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Electronically Excited Atoms and Molecules in Solid - Gas Systems

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The formation, emission, and deactivation of electronically excited atoms and molecules in solid - gas systems have been examined. The mechanisms of these processes and the influence of the nature of the solid on their course have been discussed. The bibliography contains 175 references.

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I. INTRODUCTION

In recent years there has been a marked increase in interest in the study of excited states on a surface and in particular electronically excited atoms and molecules in heterogeneous systems. This is related to the development of plasma and radiation chemistry, laser technology, and photocatalytic processes, in which the participation of electronically excited atoms and molecules is obvious, although it has been insufficiently studied.[1] Moreover, there are experimental data which indicate that electronically excited molecules are formed in thermal heterogeneous processes. In particular, certain reactions take place by a heterogeneous–homogeneous mechanism, that is electronically excited atoms and molecules are emitted into the gas phase in the course of the reaction. Thus it is clear that for an understanding of the mechanism of many heterogeneous reactions in a solid–gas system it is important to know the properties and behaviour of electronically excited atoms and molecules.

The present review deals primarily with long-lived species. The long radiative lifetimes of some electronically excited atoms and molecules in the gas phase suggest that on solid surfaces also, their stability will be sufficient for them to take part in surface processes such as the luminescence of adsorbed molecules and the formation and emission of electronically excited atoms and molecules from solid surfaces under the influence of light, chemical, mechanical, and other factors. The results of the study of the deactivation of electronically excited atoms and molecules on solid surfaces of different kinds are of considerable interest. The deactivation is due to the exchange of the excitation energy with the solid or with an adsorbed layer, and also to chemical reaction with the surface of the adsorbent (chemisorption) and with the adsorbed species—molecules and radicals.

Information of different kinds on the behaviour of various electronically excited atoms and molecules at a solid–gas interface has been published. The experimental data are generally qualitative in character. The largest number of publications in this field has been devoted to electronically excited oxygen molecules (singlet oxygen $^1O_2$); data have also been published on electronically excited nitrogen molecules, metal atoms, and metastable inert gas atoms.

II. THE FORMATION AND EMISSION OF ELECTRONICALLY EXCITED ATOMS AND MOLECULES INTO THE GAS PHASE FROM A SOLID SURFACE

Recent reviews[1-11] contain varied information on the formation of electronically excited atoms and molecules and their emission from solid surfaces. New data, not discussed in these reviews, have recently been published[12,13] on the mechanism of the photosensitised formation of singlet oxygen in solid–sensitiser–oxygen systems. It has also been found[15-18] that emission of singlet oxygen from solid surfaces takes place in many dark and photo-heterogeneous processes. The surface and the adsorption layers have been excited by different methods: the chemical reaction of oxygen atoms with metal oxides,[17,19-21] mechanochemical processes,[15] the thermal decomposition of catalysts,[16,23] the illumination of catalysts containing transition metal ions,[18,24,25] etc.

1. The Photosensitised Formation of Electronically Excited Oxygen Molecules in Heterogeneous Systems

The idea that singlet oxygen ($^1O_2$) is formed in the reaction of a triplet dye molecule with oxygen by the transfer of the triplet excitation energy was first put forward by Kautsky,[26] who observed the simultaneous quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel and oxidation of the leuco-base of Malachite Green, adsorbed on other silica gel granules. The oxidation took place in a narrow pressure range $(1.56-3.12) \times 10^{-3}$ hPa† oxygen. It was suggested that the oxidation involved electronically excited oxygen molecules, formed by the reaction

$$T + {}^3O_2 \rightarrow S_0 + {}^1O_2$$

where T and S_0 represent respectively the triplet-excited and ground states of the dye molecule, and $^3O_2$ and $^1O_2$ the ground and singlet-excited states of oxygen. Since the sensitiser and the substrate being oxidised were separated in space, the singlet oxygen could pass into the gas phase. It should be noted, however, that the oxidation stopped when the distance between the particles with the adsorbed dye sensitiser and with the substrate being oxidised was increased to several millimetres.

The discussion of the nature of the oxidising agent in these systems continued for many years. Thus according to the hypothesis of Weiss,[27] the oxidising agent could be the oxygen radical-anion $O_2^{\cdot-}$. Later, Weiss adopted the views of Franck and Livingston,[28] who suggested that hydrogen peroxide is formed in this process. The radical-anion removes a hydrogen atom either from the dye sensitiser[28] or from a water molecule adsorbed on silica gel.[29] As pointed out by Terenin,[30] however, energy considerations indicate that the $O_2^{\cdot-}$ radical-anion cannot oxidise the leuco-compound, and the formation of hydrogen peroxide should lead to an irreversible chemical change in the dye sensitiser. The energy of the triplet level of trypaflavine (48 kcal mole^{-1}) is insufficient for the removal of a proton from water molecules adsorbed on silica gel.[31] In the opinion of other authors,[32,33] the reactive species is a metastable complex (moloxide) formed by the triplet dye molecule with oxygen. Under the conditions of Kautsky's experiment, however, this complex cannot leave the surface and reach the substrate being oxidised.

Rosenberg and co-workers[34,35] studied the influence of gases on the quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel, and suggested that a vibrationally excited oxygen molecule is formed in the reaction of oxygen with the triplet sensitiser molecule.

Recently, a number of workers have interpreted the data obtained in the study of systems of this kind in terms of singlet oxygen formation.

Thus the dye-photosensitised (including trypaflavine-sensitised) decrease in the strength of textile fibres has been attributed[29,36] to the participation of singlet oxygen. This effect was observed in the absence of water at an oxygen pressure of 10^{-3} hPa; the sensitiser (a film of dye or a coloured fibre) was situated at a distance of several millimetres from the textile fibre being oxidised.

The dye- (eosin and Methylene Blue) sensitised oxidation by oxygen of diphenylanthracene and rubrene, separated from the sensitiser by layers of barium or cadmium stearate with different thicknesses (up to 500 Å), has been studied.[37] In the opinion of the authors cited, singlet oxygen is formed in this case, and can diffuse through the stearate layers and oxidise the substrate molecules.

