrogen atom for $\alpha(^2D \rightarrow {}^4S)$.[71] O_{AB} is the sum of lines O_A and O_B.

In this study[71] the first event in the mechanism for stimulation of CL is assumed to be the recombination of two $N(^4S)$ atoms. The energy of the excited triplet molecule of N_2 is then transferred to nitrogen atoms, which emit light.

The suggestion that there were two mechanisms for excitation of nitrogen atoms was based on the results of an investigation of the kinetics of liberation of N atoms from traps at different temperatures. It transpired that in no single case could the attenuation of CL on removing the heating and stabilising the temperature of the nitrogen matrix containing nitrogen atoms be represented by an exponential decay typical of a first-order kinetic reaction. The decrease in luminescence at 20.3 K corresponds closely to $1/(1 + at)^2$. The intensity of CL at 15.9 and 23 K varies according to a hyperbolic relationship, $1/t$, which is characteristic of the recombination of electron-hole pairs occurring by a tunnel mechanism.

Tribbollet and Valadier[71] proposed two equations to represent the temperature dependencies of intensity obtained in their study for one of the components of the α-band (designated by them as line *1*) in the CL spectrum recorded on warming nitrogen which had condensed at 5 K after passage through a zone of ultra-high frequency discharge. The first expression was obtained by assuming

that the CL reaction occurs by a first-order kinetic mechanism, the second was obtained for the kinetics of a bimolecular reaction:

$$I_1 = n_0 S \exp(-E/kT) \cdot \exp\left(-\frac{S}{B}\int_{T_0}^{T} \exp(-E/kT')\,dT'\right),$$

$$I_2 = n_0 S' \exp(-E/kT) \cdot \left(1+\frac{S'}{B}\int_{T_0}^{T} \exp(-E/kT')\,dT'\right)^{-2},$$

where n_0 is a factor proportional to the number of particles responsible for luminescence at temperature T_0; E is the energy of activation; S is the pre-exponential factor; B is the rate of warming; T_0 is the initial temperature.

It may be mentioned that the theoretical curve that is plotted using the second expression is a better approximation to the experimentally obtained curve.

The problem of stabilising atoms and free radicals that occur in significant concentrations in solid matrices at low temperatures also remains important at the present time. The development of low-temperature physics has revived interest in metastable systems containing atoms stabilised at helium temperatures because of the possibility of finding unique quantum properties in such systems, namely, quantum diffusion, tunnel chemical reactions involving exchange of an atom with a molecule, superfluidly doped atoms, and superconductivity. These questions are among the most interesting and important problems of contemporary physics.

The fact that in the 1950's to 1960's it was only possible to stabilise atoms and radicals in very low concentrations was due to the thermal instability of systems containing considerable quantities of high-activity particles. It was suggested that atoms or free radicals were stabilised in structural traps in the matrix and the thermal instability was due to an increase in their diffusion capabilities caused by a temperature wave coming from the centre of a random recombination. This accounted for the weak dependence of the limiting concentrations of the stabilised atoms on the temperature of the matrix and depth of the structural traps.

Experiments carried out by a group of Soviet research workers[72–77] in which an original method was used for stabilisation of atoms based on the introduction of atom-molecule clusters into superfluid helium (He *II*) through its surface[72] showed that under good heat-exchange conditions and at a low temperature ($T_0 \approx 1.5$ K) the concentration of stabilised nitrogen atoms can reach 10%,[77] and the N atoms do not recombine for at least 1.8×10^3 s. It may be concluded from this that there is virtually complete stabilisation of the nitrogen atoms in He *II*. It was found that on increasing the temperature a significant proportion of the nitrogen atoms that accumulated at T < 2 K recombined in an explosive manner at the λ-point ($T_\lambda \simeq 2.19$ K). A powerful emission of CL is recorded at the same time.[72,73] Since at the λ-point there is only a sudden change in the thermal conductivity of liquid helium, the authors concluded that the effect was due to thermal explosion of particles of molecular nitrogen containing N atoms that were suspended in the liquid.

An analysis of the thermal stability of systems containing stabilised atoms was carried out by Gordon and co-workers.[73] They came to the conclusion that the limiting concentrations of the atoms stabilised at very low temperatures (T < 4 K) are determined by the stability of the system towards temperature-wave explosion and at higher temperatures towards thermal explosion. In the first case, the conditions for stabilisation require that the temperature wave coming from the centre of a random recombination does not succeed during its existence in inducing the recombination of neighbouring atoms in the matrix; in the second case the conditions require that the rate of heat removal from recombination provides a constant temperature of the medium.

The mechanisms examined above concerning the excitation of condensates of active nitrogen assumed the occurrence of two successive processes: the diffusion-controlled recombination of $N(^4S)$ atoms on the surface or in the bulk of a solid sample and the resonant transfer of energy from the $N_2(A\,^3\Sigma_u^+)$ molecule formed to an $N(^4S)$ atom, which is converted in the process to the electronically excited ^2D state.

Gordon and co-workers[74,75] studied the effect of isolating active nitrogen in a neon matrix on the fine structure of the α-band in the luminescence spectrum of solid nitrogen condensed in superfluid helium from a region of microwave discharge. They came to the conclusion that the α-emission of the nitrogen atoms at the moment of condensation was not due to the recombination of $N(^4S)$ atoms but to the de-excitation of excited $N(^2D)$ atoms trapped from the gas phase in the matrix of molecular nitrogen. The authors made use of the fact that even the lowest energy level of an excited neon atom (E = 16.6 eV) cannot be populated using the recombination reaction of $N(^4S)$ atoms (E = 9.8 eV). Consequently, the resonant transfer of energy from the triplet $N_2(A\,^3\Sigma_u^+)$ nitrogen molecule through the neon matrix is impossible. Therefore, if the mechanism for excitation of condensates of active nitrogen includes the recombination of nitrogen atoms in the ground state followed by transfer of energy from $N_2(A\,^3\Sigma_u^+)$ through the nitrogen matrix to an $N(^4S)$ atom, as N_2 is replaced by Ne the intensity of luminescence of the nitrogen atoms due to the $^2D \rightarrow {}^4S$ transition must decrease. If the main reason for the development of $N(^2D)$ atoms in the condensate is their capture from the gas phase, the matrix isolation with neon should not affect the intensity of the α-band in He *II*.

It transpired that when the ratio Ne/N_2 was varied from 0 to 20 the intensity of luminescence due to the transition $N(^2D \rightarrow {}^4S)$ in the nitrogen–neon condensate did not change.

In one study[76] the fine structure of the α-band in the luminescence spectrum of active nitrogen condensed in superfluid helium was examined, and it was concluded that the line with $\lambda \geqslant 523$ nm was due to a phonon wing transition and the I^+ line (λ = 521.2 nm) was not due to an anti-Stokes transition[65] but corresponded to the luminescence of nitrogen atoms captured on surface traps of a molecular nitrogen matrix.