The oxidation of various organic substances in solution, photosensitised by dyes (Rose Bengal, eosin, fluorescein, etc.) deposited on chloromethylated polystyrene, has been studied.[38] Analysis of the products indicated that the oxidation is brought about by singlet oxygen, formed in the reaction of a triplet dye molecule with oxygen.

The oxidation of anthracene and 2-methylbut-2-ene in solution, photosensitised by Rose Bengal and eosin deposited on Amberlite IRA-400 ion exchange resin and by Methylene Blue deposited on Amberlite IRS-200, has been observed.[39] From the fact that the compounds obtained were identical to the products of oxidation by singlet oxygen, it was concluded that singlet oxygen is involved in the reaction.

The oxidation of tetramethylethylene, 1,3-diphenylisobenzofuran, etc. in solution, photosensitised by Rose Bengal and Methylene Blue adsorbed on silica gel and alumina gel, has been studied.[40] The efficiency of the oxidation was approximately the same in heterogeneous and homogeneous systems. The experiments of Ref.26 were also repeated using Rose Bengal adsorbed on silica gel as the sensitiser, and 9,10-diphenylanthracene adsorbed on other silica gel particles as the substrate being oxidised. When oxygen (pressure 6 hPa) was passed through a "fluidised bed" of the catalyst with illumination by a xenon lamp for 2.5 h, the degree of oxidation was 50%. It was suggested that the oxidation involves singlet oxygen.

The photosensitised formation of singlet oxygen has been detected[41,42] using a thin film of Rose Bengal as sensitiser. The conclusion that singlet oxygen is formed was reached by analysing the oxidation products of rubrene.

The photo-oxidation of the surface of a single crystal of anthracene in an oxygen atmosphere has been studied.[43] The composition of the products indicated that the reaction takes place under the influence of singlet oxygen.

Thus the conclusion that singlet oxygen plays a decisive role in photosensitised oxidation in heterogeneous solid–dye–oxygen systems was based on the fact that the products of the photosensitised oxidation and the direct action of singlet oxygen were identical. The corresponding comparison for solutions was first made in Refs.44 and 45. Other workers[46,47] studied the oxidation of substances deposited on various supports (cellulose, silica gel, etc.) by singlet oxygen, obtained in different ways. Thus in Ref.46, various substances adsorbed on silica gel were oxidised by singlet oxygen formed by heating the triphenyl phosphite–ozone adduct. The products obtained by oxidising tryptophan, thymine, and uracil, adsorbed on silica gel, by singlet oxygen obtained in a radiofrequency discharge were also identified. In Ref.47, 9,10-dimethylanthracene and other substances,

† 1 hPa = 100 Pa ≅ 0.75 Torr (Editor of Translation).

adsorbed on cellulose and silica gel, were oxidised using singlet oxygen formed in a ultrahigh-frequency discharge. On the basis of these studies, it was suggested[48] that photosensitised oxidation in systems with the sensitiser and the substrate being oxidised separated in space could be used to test for the formation of singlet oxygen. It is only recently, however, that is has been possible to observe the luminescence of singlet oxygen ($^1\Delta_g$) in the gas phase with photosensitisation by a dye film (Rose Bengal).[49,50]

Recently, semiconducting detectors were used to detect singlet oxygen in the gas phase.[17,51] This method is based on the change in the electrical conductivity of thin oxide films (ZnO, TiO_2, CdO, etc.) as a result of the adsorption of atoms and molecules.[22,114,134] The procedure requires the use of not only semiconducting films but also additional apparatus and methods for the selective determination of the concentration of the gas being determined. Singlet oxygen is detected in the presence of oxygen atoms using an apparatus in which the oxygen atoms are deactivated on the surface of mercury or silver oxides.[17,51] The influence of ordinary (triplet) oxygen can be practically eliminated either by lowering the temperature of the detector or by oxidising it beforehand.[51,113] In Ref.12, semiconducting detectors, and also calorimetry, showed unambiguously that the illumination of dyes (trypaflavine, Rose Bengal) adsorbed on quartz, and a film of trypaflavine, leads to the formation and emission of singlet oxygen into the gas phase.

The proof that singlet oxygen is formed when heterogeneous solid–sensitiser–oxygen systems are illuminated, and the quenching of the phosphorescence of the adsorbed sensitiser, observed simultaneously, confirm the view[26] that singlet oxygen is formed by the reaction of oxygen with a triplet molecule of the sensitiser. It should be noted, however, that the quenching of the phosphorescence of the sensitiser by oxygen indicates only that singlet oxygen is formed, and to investigate its subsequent behaviour (the regular features of emission into the gas phase) it is necessary to study its desorption.

Since the concentration of singlet oxygen in the gas phase is directly proportional to the intensity of excitation,[12] the change in the intensity of the phosphorescence of the adsorbed sensitiser in the reaction with oxygen is apparently given by an equation of first order with respect to the triplet molecules of the sensitiser.[34,52] The change in the intensity of the phosphorescence of the adsorbed sensitiser with change in the oxygen pressure[35] corresponds to the change in the concentration of singlet oxygen in the gas phase. Thus the intensity of the phosphorescence of the sensitiser decreases, and the concentration of singlet oxygen in the gas phase increases, with increase in the oxygen pressure. With further increase in the oxygen pressure, the intensity of the phosphorescence of the sensitiser becomes close to zero (that is all the triplet molecules of the sensitiser are quenched), but the concentration of singlet oxygen formed is a maximum, and its concentration in the gas phase is determined only by homogeneous–heterogeneous deactivation processes.[12,13] The rate constant for the reaction of a triplet molecule of trypaflavine adsorbed on quartz is 5×10^9 litre $mole^{-1}s^{-1}$. The calculation was based on the assumption that the singlet oxygen is formed by the transfer of the energy of the sensitiser molecule to oxygen in a short-lived collision complex. This value agrees satisfactorily with published data[34,52,53] obtained by measuring the quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel. In the works cited it was again assumed that the quenching of the phosphorescence of the sensitiser by oxygen takes place in a short-lived collision complex formed by the triplet molecule of the sensitiser and oxygen.