IV. Chemiluminescence in cryogenic matrices of inert gases

A large contribution to the study of reactions in cryogenic matrices was made by Pimentel and co-workers. Back in 1958 Milligan and Pimentel[78] made a visual observation of the red luminescence during the warming up of solid nitrogen which had been subjected to UV photolysis at 20 K and which contained diazomethane. It was suggested that the CL was caused by one of three reactions:

Reaction	$-\Delta H$, kcal mol^{-1}
a) $CH_2 + CH_2N_2 = C_2^*H_4 + N_2$	101
b) $CH_2 + CH_2 = C_2^*H_4$	122
c) $CH_2N_2 + CH_2N_2 = C_2^*H_4 + 2N_2$	80

Subsequently, Goldfarb and Pimentel[79,80] undertook a more detailed spectrographic and visual study of the orange-red CL recorded at 20–40 K during the warming of a nitrogen or argon

matrix containing reactive residues of diazomethane or its deuterated analogues. On increasing the temperature the intensity of CL changed substantially—from a luminescence scarcely visible to the eye adapted to darkness to a bright orange-red emission which could be discerned even in a light sufficient for reading.

It should be noted that the photolytic method for obtaining active particles stabilised in cryogenic matrices proved very convenient and the majority of the subsequent studies concerned with low-temperature CL were carried out using UV photolysis. One of the studies of Goldfarb and Pimentel[79] is also of interest as a complex method for studying the mechanism of solid-state CL was used in it—IR absorption spectroscopy and emission spectroscopy and isotope substitution. Many subsequent studies were carried out using a similar approach.

Two decades after the discovery of CL in ethylene, Pimentel returned to cryogenic matrices containing diazomethane in order to study once again the luminescence spectrum, to elucidate the role of oxygen impurities, to obtain additional evidence for the presence of CH_2 radicals in a photolysed matrix, and to identify the emitter of chemiluminescence and the electronic transitions responsible for the emission of light.[81] During the intervening period there had been a considerable increase in the scope for recording low-temperature CL and knowledge about the energy levels of the excited states of ethylene had broadened. With the use of EPR and photoelectron spectroscopy new information about CH_2 radicals was obtained and an attempt was made to identify the possible products from the photolysis of diazomethane in matrices of inert gases.

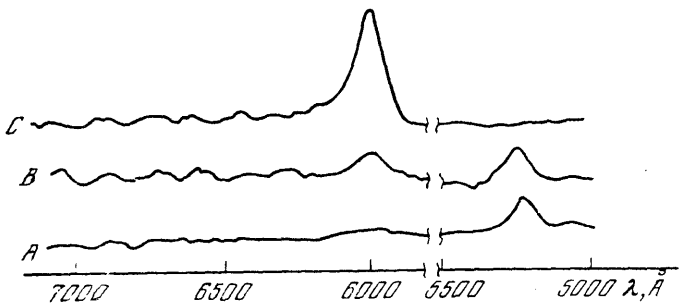


Figure 6. Luminescence spectrum recorded on warming a UV-irradiated nitrogen matrix containing CH_2NN (CH_2NN/N_2 = 1/300).[81]
Temperature, K: *A*, 8–10; *B*, 11–12; *C* 15–16.

Samples obtained by coprecipitation of diazomethane and argon (CH_2N_2:Ar = 1:300) on a copper sheet at 6 K were irradiated with the full light of a medium-pressure mercury lamp for 2.5 h, and the CL spectra were recorded at a slow rate of warming (1–2 deg/min).[81] The early observations[79–80] were confirmed, and with better resolution of the spectroscopic apparatus used, additional structural features were detected in the spectrum. Below 10 K, a broad band with a maximum at 522.0 ± 0.4 nm (Fig. 6, spectrum *A*) predominated in the spectrum. At 11–12 K, a broad band appeared in the region 598.7 ± 0.5 nm, and there were also weak bands over the range 600–760 nm (Fig. 6, spectrum *B*). When the temperature was increased further the emission at 522.0 nm decreased and at 15 K was no longer recorded. At the same time the intensity of the band at 598.7 nm increased, reaching a maximum value at 18 K. This luminescence could be recorded up to about 35 K (Fig. 6, spectrum *C*).

The determination of the nature of the CL emitter was given prominence in this study.[81] Each of the maxima in the luminescence spectrum at 522.0 and 598.7 nm is a separate broad peak without any signs of vibrational structure. This type of spectrum is typical for a monoatomic emitter or a molecular transition between states with almost the same molecular geometry. The nitrogen atom and N_2, CH_2NN, CH_2NH, and C_2H_4 molecules were examined as probable sources of CL. The authors[81] considered the most probable CL emitter to be the ethylene molecule formed in reactions (a) and (b). This interpretation was confirmed not only by the observed correlation between the brightness of luminescence and the concentration of ethylene in the sample but also by the existence in a C_2H_4 molecule of electronic transitions between states with the same geometry. The latter circumstances accounts for the frequencies of the observed spectroscopic bands and the absence of vibrational structure in the CL spectrum. An argument in favour of a C_2H_4 molecule participating in the chemiluminescent reaction was the band detected in the IR region at 1115 cm^{-1}, which corresponded to the deformational vibration of the ground state of CH_2.[81] Consequently, on warming the matrix either diffusion and subsequent recombination of CH_2 radicals was possible or they could react with diazomethane [reactions (b) and (a) respectively]. The authors proposed that the long-wavelength CL maximum at 598.7 nm was due to electronic transitions from the second singlet ($^1A_1$, 43 000 cm^{-1}) or the first singlet ($^1B_2$, 43 769 cm^{-1}) state to the triplet ($^3A_2$, 24 700 cm^{-1}) state of the ethylene molecule. No definite conclusion was reached about the nature of the CL with a maximum at 522.0 nm.

At the start of the 1970's, owing to the efforts of inorganic chemists and organometallic chemists interest was once again stimulated in processes occurring in low-temperature matrices. The focus in studies of this type was shifted from the physical aspects of the chemistry towards synthesis, structure, and reactivity. Laser Raman spectroscopy, Mössbauer spectroscopy, magnetic circular dichroism, developed for application in matrix studies, proved a useful addition to the methods of EPR, absorption, and emission spectroscopy. CL also underwent further development.

Starting in 1974 a whole series of studies was published on low-temperature solid-state CL reactions involving sulphur atoms. In one of the first reports[82] there is information about a blue luminescence observed during the warming of Ar, N_2, or CO matrices which had previously been photolysed at 20 K and which contained hydrogen sulphide. The observed phenomenon was attributed to the formation of HS radicals, and hydrogen and sulphur atoms during photolysis. It was assumed that at 30 K diffusion of sulphur atoms starts, leading to their recombination and radiative deactivation of the excited sulphur molecule formed. The correctness of such an interpretation was confirmed by experiments involving photolysis of OCS.[83,84]

Direct evidence for the formation of S(^1S) atoms by photodecomposition of OCS in an argon matrix at 4 K on exposure to light with λ = 147 nm was obtained by Brom and Lepak.[83] They observed a broad emission band with a maximum at 775 nm, which was readily identified as the $^1S \rightarrow {}^1D$ transition in a sulphur atom.

The chemiluminescence of SO_2 on warming cryogenic matrices that had been irradiated with UV light and which contained SO_2 was first observed by French research workers,[85] who proposed that

the luminescence developed as a result of the reactions S + O_2 and O + SO. Long and Pimentel[86] interpreted the CL spectrum recorded on warming an argon matrix that had been photolysed at 8.5 K and which contained OCS and O_2 molecules by comparing it with the spectrum of the gas-phase phosphorescence of SO_2 and also by measuring the isotope shifts of the vibrational bands of the CL spectrum when $^{16}O_2$ was replaced by $^{18}O_2$. It was concluded that CL develops during the reaction of sulphur atoms with an oxygen molecule, which occurs with an energy of activation almost equal to zero at 10–40 K:

$$S(^3P_2) + O_2(X\,^3\Sigma_g^-) \rightarrow S{\cdot}O_2 \rightarrow SO_2(X\,^1A_1) + h\nu.$$

French research workers[84] detected a considerable diffusion of sulphur atoms in an argon matrix even at 6 K. This study was the extension of a previous one,[85] in which the occurrence of CL on warming a matrix containing SO_2 was attributed exclusively to the emission of SO_2 formed in an electronically excited state as a result of reaction in the lattice $S(^3P) + O_2(X^3\Sigma_g^-)$. However, the high intensity of SO_2 phosphorescence could have masked the emission of $S_2(B^3\Sigma_u^-)$ and in order to detect CL of the sulphur molecule, the French research workers turned to other sulphur-containing compounds giving sulphur atoms by photodissociation. In their later study[84] they observed two clearly distinguishable types of luminescence—the photoluminescence during photolysis at 5–6 K of Ar matrices containing OCS or CS_2 molecules, and CL when the temperature of the sample was increased after the completion of irradiation with light of wavelength 147 nm. Since the energy of the photons (8.3 eV) was insufficient for photoionisation of CS_2 or OCS, the observed luminescence was not due to recombination of charges, as occurs in radiothermoluminescence, but was due to the recombination of atoms, forming molecules in an electronically excited state, in other words, it was CL by its very nature.

It was also established that the CL emitter in matrices containing both OCS and CS_2 was an electronically excited molecule of sulphur, which emits light from the transition $(B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-)$. As well as emission from S_2, emission of SO_2 was recorded in the matrices containing OCS, which was borne out by the similar shape of the temperature curves of intensity of luminescence for S_2 and SO_2 molecules,[84,86] which was an indication of the identity of the particles responsible for luminescence (Fig. 7). In the case of CS_2, bands relating to CS particles $(a^3\Pi \rightarrow X^1\Sigma^+)$ were observed in the CL spectrum. These results indicate that carbon atoms can also diffuse for a considerable distance to form $CS(a^3\Pi)$ particles according to the reaction

$$C(^3P) + S(^3P) \rightarrow CS(a\,^3\Pi),$$

and the rate of diffusion of the carbon atoms is higher than that for the sulphur atoms—Cs bands are observed at lower temperatures than for S_2 bands.

The reliably established evidence for the formation of S_2[83,84] and O_2[87] molecules in an electronically excited state as a result of solid-state chemical reactions stimulated the study undertaken by Lee and Pimentel[88] on low-temperature matrices aimed at obtaining SO molecules in an electronically excited state; there was no information about the existence of these molecules in the gas phase. The authors introduced NO_2, O_2, and SO_2 molecules into an argon matrix for the photogeneration of oxygen atoms, and to obtain sulphur atoms they introduced OCS and SO_2. When the photolysed matrices ($OCS/O_2/Ar$; $OCS/NO_2/Ar$; SO_2/Ar) were warmed up, they observed CL, with a spectrum containing two emission bands—in the region 390–520 nm, due to the transitions $SO_2(\tilde{a} \rightarrow \tilde{X})$, and a progression in the region 520–770 nm. In the system $OCS/O_2/Ar$ the $S_2(\tilde{c}^1\Sigma_u^- \rightarrow \tilde{a}^1\Delta_g)$ was also observed.[89]

The progression in the region 520–770 nm was identified by Gordon and co-workers[74] as SO emission, which was identified from the proximity of ω_e'' to the vibrational frequency of the progression and arose from the low electronically excited states of the SO molecule. Experiments with $^{18}O_2$ showed that the CL emitter contained oxygen.

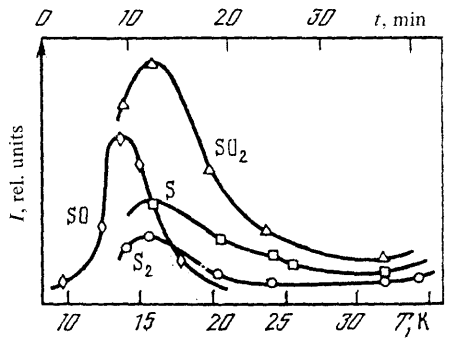


Figure 7. Dependences on temperature and time for the intensity of chemiluminescence of SO, S_2, S, and SO_2 molecules, recorded on warming UV-irradiated Ar matrices containing O_2 and COS ($COS:O_2:Ar = 1:1:200$).[88]

By analysing the experimentally obtained and calculated data on the energy levels of the SO molecule, Lee and Pimentel[88] were able to conclude that the chemiluminescence of SO was due to the radiative transition $\tilde{c}^1\Sigma^- \rightarrow \tilde{a}^1\Delta$. The $\tilde{c}^1\Sigma^-$ state is populated as a result of the reaction $S(^3P_2) + O(^3P_2)$ taking place either directly or via the higher $\tilde{A}''$ and/or $\tilde{A}'$ states, which rapidly relax to the $\tilde{c}$ state. Thus, in this study[88] spectroscopic information about the $\tilde{c}^1\Sigma^-$ state of the SO molecule was obtained for the first time.

In all the studies examined above CL spectra were recorded either photographically or by using a photoelectron multiplier (PEM). The main disadvantage of the latter system is the variation in the light flux, the intensity of which is proportional to the concentration of emitting particles such as SO_2^* or S_2^* during the interval of time necessary to record the spectrum. Consequently, the ratio of intensities of the bands at the limits of an emitting system can only be determined approximately.