In this case also, however, it is necessary to take account of the specific features of heterogeneous systems. Thus the quenching of the phosphorescence of trypaflavine adsorbed on silica gel does not obey the Stern–Volmer relationship. In Refs.53–59, the regular features of the change in the intensity of the phosphorescence and the lifetime of the triplets of trypaflavine adsorbed on silica gel with change in the oxygen pressure in the gas phase were explained in terms of the dynamic character of the quenching (according to Terenin[60]), that is the process takes place in a short-lived collision complex. Thus from the practically instantaneous and ready reversal of the quenching as far as −60 °C it was concluded[55] that the form of the quenching curves is independent of the adsorption of oxygen. In Ref.53 it was established that all the luminescence centres of trypaflavine adsorbed on silochrome react with oxygen at the same rate at all stages of the non-exponential quenching of the phosphorescence, and it was concluded that the quenching is dynamic in character. In Refs.54 and 56–58 the deviations from the Stern–Volmer relationship were attributed to the molecular-sieve and trajectory effect. The sensitiser molecules may be situated in macro-pores of the adsorbent, readily accessible to oxygen, or in micro-pores (cracks), which are not readily accessible. The distribution of the sensitiser in the macro- and micro-pores determines what fraction of the triplet molecules of the sensitiser will contribute to the phosphorescence, and what fraction will be quenched. It is difficult to imagine, however, that a pore which is accessible to the fairly large molecule of the sensitiser (trypaflavine) will not be filled by oxygen molecules, whose dimensions are appreciably smaller. Moreover, it was assumed that only part of the trajectory of the random movement of the active product of the photodissociation of the trypaflavine molecule (polaron, H, exciton, etc.) in the matrix is accessible to oxygen molecules. Thus in the opinion of the authors cited, the nature of the solid on which the sensitiser is adsorbed has a decisive influence on the quenching of the phosphorescence of the sensitiser (and hence the formation of singlet oxygen). As noted in Ref.53, the regular features of the quenching of the phosphorescence of adsorbed trypaflavine can also be explained by assuming that there is a distribution of the luminescence centres with respect to lifetime. This view was put forward in Ref.61. It was found that trypaflavine is adsorbed as monomers and dimers, and that the lifetime of the triplets in the dimeric form is shorter than for the monomeric form. Moreover, the lifetime of the triplets of the adsorbed trypaflavine was independent of the oxygen pressure over a wide range (10^{-6}–1 hPa), whereas the intensity of the phosphorescence changed by several powers of ten. It was therefore suggested that a decisive role in the quenching of the phosphorescence of adsorbed trypaflavine is played by adsorbed oxygen. In Ref.62, the quenching of the phosphorescence of biphenyl, naphthalene, and chloronaphthalene on silica gel was brought about by adsorbed oxygen, that is the quenching was static in character.

There are thus two views of the quenching of the phosphorescence of adsorbed molecules by oxygen and the associated formation of singlet oxygen. Up to the present (see earlier reviews[2–11]) the predominant view has been that singlet oxygen is formed in a short-lived collision complex (triplet sensitiser molecule–oxygen), that is the dynamic mechanism of the quenching of the phosphorescence has been assumed. Recently, however, direct proof that adsorbed O_2 molecules take part in the formation of singlet oxygen has been obtained. Thus in Refs.12 and 13 it was shown that singlet oxygen is formed with the photosensitisation of trypaflavine adsorbed on quartz, or a film of trypaflavine, and previously adsorbed oxygen.

The formation and emission of singlet oxygen into the gas phase was observed under conditions of continuous evacuation at a residual gas pressure of 10^{-6} hPa, and the intensity of the emission decreased regularly with time. The emitting power of these systems was preserved for several tens of minutes, evidently due to oxygen adsorbed on the surface. At an oxygen pressure in the gas phase of 10^{-6} hPa, the quenching of the phosphorescence of adsorbed trypaflavine is not observed.[35] Moreover, singlet oxygen is not formed if the sensitiser is evacuated for several hours at a temperature of ~100 °C.

Similar data were obtained using vanadium[24] and molybdenum[25] ions deposited on quartz as sensitiser. The results of these experiments show convincingly that adsorbed oxygen plays a decisive role in the formation of singlet oxygen in heterogeneous systems. The residence time of the oxygen molecule on the solid surface, even in the case of physical adsorption, is greater by several powers of ten than the lifetime of the collision complex, so that the efficiency of the formation of singlet oxygen should be greater by several powers of ten in this case. Thus in the gas phase the efficiency of the formation of singlet oxygen is ~10^{-3} (from data on the quenching of the phosphorescence of the sensitiser[9]), whereas in solutions it is close to 1, because of the cage effect.[63-65] In Ref.40 it was shown that the efficiency of the photosensitised oxidation in heterogeneous systems is not lower than that under homogeneous conditions for solutions. According to Ref.61, for trypaflavine adsorbed on silica gel, the efficiency of the formation of singlet oxygen is close to 1. The question of possible centres for the adsorption of oxygen can be considered. It may be assumed that oxygen is adsorbed on the surface of the solid, migrates over the surface, and collides with triplet molecules of the sensitiser. Simple calculation of the concentration of singlet oxygen in the gas phase shows, however, that in this case the efficiency of its formation should be much smaller than 1. It is natural to assume that the oxygen molecules involved in the quenching are adsorbed on the molecules of the sensitiser.

The quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel is a practically activationless process.[34,53] On the other hand, in Refs.12 and 13 it was found that the concentration of singlet oxygen in the gas phase increases considerably with increase in the temperature of the sensitiser. The concentration of singlet oxygen in the gas phase is apparently determined by the desorption of singlet oxygen from the surface. It is still not clear from which centres the singlet oxygen is desorbed, that is whether it is desorbed from a sensitiser molecule or from the quartz surface. The increase in the concentration of singlet oxygen in the gas phase with increase in the temperature of the sensitiser, detected in Ref.13, can be attributed to a decrease in the residence time of the singlet oxygen molecule either on the quartz surface or on the sensitiser molecule. Correspondingly, the activation energy of the effective rate constant for the formation of singlet oxygen, 10 kcal mole^{-1},[13] can be taken as the heat of adsorption of singlet oxygen on the quartz surface or as the heat of adsorption on the sensitiser molecule. In Ref.34, the quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel stopped at the temperature of liquid nitrogen. The heat of adsorption of singlet oxygen, calculated with allowance for this experimental fact, was found to be 6 kcal mole^{-1}. Unfortunately, there are no direct data on the adsorption characteristics of singlet oxygen.

Thus it is not yet possible to give a definite answer to the question raised. The estimated activation energy of the desorption of oxygen from the surface of trypaflavine (12 kcal mole^{-1}),[66] however, indicates that desorption of singlet oxygen from the sensitiser molecule is more probable.

A possible scheme for the formation and emission of singlet oxygen into the gas phase is given below:

$$^1S_0 + {}^3O_2(gas) \rightleftarrows [^1S_0 \ldots {}^3O_2(ads)]$$
$$[^1S_0 \ldots {}^3O_2(ads)] \xrightarrow{h\nu} [^1S_1 \ldots {}^3O_2(ads)]$$
$$[^1S_1 \ldots {}^3O_2(ads)] \rightarrow [^3S_1 \ldots {}^3O_2(ads)]$$
$$[^3S_1 \ldots {}^3O_2(ads)] \rightarrow [^1S_0 \ldots {}^1O_2(ads)]$$
$$[^1S_0 \ldots {}^1O_2(ads)] \rightarrow {}^1S_0 + {}^1O_2(gas)$$

where $[^1S_0 \ldots {}^3O_2(ads)]$, $[^1S_1 \ldots {}^3O_2(ads)]$, $[^3S_1 \ldots {}^3O_2(ads)]$, and $[^1S_0 \ldots {}^1O_2(ads)]$ are the complexes of oxygen with the sensitiser molecule in the ground state $^1S_0$, the singlet excited state $^1S_1$, and the triplet state $^3S_1$, and $^3O_2(gas)$, $^1O_2(gas)$, $^3O_2(ads)$, and $^1O_2(ads)$ the ground and singlet excited states of oxygen in the gas phase and in the adsorbed phase respectively. The nature of the complex in which singlet oxygen is formed must be determined in each specific case.

Until recently it was usually assumed that singlet oxygen is formed in a short-lived collision complex with transfer of energy,[9] and not in a complex with charge transfer, except in the case of aromatic substances.[67] It has been found, however, that the formation of singlet oxygen in a complex with charge transfer is characteristic of alkenes[10] and a number of other substances.[4,68] As noted in Ref.69, the detection of magnetic effects (the influence of a magnetic field and chemical polarisation of the nuclei) in a number of cases helps to decide between energy transfer and electron transfer processes. A detailed review of the influence of a magnetic field on the reaction of triplet molecules with oxygen has been published.[70] There is apparently only one published paper on the influence of a magnetic field on the efficiency of the formation of singlet oxygen in heterogeneous systems. This is a paper by Frankevich and Sokolik[71] on the solid-phase photo-oxidation of tetracene. The reaction of oxygen with tetracene molecules in the triplet state gives a charge-transfer complex with a lifetime of 10 s at room temperature. The application of a magnetic field (H = 2 kOe) increases the rate constant for the reaction of oxygen with the triplet molecule of tetracene (that is the efficiency of the formation of singlet oxygen) by 50 ± 10%. The authors cited consider that all the singlet oxygen formed is used up in the oxidation of tetracene. The existence of emission by singlet oxygen from the surface of tetracene into the gas phase does not cast doubt on the main conclusions of the work cited, but it must be taken into account in the explanation of the temperature dependence of the rate of the photo-oxidation of tetracene.

This work clearly demonstrates the important information that can be obtained by studying the influence of a magnetic field on the efficiency of the formation of singlet oxygen in heterogeneous systems.

In Ref.4 it was suggested that singlet oxygen is formed via an intermediate moloxide stage. In a recent theoretical paper,[72] the quenching of the phosphorescence of ethylene by oxygen (and the formation of singlet oxygen) was also attributed to moloxide formation.

It is also possible to use inorganic molecules deposited on a solid surface as sensitiser. Thus when a quartz surface promoted by vanadium[18,24] or molybdenum[25] ions is illuminated in the presence of oxygen, singlet oxygen is formed and emitted into the gas phase. From the regular features of the emission of singlet oxygen in V/SiO_2 and Mo/SiO_2 systems, and also from data on the quenching by oxygen of the phosphorescence of transition metal (vanadium, molybdenum) ion complexes on a quartz surface,[73] the following mechanism can be proposed for the formation and emission of singlet oxygen into the gas phase in these systems.[18,24] When the V/SiO_2

system is illuminated, surface charge-transfer complexes are formed:[74]

$$|V^{5+}O^{2-}| \xrightarrow{h\nu} |V^{4+}O^{-}|_s^*$$

where s = surface. In the quenching of the phosphorescence of the complex on the surface of the adsorbent, the excitation energy of the complex is transferred to the adsorbed oxygen molecule to give singlet oxygen, which is subsequently desorbed. In this case the dependence of the concentration of singlet oxygen in the gas phase on the intensity of the exciting light and the oxygen pressure is similar to that for solid–dye–oxygen systems.[12,13] A decrease in the concentration of the metal–oxygen complexes on the quartz surface, brought about by preliminary photo-reduction of the specimen with hydrogen (when the V and Mo complexes decompose[75]), leads to a decrease in the intensity of the liberation of singlet oxygen.