This difficulty is eliminated when a photographic method is used, when all the emission distributed in the spectrum is recorded at the same time. However, because of the relatively low sensitivity and the logarithmic dependence of the degree of darkening of photoemulsions on the duration of exposure, it is only possible to use this method successfully with bright CL systems. These disadvantages are eliminated by an optical multichannel analyser in which the integral (multichannel) resources of a photographic plate are combined with the high sensitivity and linear characteristics of the PEM.

By using an optical multichannel technique it was possible for the first time to record simultaneously low-temperature CL spectra on warming cryogenic matrices.[90] The time of scanning a section of the spectrum with width 275 nm was 32.8×10^{-3} s. In each experiment up to 1000 individual scans were carried out using 500 channels. The studies were carried out over the spectroscopic range 200–650 nm. Frozen mixtures of inert gases (Ar, Kr, Xe) with added amounts of O_3, $H_2S + O_2$, and $O_3 + H_2S$ at 8 K were irradiated with UV light. The successive warming up of the irradiated samples over the range 8–20 K led to the appearance of intense chemiluminescence in the visible region of the spectrum.

In the CL spectrum observed on warming an irradiated matrix containing ozone there was the Herzberg I system due to $O_2(A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-)$ emissions. This system (340–640 nm) was observed by Broida and Peyron[56] when they studied the luminescence of solid condensates from ultra-high frequency discharge in gaseous N_2 containing traces of oxygen. However, in contrast to Broida and Peyron, who postulated an excitation mechanism that included the transfer of energy from an electronically excited N_2 molecule, Smardzewski[90] considered that excitation of O_2 occurred as a result of diffusion and emissive recombination of oxygen atoms formed by photolysis of ozone:

$$O(^3P) + O(^3P) + M \rightarrow O_2(A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-) + M.$$

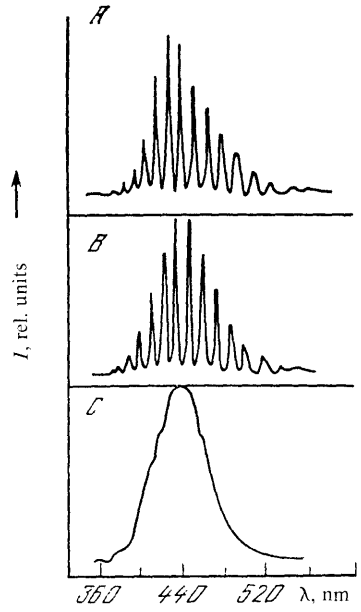


Figure 8. Chemiluminescence spectra observed on warming (from 8 to 13–15 K) H_2S-containing matrices subjected to UV-photolysis during their condensation at 8 K.[90] $M : H_2S = 100 : 1$; *A*, M = Ar; *B*, M = Kr; *C*, M = Xe.

By using different inert gases as matrices it was possible to study the effect of the matrix environment on the CL spectra. There could be two causes of such an effect—diffusion effects and the interaction of trace particles and atoms or molecules of the cryogenic matrix. In densely packed structures of solid inert gases, the dimensions of the interstices and vacancies increase with atomic weight. If the dimensions of trace particles having a low atomic (molecular) weight are comparable with the dimensions of the vacancies in the matrix, diffusion of such particles can take place at an appreciable rate.

It was shown,[90] in fact, that the $(A \rightarrow X)$ emitting system of O_2 molecules formed in an excited state by recombination of oxygen atoms has high intensity in solid argon, low intensity in krypton, and is not recorded at all in solid xenon. This was attributed to the fact that in matrices of heavy inert gases (Kr, Xe) the diffusion mobility of oxygen atoms is quite high even at the temperature of photolysis (8 K) so that even before the sample is warmed up the oxygen atoms have time to react with each other to give O_2 or O_3. Such an interpretation is consistent with an earlier study,[59] in which the radiative $(A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-)$ transition of molecular oxygen was observed during electron bombardment of Kr and Xe matrices containing O_2.

In experiments with matrices containing H_2S, Smardzewski[90] observed CL, the spectra of which are shown in Fig. 8. In the case of the Ar and Kr matrices, CL was due to $S_2(B\,^3\Sigma_u^- \rightarrow X\,^3\Sigma_g^-)$ emission in the region 365–560 nm. The same type of emission was observed[83,84] when photolysed Ar matrices containing OCS and CS_2 molecules were warmed up.

The recombination of sulphur atoms in the ground state was considered to be a fundamental part of the CL mechanism by both Smardzewski and other authors.[83,84] However, it was known from gas-phase studies that the $B\,^3\Sigma_u^-$ state of S_2 is not populated by direct reaction of two $S(^3P)$ atoms. In order to overcome this difficulty, it was assumed that when the $S(^3P)$ atoms recombine, S_2 is formed in the predissociative state 1_u, whose potential curve intersects the potential curve of the $B\,^3\Sigma_u^-$ state. The $B\,^3\Sigma_u^-$ state is then formed as a result of a nonradiative transition:

$$S(^3P) + S(^3P) \xrightarrow{M} S_2(1_u) \xrightarrow{M} S_2(B\,^3\Sigma_u^-,\ v' = 0).$$

The results of the study by Smardzewski[90] indicate that the effect of the matrix on the course of reactions involving recombination of O and S atoms varies substantially. In fact, the product of mass times radius of the sulphur atom is more than four times the corresponding value for an oxygen atom, and so naturally a lower mobility of S atoms compared to O atoms is to be expected. The diameter of the oxygen atom is ~1.2 Å, in other words, approximately equal to or slightly less than the average diameter of an interstice in solid krypton (1.28 Å) and considerably less than the corresponding distance in solid xenon (1.39 Å) at 4 K. The size of the sulphur atom (2.54 Å) and also its large mass impede the diffusion of the latter in all three matrices before the process of warming up the sample. Thus, the occurrence of chemiluminescence for S_2 and the absence of luminescence for O_2 in solid Xe is due to the different rate of diffusion of the S and O atoms in a Xe matrix at low temperatures.

Matrix effects of the second type, which are due to interaction of trace particles with the matrix material, are quite complex. Thus, in experiments concerned with studying CL in S_2 molecules, structured spectra were observed in Ar and Kr matrices, while for the Xe matrix an unexpected result was obtained—instead of a progression of sharp bands, the CL spectrum comprised a broad featureless band in the region 365–532 nm (Fig. 8, spectrum *C*).

Two possible causes of the broadening of the band were investigated.[90] One of these was fluorescence from vibrationally nonrelaxed states. In the Xe matrix, where the diameter of vacancies reaches 4.34 Å, two sulphur atoms could recombine on

warming the matrix to form an excited S_2 molecule, whose dimensions in the $B^3\Sigma_u^-$ state (~4.2 Å) would be less than the space occupied by a vacancy. If the radiative lifetime of such a particle is small, highly excited vibrational states ($v' \leqslant 9$) would not be attenuated and they would contribute to the emission spectrum. The absence of low-frequency bands and the short lifetime of S_2^* (45.0 ± 0.6 ns) are evidence for the possibility that $S_2(B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-)$ fluorescence takes place at the same time as nonradiative vibrational relaxation. In this particular case, superposition of $(n + 1)$ Franck–Condon emission maxima from each of the excited v_n' levels would give a total effect of broadening the S_2 fluorescence into the blue region of the spectrum. In the case of Ar and Kr matrices, which have smaller diameters for vacancies amounting to 3.76 and 3.99 Å respectively, vibrationally excited states will be attenuated as a result of collisions.

The alternative explanation for the broadening of the fluorescence lines, as proposed by Smardzewski,[90] assumes the formation of an S_2^*–Xe Van der Waals complex.

The CL emitters and electronic transitions that are responsible for the emission of bands in the regions 490–870 and 385–600 nm on warming matrices containing sulphur and oxygen atoms were established by Tevault and Smardzewski.[91] It was found that luminescence was due to the transitions $c\,^1\Sigma^- \rightarrow a\,^1\Delta$ and $A'\,^3\Delta \rightarrow X^3\Sigma^-$ from SO molecules formed in reactions involving recombination of sulphur and oxygen atoms. The interpretation of the spectra was based on the results of experiments with $^{18}O_2$ and ^2H isotopes, which showed that the emitting molecule did not contain hydrogen atoms and had one oxygen atom. An optical multichannel analyser was used as the primary photodetector,[91] so that it was possible to follow several CL systems simultaneously over a practicable time-scale.

Lee and Pimentel[89] extended the spectroscopic range for observing CL caused by reactions involving sulphur atoms to the near IR region. In the CL spectrum observed over the range 8–44 K on warming photolysed Ar, Kr, and SF_6 matrices containing CS_2 and COS molecules, three progressions were recorded. The progression in the region 340–552 nm was due to the familiar[83,84,86,90] $B^3\Sigma_u^-$ $(B''\,^3\Pi_u) \rightarrow X^3\Sigma_g^-$ radiative transition of the S_2 molecule, while the two new bands in the regions 558–689 and 668–875 nm were identified as $A'\,^3\Delta_u \rightarrow X^3\Sigma_g^-$ and $c\,^1\Sigma_u^- \rightarrow a\,^1\Delta_g$ transitions respectively.

Fluorescence spectra and recombination emission of S_2 molecules, recorded on photolysis with light at $\lambda = 257.3$ nm (frequency doubled pulsed Ar^+ laser) of CS_2/Ar mixtures frozen at 15 K were observed by Hamaguchi and Tasumi.[92] These spectra contained two series of vibrational bands attributed to transitions of the S_2 molecule—$B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ and $B''\,^3\Pi_u^- \rightarrow X^3\Sigma_g^-$. The excitation mechanism includes the primary photodissociation of CS_2 molecules:

$$CS_2 + h\nu \rightarrow CS\,(a\,^3\Pi) + S\,(^3P)$$

followed by a process involving recombination luminescence:

$$S\,(^3P) + S\,(^3P) \rightarrow S_2^*\,(B''\,^3\Pi_u) \rightarrow S_2\,(X\,^3\Sigma_g^-) + h\nu.$$

CL systems containing nitrogen oxides[93] and carbon oxides[94,95] have been detected. When a photolysed argon matrix containing NO_2 and O_2 molecules was warmed up, two emitting systems from NO_2 and O_2 were recorded. Irradiation at 7.5 K of an Ar matrix containing N_2O with light of wavelength 147 nm was accompanied by emission of Vegard–Kaplan bands of the N_2 molecule $(A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+)$ and fluorescence of oxygen atoms $(^1S \rightarrow {}^1D)$ and nitrogen atoms $(^2D \rightarrow {}^4S)$.[94] It follows from this that the primary processes in the photolysis of N_2O are:

$$N_2\,(X\,^1\Sigma_g^+) + O\,(^1S); \quad N_2\,(A\,^3\Sigma_u^+) + O\,(^3P);$$
$$NO\,(X\,^2\Pi_{1/2}) + N\,(^2D).$$

On warming the irradiated samples, starting at 9 K, CL, resulting from the recombination of oxygen atoms was recorded

$$O\,(^3P) + O\,(^3P) \rightarrow O_2\,(A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-).$$

Under the experimental conditions of the study,[94] the distance between the oxygen atoms was estimated to be 50 Å; it would be necessary for the oxygen atoms to complete about 170 random jumps in order to cover the space separating them and undergo reaction.

In the presence of CO the CL spectrum changes. Instead of a radiative O_2 transition, a continuum is recorded in the region 380–500 nm, due to emission of CO_2 molecules excited in the reaction

$$CO\,(X\,^1\Sigma^+) + O\,(^3P) \rightarrow CO_2\,(^3B_2 \rightarrow X\,^1\Sigma_g^+).$$

The photolysis of CO_2 in Ne, Ar, and Kr matrices at 4.5 K with UV light ($\lambda = 147$ nm) and the reactions occurring when the samples were subsequently warmed up were studied.[95] The CL spectrum consisted of four bands of an $O_2(A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-)$ Herzberg system, which were absent in the photoluminescence spectrum. It was shown that the recombination of $O(^3P)$ atoms on irradiation of CO_2 in solid Ar or Kr did not take place even when photolysis was carried out at 30 or 40 K. Increasing the temperature of the samples was a necessary condition. At the same time, in a Ne matrix the recombination of oxygen atoms, appearing as CL, took place under isothermal conditions even at 4.5 K. It was not possible to account for this behaviour on the basis of differing rigidities of the matrices since they are the same for Ne at 4.2 K and for Kr at 20 K. Fournier and co-workers[95] proposed a model according to which the oxygen atoms in the Ne matrix do not interact with the atoms of inert gas while in the case of Ar, Kr, and Xe matrices they are stabilised by formation of oxides of the respective inert gas.

The suggestion about the formation of Van der Waals complexes had been put forward previously,[96] when the luminescence stimulated by synchrotron irradiation was attributed to radiative transitions of ArO and KrO. The formation of XeO was detected in an argon matrix containing Xe, CO_2, or O_2 when it underwent UV photolysis with light at $\lambda = 121.5$ nm.[97] In the photoluminescence spectrum of a frozen mixture of Ar/Xe/CO_2, a system of bands was observed, corresponding to a XeO transition $(d^1\Sigma^+ \rightarrow a^1\Sigma^+)$ in the region 520–570 nm and Cameron bands due to CO.