With increase in the temperature of the sensitiser, the concentration of singlet oxygen in the gas phase increases. The activation energy of this process is 1.5 kcal mole^{-1}. This value is appreciably lower than the activation energy of the formation and emission of singlet oxygen into the gas phase when a dye (trypaflavine) is used as sensitiser.[13] It has been suggested[24] that the increase in the intensity of the emission of singlet oxygen with increase in the temperature of the sensitiser in this case is related to a decrease in the residence time of the singlet oxygen on the surface of the adsorbent, and to a consequent decrease in the rate of the deactivation of singlet oxygen on the solid surface.

Thus in the investigation of the mechanism of photo-oxidative processes on deposited catalysts it is apparently necessary to take account of the extremely probable role of singlet oxygen molecules. It also follows from Refs.15, 18, 24, and 25 that some oxidative photo-heterogeneous processes may take place by a heterogeneous–homogeneous mechanism.

2. The Influence of the Nature of the Sensitiser Carrier on the Efficiency of Formation of $^1O_2$

There are practically no published data on the influence of the solid on the photosensitised formation and emission of singlet oxygen into the gas phase. In a number of cases it is difficult to relate unambiguously the change in the efficiency of the formation of singlet oxygen to a specific mechanism of the influence of the solid.

Thus for example the quenching of the phosphorescence of trypaflavine adsorbed on silica gel does not obey an exponential law.[77–79] In Ref.77, the phosphorescence quenching curves were represented as the sum of two exponents, corresponding to two metastable levels of the sensitiser molecule. In Ref.79 this suggestion was rejected on the basis of the fact that the phosphorescence quenching curve is non-exponential at low temperatures, when the lifetime and phosphorescence spectra are independent of temperature. The non-exponential nature of the quenching of the phosphorescence, which could not be represented as the sum of two exponents, was attributed to a difference in the nature of the trypaflavine adsorption centres on the silica gel.

In Ref.82 it was found that the kinetics of the quenching of the phosphorescence of naphthalene and anthracene adsorbed on γ-Al_2O_3 at degrees of covering $\ll 1$ do not obey an exponential law, but are described by a sum of two exponents. The observed regular features were attributed to a difference in the nature of the adsorption centres. In Ref.78, a mechanism for the quenching of the phosphorescence was proposed, involving the reversible dissociation of the excited sensitiser molecule and the migration of one of the products (HO_2, H^+, exciton, etc.) in the cage. In Ref.61, the deviation from the exponential relationship was attributed to the presence of monomeric and dimeric forms of the sensitiser. The phosphorescence which was quenched rapidly was assigned to sensitiser dimers, and that which was quenched more slowly was assigned to the monomers. This view is confirmed by the fact that the changes in the absorption and luminescence spectra of trypaflavine adsorbed on silica gel are slight compared with aqueous solutions, indicating that trypaflavine is physically adsorbed on the silica gel surface.[77] This is also indicated by the fact that the form of the phosphorescence quenching curve is independent of the pH at which the adsorption is carried out.[79] In Refs.80 and 81 it was shown that the chemisorption of the dye takes place only if the overlap integral of the wavefunctions of the adsorbate and the adsorbent is sufficiently large to displace the hydrogen bond.

In Ref.61, therefore, the form of the curve for the quenching by oxygen of the phosphorescence of adsorbed trypaflavine was attributed to a difference between the efficiencies of the reaction of oxygen with the triplets of trypaflavine in the monomeric and dimeric forms (and hence a difference in the efficiences of the formation of singlet oxygen). The values are 0.980 ± 0.05 for the monomeric form, and 0.86 ± 0.04 for the dimer.

A decrease in the sensitivity of the phosphorescence of adsorbed trypaflavine to the presence of oxygen on dehydroxylation of the silica gel has been observed.[55] The opposite conclusion was reached, however, in a study[83] of the influence of the moisture content and nature of the support on the quenching by oxygen of the phosphorescence of various adsorbed organic substances (including substances adsorbed on silica gel).

It was also found[18,25] that adsorbed vanadium and molybdenum ions are good sensitisers of the formation of singlet oxygen, but when an oxide phase appears, singlet oxygen is not formed. The quartz surface on which the ions are adsorbed takes part in the formation of surface complexes which photosensitise the formation of singlet oxygen. When a bulk oxide phase is produced, these complexes are not formed,[14] and singlet oxygen is not generated.

Thus the carrier influences the nature and state of the sensitiser, and this may be revealed by a change in the nature of the deactivation of its excited states. In addition, dimerisation or aggregation of the sensitiser and modification of its electronic structure by the adsorbent are possible. All this must be taken into account in the study of the photosensitised formation and emission of singlet oxygen into the gas phase in heterogeneous solid–gas systems.

The nature of the solid may also influence the formation and emission of singlet oxygen into the gas phase. Thus the formation of singlet oxygen has been studied in experiments in which the support for the sensitiser (trypaflavine) was zinc oxide, whose electronic properties could be altered.[84] The formation and emission of singlet oxygen into the gas phase was observed only after extensive oxidation of ZnO. After the reduction of the oxidised zinc oxide in the course of the experiment, the formation of singlet oxygen stopped. This result can be understood if account is taken of the effect of the spectral sensitisation by dyes of the photoconductivity of zinc oxide.[60] When oxygen is adsorbed on the surface of zinc oxide, thermally activated capture of electrons takes place on the surface levels of the adsorbed oxygen. According to Ref.85, it is on these levels that effective transfer of the excitation energy of the adsorbed sensitiser takes place. In reduced ZnO, the concentration of surface ionised zinc is high.[86] When oxygen is adsorbed, a high density of surface levels is created, and effective transfer of the excitation energy of the sensitiser (trypaflavine) to the support (zinc oxide) takes place. When ZnO is treated

with oxygen atoms (extensive oxidation), the quantity of surface superstoichiometric zinc atoms and the density of surface levels decrease sharply.[86] In this case the transfer of the excitation energy of the sensitiser to oxygen, that is the formation of singlet oxygen, becomes more effective.