The range of CL systems in cryogenic matrices is constantly expanding. There are interesting studies on the laboratory simulation of processes occurring in dust clouds in interstellar space. Studies of this type have theoretical importance for our understanding of chemical and prebiological evolution.[10] Thus, on warming argon matrices containing water vapour and/or ammonia which had been irradiated at 10 K with light from a hydrogen lamp ($\lambda = 150$–170 nm), CL from O_2, NO, N_2, and NH molecules was detected.[98] The occurrence of electronically excited diatomic molecules on warming the photolysed matrices for all cases except NH and the β-bands from NO was attributed to the diffusion and subsequent recombination of nitrogen and oxygen atoms in the

ground state. In similar experiments with $Ar/CH_4/H_2O$ mixtures, which also simulated the "dirty ice" on dust particles in dense nebulae, as well as an O_2 system in the CL spectrum, Cameron bands were observed, caused by $a^3\Pi \rightarrow X^1\Sigma^+$ transitions of CO, as were unidentified bands, which were later[99] identified as radiative $d^3\Pi_g \rightarrow a^3\Pi_u$ transitions from C_2 molecules.

There are many unresolved problems in the chemistry of atomic carbon, which is mainly due to the difficulty of obtaining C atoms and their high reactivity. The rate of a chemical process can be considerably reduced by cooling the reaction system. Krogh and co-workers[99] did precisely that, having used the method of matrix isolation to study the dynamics of reactions involving products from the UV photolysis of cyanazide. The highly active intermediates formed were identified from the results obtained using IR spectroscopy and low-temperature CL. The source of carbon atoms was NCN_3 which dissociated when photolysed. The first report about CL from warming an Ar matrix containing products from the photolysis of NCN_3 was produced by Milligan and co-workers,[100] who established that the primary product of the photodissociation of cyanazide is the NCN radical.

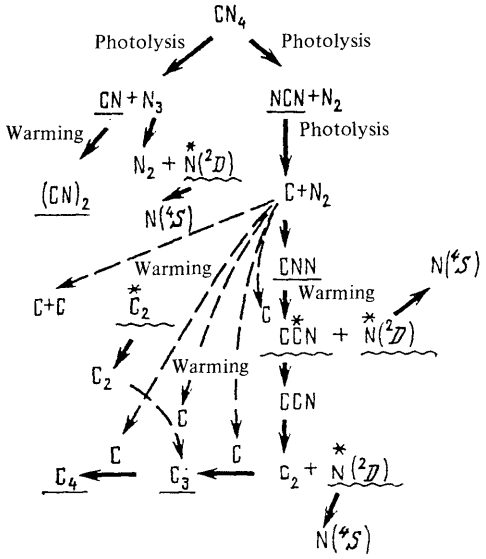


Figure 9. Mechanism for the reaction involving the photolysis products of NCN_3 in an argon matrix.[99] The data of IR measurements are emphasised with a straight line, the curved lines indicate the results obtained using an optical multichannel analyser.

In the CL spectrum[99] recorded using an optical multichannel analyser when a photolysed argon matrix containing NCN_3 was warmed up, 5 Swan bands from $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$ and bands due to emission by the CCN radical ($A^2\Delta_i \rightarrow X^2\Pi_i$) and the nitrogen atom ($^2D \rightarrow {}^4S$) were detected. It was shown that $N(^2D)$ atoms were mainly formed during thermal decomposition of N_3 radicals formed as a metastable cyclic isomer by photolysis. The reaction scheme occurring on photolysis of NCN_3 followed by warming of the matrix is depicted in Fig. 9. Krogh and co-workers[99] concluded that despite the complexity of the process, photolysis of cyanazide could serve as a powerful source of carbon atoms.

During the last ten years low-temperature solid-state chemiluminescence has been detected for several diatomic (O_2, S_2, CO, CS) and triatomic (NO_2, SO_2, CO_2, CCN) molecules which are formed as a result of the thermally induced diffusion and subsequent interaction of highly active particles stabilised in cryogenic matrices. There is a clear trend towards extending the CL method to study low-temperature reactions involving polyatomic molecules. The first results in this direction have already been obtained. Thus, in one study examined above[81] CL was detected in ethylene. Subsequently, when an Ar matrix which had undergone UV irradiation at 8 K and which contained diazomethane and oxygen was warmed up, CL was detected,[101] and in the spectrum two new progressions in the regions 310–360 and 390–490 nm were detected together with the known $O_2(A'^3\Delta_u \rightarrow X^3\Sigma_g^-)$ emission.

By analysing isotope shifts in experiments with $^{18}O_2$ it is possible to interpret the vibrational numbers v'' in two ways for both emission systems. The spectroscopic parameters obtained indicate that the observed progressions belong to the $a^3A'' \rightarrow X^1A'$ and $A'^1A' \rightarrow A^1A''$ transitions of the HCOOH molecule. This is the first observation (not only as luminescence but also when using any other methods of excitation) of such transitions in formic acid, whose molecules are excited in an argon matrix according to the reaction:

$$CH_2(^3B_1) + O_2(^3\Sigma_g^-) \rightarrow HCOOH.$$

In all of the previously examined reports on low-temperature CL in cryogenic matrices, reactions whose initial stage was recombination of radicals were studied. The recently discovered chemiluminescence of BaO, which is excited in the reactions

$$Ba + N_2O \rightarrow Ba^*O + N_2 \text{ and } Ba + O_3 \rightarrow Ba^*O + O_2,$$

presents a new class of CL reactions, with a mechanism that involves atom transfer.[88]

In the case of an argon matrix containing barium atoms and an oxidising agent (N_2O or O_3) a sharp increase in temperature of the sample is found when it is warmed up. Matrices containing Ba and N_2O (or O_3) at about 15 K warm up unexpectedly rapidly to 40 K, which results in evaporation of the sample. Chemiluminescence is usually recorded, starting at 8 K, then its intensity increases steadily as the temperature is raised. In the region 13–15 K a sharp increase in the intensity of luminescence occurs and the subsequent sudden jump in temperature of the sample is accompanied by an extremely bright emission. In the opinion of Pimentel and co-workers[102] the rapid rise in the temperature of the matrix is caused by decomposition of the unstable oxidising agents N_2O and O_3, catalysed by barium oxide or barium atoms.