In addition to the transfer of the energy of electronic excitation of the sensitiser to the solid, its vibrational degradation as a result of the interaction of the sensitiser molecule with the solid is also possible. The formation and emission of singlet oxygen into the gas phase with photosensitisation by a film of dye (trypaflavine) has been detected.[12,13] The dye molecules in the solid phase to a large extent retain their individual properties, since they are joined by weak dispersion forces.[60] A film of this kind can be regarded as a strongly absorbing surface layer on a support. It is apparently these characteristic features of the behaviour of the dye molecule in the solid phase that determine the regular features of the formation and emission of singlet oxygen into the gas phase. A hundred-fold increase in the rate constant for the degradation of the energy of the triplet excitation of the sensitiser compared with the adsorbed state has been detected.[84] This increase was related to the vibrational degradation of the excitation energy of the sensitiser as a result of reaction with the support. Thus in the study of the regular features of the formation and emission of singlet oxygen into the gas phase in heterogeneous solid–sensitiser–oxygen systems it is necessary to take account of the distribution of the excitation energy of the sensitiser between the solid and oxygen.

The dependence of the concentration of singlet oxygen in the gas phase on the oxygen pressure with sensitisation by adsorbed trypaflavine differs considerably for silica and quartz surfaces.[13] In the case of silica gel, the formation and emission of singlet oxygen into the gas phase is observed in a narrower range of oxygen pressures, and its maximum concentration is displaced to low pressures. This difference can be attributed to the effective deactivation of singlet oxygen in the pores of the silica gel. Thus the efficiency of sensitisers adsorbed on silica gel is low in photo-oxidation processes.

The influence of the adsorption characteristics of singlet oxygen on the efficiency of its formation and emission into the gas phase has not been studied, since there are no data on the adsorption of singlet oxygen.

The photosensitised formation of singlet oxygen when the role of the sensitiser is played by the solid is of considerable interest. Thus even in Ref.87 it was suggested that when zinc oxide with oxygen adsorbed on its surface is illuminated, the formation and emission of singlet oxygen into the gas phase should take place in the intrinsic absorption band. It has recently been suggested that singlet oxygen is formed in the photo-desorption of oxygen from zinc oxide[88] and in the photocatalytic osidation of hydrogen on potassium bromide.[89] No direct proof that singlet oxygen is formed was given, however.

In addition to the mechanism examined (it can be described as physical), which involves the transfer to oxygen, most probably adsorbed, of the energy of optical excitation by surface centres or adsorbed molecules, a chemical mechanism also exists. Its chief characteristic is the chemical reaction taking place on the surface to give singlet oxygen. Thus data have been obtained,[90] indicating that singlet oxygen is formed when a highly hydroxylated titanium dioxide surface is illuminated. The authors of the works cited, who had previously carried out extensive work on the photo-desorption of oxygen from the surface of TiO_2, found that when titanium dioxide, previously activated with chlorine and impregnated with a solution of caesium anthracene-9,10-bis(ethanesulphonate) (AES), which is an effective absorber of singlet oxygen, was illuminated, the quantity of oxygen desorbed was much smaller than in the absence of AES. It was concluded that in this system, singlet oxygen is formed on the TiO_2 surface. The mechanism of formation of $^1O_2$ includes: 1) the formation of H_2O_2 in the course of the photo-desorption of O_2 from the hydroxylated TiO_2 surface; 2) the oxidation of surface chloride ions to ClO^- when TiO_2 is illuminated in an O_2 atmosphere; and 3) the reaction of surface ClO^- ions with hydrogen peroxide:

$$ClO^- + H_2O_2 \rightarrow H_2O + Cl^- + {}^1O_2$$

Thus in this system the mechanism of formation of $^1O_2$ is chemical in character, like the homogeneous production of $^1O_2$ as a result of the reaction of H_2O_2 with the ClO^- ion in solution.[91]

The liberation of singlet oxygen after heating a sensitiser previously irradiated with light at a low temperature has been observed.[92,93] Thus in Ref.93, alcoholic solutions of Rose Bengal and Methylene Blue were illuminated at −60 °C, and singlet oxygen was liberated after heating to room temperature. In Ref.92, illumination of polyvinylnaphthalene at 0 °C followed by heating without illumination to 30 °C also led to the emission of singlet oxygen. In the opinion of the authors cited, singlet oxygen is formed by the decomposition of peroxides stable at a low temperature, which in turn are produced as a result of the reaction of the substances inidcated with singlet oxygen. Thus accumulation of singlet oxygen, which is subsequently readily liberated, takes place.

Many questions have still to be answered. Thus it is not clear whether the singlet oxygen in heterogeneous systems is produced in the state $^1\Delta_g$ or $^1\Sigma_g^+$, there are no accurate data on the efficiency of its formation, the possible formation of singlet oxygen by reaction with singlet-excited molecules has not been studied, and a number of other problems, which have been successfully resolved for homogeneous systems, still remain.

The general character of the problems examined for the case of singlet oxygen has been demonstrated[94] in a study of the triplet–triplet transfer of energy from solid organic substances (naphthalene, 9,10-anthraquinone, etc.), excited by light, to molecules of the gas phase (penta-1,3-diene), leading to the *cis–trans* isomerisation of these molecules.

3. The Formation of Electronically Excited Oxygen Molecules as a Result of the Adsorption of Oxygen, Chemical Reactions, and Structural-chemical Transformations on Solid Surfaces

EPR has been used to study the reaction of oxygen with chromium ions deposited on silica gel, and the formation of the complex $[Cr^{5+}O_2]$ was detected.[159] The parameters of the EPR spectrum of this system agreed with the suggestion that the O_2 molecule in this complex is in the singlet-excited state. An analysis[161] of a large number of EPR studies of complexes of O_2^- radical-ions with Ti^{4+} and V^{5+} ions showed that the ground state of molecular oxygen in the coordination sphere of these metals must be singlet.

The adsorption of oxygen on the (100) and (110) faces of a single crystal of copper has been studied.[160] Ultraviolet photoelectron spectroscopy identified several forms of adsorbed oxygen, including a molecular form, stable at temperatures of 100–300 K, whose photo-electron spectrum consists of three bands. The authors cited consider that this form is an electronically excited O_2 molecule in the state $^1\Sigma_g^+$ (for the triplet O_2 molecule the photo-electron spectrum consists of five bands). This state of singlet oxygen, which is unstable in the gas phase, in the opinion of the authors cited is stabilised on the copper surface as a result of adsorption, and can react with various molecules.

The formation and emission into the gas phase of excited oxygen molecules can take place during the recombination of O atoms (a strongly exothermic reaction, $Q = 118$ kcal mole^{-1}) on solid surfaces. Thus it has been shown[76] that an appreciable proportion of the energy liberated in the recombination of oxygen atoms on metal surfaces is carried into the gas phase. The authors cited, however, do not indicate precisely in which energy state (vibrationally or electronically excited) the oxygen molecules leave the surface. In Ref.21 it was proved spectroscopically that electronically excited $^1O_2$ molecules are formed during the recombination of O atoms on nickel films. The authors cited consider that the production of an electronically excited $^1O_2$ molecule by the reaction:

$$NiO + O \rightarrow Ni + {}^1O_2 \quad (1)$$

is unlikely. The formation of the $^1O_2$ molecule in this system may take place by the reaction of an adsorbed O atom and an O atom leaving the gas phase:

$$NiO.O(ads) + O(gas) \rightarrow NiO + {}^1O_2 \quad (2)$$

Here, the excitation energy is determined by the dissociation energy of O_2 after subtraction of the energy of the bond formed by O(ads) with the NiO surface.

The emission of singlet oxygen as a result of the recombination of O atoms on Pyrex has been detected.[158] The probability of the formation of $^1O_2$ in this process is 0.2–0.4 (depending on the conditions of the experiment).

$^1O_2$ molecules can also be obtained as a result of the reaction of oxygen atoms with metal oxides. Mercury oxide has been studied in most detail in this connection. Even in early studies of the formation of singlet oxygen in electrical discharges in oxygen[19,20] it was noted that when the stream of active particles from the discharge passes over a film of mercury oxide there is a significant increase in the concentration of singlet oxygen in the gas phase, determined from the intensity of the spectral bands of $^1O_2$. The authors cited[20] consider that the singlet oxygen molecules are formed as a result of the reaction of oxygen atoms with mercury oxide.

In Ref.17, semiconducting detectors of singlet oxygen were used for the first time to study the emission of $^1O_2$ in this system. The O atoms were generated on a platinum filament and diffused to a film of HgO.

The dependence of the intensity of the signal of the detector (which was at room temperature) on the temperature of the thermal-decomposition filament was used to calculate the activation energy (53 kcal mole^{-1}) of this process, which was found to be approximately half the energy of rupture of the bond in the oxygen molecule. The result indicates that the magnitude of the signal in these experiments is proportional to the concentration of singlet oxygen, and that the emission of $^1O_2$ from the HgO surface is a reaction of first order with respect to oxygen. According to data on the change in the electrical conductivity of the detector, the ratio of the intensities of the fluxes of the O atoms falling on the HgO surface and the $^1O_2$ molecules leaving is close to 1, that is this reaction has a high efficiency.

The data obtained agree with the mechanism proposed in Ref.20:

$$HgO + O \rightarrow Hg + {}^1O_2 \quad (3)$$

The activation energy of reaction (3) is 5 kcal mole^{-1}, which is characteristic of processes involving oxygen atoms.[86]

As shown by Eqn.(3), the oxygen atoms reduce the mercury oxide surface, and this was observed visually from the darkening of the HgO film. As reduction proceeds, another process, competing with reaction (3), begins to play a larger role, namely the oxidation of the newly formed mercury atoms, leading to a decrease in the intensity of the flux of $^1O_2$ molecules from the HgO surface:

$$Hg + O \rightarrow HgO$$

During the experiment, the high initial intensity of the $^1O_2$ flux decreased regularly to a stationary value. Thus with a constant flux of primary active species, that is O atoms, the state of the HgO surface reflects redox reactions taking place simultaneously to establish a stationary flux of $^1O_2$ molecules into the volume.

Comparison of the results with published data[20,96] indicates that metal oxides whose surface layers can be even partially reduced by oxygen atoms (for example lead, silver, or mercury[96]) liberate $^1O_2$ molecules in the course of this reaction. This effect is observed because the energy of the bond formed by oxygen in the surface layer of, for example, PbO is half the standard enthalpy of formation of this oxide[97] and amounts to 40 kcal mole^{-1}. In other words, the emission of $^1O_2$ in reactions of this kind is possible only for those oxides whose surface oxygen atoms are relatively weakly bound in the crystal lattice.

Zav'yalov and Myasnikov[15] described for the first time a study of the formation and emission of singlet oxygen when a disordered quartz surface was heated in an oxygen atmosphere. In this case the energy necessary for the excitation and emission of the oxygen molecules is accumulated during the preliminary disordering of the surface layer of the solid, and is liberated during the relaxation of the disordered surface. It was discovered for the first time that singlet oxygen is liberated when quartz, freshly ground in oxygen (0.13 hPa) or in a vacuum, is heated in O_2. The temperature dependence of the intensity of the $^1O_2$ flux from the quartz surface in the range 200–600° is given by a curve with a maximum at 400 °C. The ascending branch of the curve corresponds to an intensification of the ordering of the structure of the surface layer (annealing of defects) with increase in temperature, and the descending branch is possibly related to a decrease in the concentration of defects in the surface layer of the adsorbent. It was noted that the emission of $^1O_2$ molecules is accompanied by a decrease in the intensity of the EPR signal, apparently as a result of the annealing of paramagnetic defects in the quartz. It is significant that the emission of $^1O_2$ molecules was not observed on fused quartz (which does not contain surface paramagnetic defects).