Local warming and evaporation of even small sections of the matrix in such exothermic processes leads to a loss of vacuum in the space surrounding the sample and consequently results in warming and evaporation of the whole matrix. This phenomenon restricts the temperature region for recording CL spectra to 10–13 K. However, it transpired that emission spectra obtained during condensation of a sample were identical to the CL spectra from warming the matrix. Two molecular progressions of BaO with ν_{00} = 17 035 and 17 195 cm^{-1} and ω_e'' = 657 and 651 cm^{-1} were detected in the CL spectrum. They were related to radiative $\tilde{a}^3\Sigma^+ \rightarrow \tilde{X}^1\Sigma^+$ transitions of the BaO* molecule stabilised in different positions relative to the matrix environment. The possibility of an $\tilde{A}^1\Sigma^+ \rightarrow \tilde{X}^1\Sigma^+$ transition occurring was also not

ruled out. The proposed mechanism for excitation of BaO molecules involves population as a result of the chemical reactions of one or two singlet states ($\tilde{A}\,^1\Sigma^+$ and/or $\tilde{A}'\,^1\Pi$) followed by a rapid intercombination transition to the $\tilde{a}\,^3\Sigma^+$ state. The $(6s6p\,^1P) \rightarrow (6s^2\,^1S)$ radiative transition of the Ba atom was also observed. Excitation occurs by transfer of energy from the electronically excited BaO* molecule to a barium atom:

$$Ba^*O(\tilde{A}\,^1\Pi) + Ba(6s^2\,^1S) \rightarrow BaO(\tilde{X}\,^1\Sigma^+) + Ba^*(6s6p^1P).$$

There is a considerable difference between atom transfer reactions and radical recombination reactions. For the former the selection rules are less strict, which ensures the existence of several reaction pathways. In the case of a radical reaction the total excess of energy is concentrated in the excited product, while in an atom transfer reaction a redistribution of energy takes place between the products. The relaxation pathways of such excited products can be studied directly by CL.

V. Chemiluminescence in hydrocarbon matrices at 77 K and above

In addition to the investigation of CL reactions in cryogenic matrices, CL has also been studied in low-temperature systems. A series of studies has been published on CL occurring as a result of the interaction of a stream of active nitrogen on the surface of hydrocarbons frozen at 77 K.[103-103]

When the surface of frozen benzene, fluorobenzene, and chlorobenzene was treated with active nitrogen, Devolder[103,104] observed CL, with spectra that matched the phosphorescence spectra of benzonitrile, a mixture of the three isomers of fluorobenzonitrile, and an isomeric mixture of chlorobenzonitriles respectively.

Studies were also made on the CL spectra of polycrystalline benzene with added amounts of naphthalene, carbazole, acetonitrile, and benzaldehyde, for which the energy of the phosphorescent triplet state was lower than the corresponding energy for benzonitrile. The CL spectra observed were dependent on the concentration of the added components (guests). At high concentrations of guests ($\sim 10^{-1}$ M), only the phosphorescence spectrum of the guest was observed, whereas at low concentrations ($\sim 10^{-4}$ M), phosphorescence due to both the guest and benzonitrile was recorded. This indicates that the triplet states of the guests and benzonitrile are populated in concurrent processes and that the guest can play the role of quencher relative to the triplet state of benzonitrile. Since the intensity of CL proved to be proportional to the square of the concentration of $N(^4S)$ nitrogen atoms in a stream of active nitrogen and from the known fact that the $A\,^3\Sigma_u^+$ state of the N_2 molecule is a very effective energy donor the following two-stage mechanism for CL stimulation was proposed. Recombination of N atoms occurs on the cold surface of benzene with the formation of $N_2(A\,^3\Sigma_u^+)$ molecules in the triplet state followed by the transfer of energy to a phosphorescent state of the guest or to benzonitrile formed from benzene in a chemical reaction.

The initial studies[103,104] of CL reactions of active nitrogen with hydrocarbons were continued with a spectroscopic investigation.[105] The correlation of the CL spectra carried out in the earlier studies[103,104] was confirmed by the results of a parallel study of the reactions of active nitrogen with mixed polycrystals (an aromatic polycrystalline substrate activated with the corresponding benzonitrile derivatives). It was proposed that when benzonitrile is formed during reaction, a phenyl radical appears as an intermediate.

In another study[107] there is an investigation into the nature of the so-called delayed luminescence occurring as a result of the reaction between nitrogen and polycrystalline mixtures of aromatic compounds at 77 K. When hydrocarbons initially condensed on a cold surface are treated with a stream of active nitrogen, CL similar to that reported previously[103-105] is observed. If the supply of nitrogen is then cut off and a vacuum ($\sim 10^{-2}$ mm Hg) is created in the system, the luminescence diminishes exponentially for several minutes until a very low but still finite level is reached. This residual luminescence was called delayed luminescence by analogy with the very familiar delayed luminescence that occurs after ionisation of solids with UV or γ-radiation.

Three types of delayed luminescence were studied: isothermal luminescence at 77 K; isothermal luminescence stimulated by visible or IR light; and thermoluminescence.

The following mixtures (guest + matrix) were studied: naphthalene + benzene, naphthalene + benzene-d_6, acetonitrile + benzene-d_6, benzonitrile + fluorobenzene, *p*-cyanotoluene + toluene. It was found that the delayed luminescence spectrum matched the phosphorescence spectrum of the guest molecules.

When efficient electron acceptors—CCl_4 or benzyl chloride—were introduced into the sample, neither the intensity nor the composition of the CL spectrum obtained when active nitrogen was reacted with hydrocarbons changed, whereas the isothermal luminescence was very considerably reduced and the stimulated luminescence was not observed at all. The experimental results obtained were interpreted on the basis of ideas about the ionisation of mixed polycrystalline samples at 77 K during the primary reaction of active nitrogen with a cooled surface of hydrocarbons. Two possible mechanisms for chemiluminescence were proposed: either by energy transfer from high vibrational levels of $^3\Sigma_u^+$ nitrogen molecules to a high-energy triplet level (T_i) of molecules of the matrix (M) or guest (G):

$$N + N \rightarrow N_2(^3\Sigma_u^+, \text{high } v);$$
$$N_2(^3\Sigma_u^+, \text{high } v) + M \rightarrow N_2(^1\Sigma_g^+) + M(T_i)\ [\text{or } G(T_i)];$$
$$M(T_i)\ [\text{or } G(T_i)] \rightarrow M^+\ (\text{or } G^+) + e^-,$$

or as a result of triplet-triplet annihilation of the guest with an $N_2(^3\Sigma_u^+)$ molecule which has relaxed to a state with low vibrational levels:

$$N_2(^3\Sigma_u^+, \text{low } v) + G(T_1) \rightarrow G^+ + e^- + N_2(^1\Sigma_g^+).$$

In a study by Devolder and co-workers,[107] together with the results already discussed in previous reports[103-106] there are additional data on the reactions of active nitrogen with hydrocarbons using chemiluminescence and EPR. It was established that the phase state of the matrix plays a substantial part in the mechanism for excitation of the triplet state in the guest. Thus, in polycrystalline matrices—both in aromatic (benzene, toluene, pyridine) and aliphatic (cyclohexane) matrices—the CL spectrum consists of phosphorescence from the guests (in the case of toluene, fluorescence from the benzyl radical was observed at the same time as phosphorescence from toluene). In vitreous matrices (ethanol, methylcyclohexane, isopentane) CL did not occur. In the EPR spectra mainly cyclohexadienyl-type radicals were detected.

The main difficulty in establishing the mechanism for the reaction of active nitrogen with organic compounds is principally connected with the existence of several reactive particles in active nitrogen generated by ultra-high frequency discharge in gaseous N_2. These particles are long-lived $N(^4S)$ atoms and $N_2(A\,^3\Sigma_u^+)$ molecules. There is one report[108] on a simple method for obtaining "pure" $N_2(A\,^3\Sigma_u^+)$ by passing active nitrogen through a trap filled with

liquid nitrogen. The removal of nitrogen atoms from $N_2(A^3\Sigma_u^+)$ is achieved in this method as a result of the recombination of the former on the cold surface of the trap. Dessaux[108] observed CL in the reaction of $N_2(A^3\Sigma_u^+)$ with benzene, chlorobenzene, and fluorobenzene at 77 K. The CL spectrum obtained in experiments with benzene matched the phosphorescence spectrum of benzene displaced to lower frequency, from which it was concluded that the CL emitter in this case is a charge transfer complex $N_2(A^3\Sigma_u^+)^{\pm} \ldots C_6H_6^{\mp}$.

This interpretation of the phenomenon was questioned by Mitsumori and Hiraoka.[109] They investigated the CL spectrum recorded at 77 K in reactions of $N_2(A^3\Sigma_u^+)$ with benzene and toluene, and also with given matrices containing biacetyl. If the luminescence emitter were the charged intermediate complex $N_2(A^3\Sigma_u^+)^{\pm} \ldots C_6H_6^{\mp}$ formed on the surface of solid benzene, as proposed by Dessaux, deactivation of its electronically excited state by energy transfer to guest molecules would be inefficient because of localisation of the complex in the benzene matrix. It was shown, however, that introduction of biacetyl into solid benzene substantially quenches the luminescence of pure benzene and leads to the appearance of characteristic phosphorescence from biacetyl.[109] This result indicates that there is migration of triplet excitation energy over a considerable distance in solid benzene. Mitsumori and Hiraoka[109] came to the conclusion that the CL accompanying the reaction of $N_2(A^3\Sigma_u^+)$ with solid benzene was caused by several products formed in the benzene matrix, possibly benzene isomers.

The absence of CL in reactions of $N_2(A^3\Sigma_u^+)$ with solid hexane or cyclohexane at 77 K and also the very weak (1000 times less than in benzene) phosphorescence of biacetyl (0.1 mol %) indicate either that there is no transfer of energy from $N_2(A^3\Sigma_u^+)$ to alkanes or that migration of triplet excitation energy does not occur in the solid matrices studied.

Chemiluminescence in a vitreous hydrocarbon matrix at temperatures above 77 K was first observed by Trozzolo and co-workers.[110] On warming a UV-irradiated glass containing diphenyldiazomethane and oxygen, emission of blue light was observed, with a spectrum that matched the phosphorescence spectrum of benzophenone. In samples that contained no oxygen, luminescence was absent. On the basis of the results obtained and also the fact that the matrices were warmed up several hours after irradiation, it was concluded that the observed luminescence belonged to CL accompanying the reaction of oxygen with the photolytically obtained diphenylmethylene. This CL reaction was observed on warming a 10^{-4} *M* solution of diphenyldiazomethane in 2-methyltetrahydrofuran which had been photolysed at 77 K.[111] Although the suggestion was made in these studies that the CL emitter was benzophenone in the triplet state, the CL spectrum was not published.

On freezing vitreous freon-113 (chosen because of the high solubility of oxygen in it) containing diphenylcarbene obtained photolytically at 77 K, Turro and co-workers[112] were the first to observe emission of light lasting 5–15 s which was visibie to the eye in a darkened room. Using an optical multichannel analyser it was established that CL occurs not only in the reaction between O_2 and diphenylcarbene but also in the oxidation of phenyltrifluoromethylcarbene or phenylchlorocarbene.

The CL spectrum corresponds qualitatively with the phosphorescence spectrum of the ketone which is a source of the carbene: benzophenone in the photolysis of diphenyldiazomethane, tetraphenyloxirane, 2,2,4,4-tetraphenyloxetanone, or diphenylketene; trifluoroacetophenone in the photolysis of phenyltrifluoromethyldiazirene; chlorobenzaldehyde in the photolysis of phenylchlorodiazirene. The CL spectra have an anomalous distribution of intensities of the components as compared with the photoluminescence of the corresponding ketones. The nature of this interesting phenomenon has not been determined, but in the opinion of Turro and co-workers[112] the rigid matrix of fluorocarbon glass, which inhibits the (0,0) transition because of the particular geometry of the chemically excited ketone, may be the cause.

It was established that CL may also occur at 77 K and not only when a vitreous matrix is warmed up.[112] This indicates that there is a low energy of activation for the process. It has been proposed that the reaction takes place via the formation (by a reaction between carbene and oxygen) of a $Ph_2C{=}O^+O^-$ Criegee intermediate, which reacts with oxygen to give the ketone (including that in an electronically excited state) and ozone. The latter has not been detected but is only postulated.

It was concluded[112] that CL from the reaction of carbenes with O_2 is a general phenomenon which does not depend on the multiplicity of the carbene or the source used to prepare it.

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Thus, in the studies on low-temperature CL important results have been obtained on the mobility and reactivity of a number of atoms and molecules at very low temperatures. The ability to diffuse proved very high for nitrogen, oxygen, sulphur, carbon, and barium atoms in matrices of inert gases; even at 5–10 K they diffuse over a distance of several tens of Ångstroms within comparatively short intervals of time (minutes-tens of minutes).

The increased interest shown in recent years towards CL in cryogenic matrices is due to the possibility of obtaining unique information. This primarily relates to the spectroscopic identification of new electronically excited states which often cannot be observed by other methods. It should be noted that CL spectra in matrices of inert gases have a fine structure that is similar to the spectra of gas-phase luminescence. This feature of low-temperature solid-state CL makes it possible to determine the luminescence emitter and reaction pathway and energetics with great accuracy. Chemiluminescence provides information on the population of excited states and makes it possible to assess the most precise details of the elementary event of a reaction and also the effect of matrices of varying types on relaxation processes. Thus, studies on low-temperature CL make a considerable contribution to the understanding of the role of excitation in exothermic reactions in solid matrices.

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