On isothermal heating, the rate of the liberation of singlet oxygen gradually decreases, and the kinetics of this process do not obey the equation for a unimolecular reaction. Thus the formation and emission of singlet oxygen molecules from the quartz surface are more complex than the simple decomposition of surface compounds with the liberation of $^1O_2$ into the gas phase, and are apparently determined by the annihilation of defects in the quartz layers next to the surface in the presence of O_2.

Another method can also be used to activate a quartz surface with respect to $^1O_2$ emission. In Ref.98 it was discovered that when a quartz vessel in which a stoichiometric $H_2 + O_2$ mixture had previously been exploded was heated under programmed conditions to temperatures of 400–500 °C at an O_2 pressure of 0.13 hPa, emission of singlet oxygen into the gas phase begins. The temperature dependence of the emission of $^1O_2$ in this case is similar to that for the surface of ground quartz. Thus for quartz surfaces "perturbed" in different ways, the relaxation of the disordering of the surface layers in the presence of O_2 is accompanied by the production of singlet oxygen. The result is also of interest in relation to the participation of the walls of a reaction vessel in the production and emission of excited species in chain processes taking place at low pressures.

The conditions of the formation and emission of singlet oxygen from the surface of an Li–Sn–P catalyst have been studied.[16] When oxygen (4 hPa) or air is blown through a U-shaped quartz reaction vessel containing tablets of an oxide catalyst (58.4% Sn, 10% P, and 1.5% Li), heated to 650 °C, singlet oxygen is liberated into the volume, as established from the change in the concentration of a solution of rubrene in hexadecane, placed in a cell separated from the reaction vessel (rubrene is a specific reagent for singlet oxygen[7]). More than 20 oxide catalysts were studied. The intensity of the emission of singlet oxygen from the catalyst surface was estimated from the degree of transformation of rubrene 1 h after the start of the experiment. This quantity was 30–50% for the lithium–tin–phosphate catalysts, and 1% in the absence of lithium, as in the case of manganese and cobalt oxides.

The rate of the liberation of $^1O_2$ increased with increase in temperature. The duration of the emission was 4 h. The process did not stop when oxygen was replaced by argon. The authors cited concluded that this indicates that $^1O_2$ is formed with the participation of surface oxygen on centres which break down in the course of the reaction or on the decomposition of unknown impurities in the catalyst. It is suggested that lithium in this system is converted into the superoxide, facilitating the generation of singlet oxygen. Singlet oxygen was not liberated when other catalysts, ZnO, Ag/Al_2O_3, CaO/Al_2O_3, Cr_2O_3/Al_2O_3, etc. were heated.

The emission of singlet oxygen from the surface of vanadium pentoxide, a widely encountered oxidation catalyst, has been observed.[23] $^1O_2$ molecules are emitted into the gas phase when V_2O_5 powder is heated in an atmosphere of ordinary oxygen to 300–500 °C. The initial intensity of the liberation of $^1O_2$ increases with increase in temperature. At a constant O_2 pressure (0.13 hPa) and a constant temperature, the emission of $^1O_2$ continues for several hours. The activity of the catalyst is restored after heating in O_2 at a temperature of 600 °C and atmospheric pressure. In contrast to the experiments at low O_2 pressures, the intensity of the $^1O_2$ flux remains unchanged with time at atmospheric pressure. From this the authors cited conclude that the emission of singlet oxygen from the V_2O_5 surface may be due to reversible structural-chemical transformations in the catalyst, taking place at high O_2 pressures and high temperatures. The observation that continuous emission of $^1O_2$ from a V_2O_5 surface takes place at atmospheric pressure of oxygen is important for an understanding of the mechanism of stationary oxidation reactions on this catalyst.

This is confirmed by the results of a comparison[99] of the regular features of the emission of singlet oxygen from a vanadium pentoxide surface and the oxidation of naphthalene on the same catalyst. The intensities of the two processes (the emission of $^1O_2$ and the formation of phthalic anhydride) changed in the same sense with change in the conditions of the experiments (treatment of the catalyst with the reaction mixture, heating in a vacuum, etc.). It was also established that naphthaquinone, one of the intermediate products of the oxidation of naphthalene, is formed at a low concentration of singlet oxygen. Thus the participation of singlet oxygen in the heterogeneous catalytic oxidation of organic substances was proved experimentally for the first time for the case of the oxidation of naphthalene to phthalic anhydride on a vanadium catalyst. These data indicate that singlet oxygen plays an important role in oxidation processes taking place by both heterogeneous and heterogeneous–homogeneous mechanisms.

Finally, it is appropriate to draw certain conclusions about the regular features of the emission of singlet oxygen from solid surfaces into the gas phase. The improvement of old methods for detecting singlet oxygen and the development of new methods, in particular the use of semiconducting $^1O_2$ detectors,[17,51] have made it possible to extend considerably the range of the study of physico-chemical processes leading to the formation and emission of singlet oxygen and to establish various characteristic features of their mechanism. In all cases, singlet oxygen is formed as a result of the transfer of excitation energy from a solid or an adsorbed layer to oxygen molecules. The source of this energy may be light (photochemical reactions), the energy of the recombination or reaction of atomic oxygen with metal oxides (chemical reactions), thermal energy (the decomposition of various metal oxides), or energy liberated in the disordered surface layers of a solid during their ordering (structural-chemical processes). All this indicates that it is highly probable that singlet oxygen also appears in other processes in which a solid is excited in the presence of oxygen, for example under the influence of electrons, ions, radiation of different kinds, and in general as a result of reactions leading to marked and reversible breakdown of the structure of the surface layers of solids.

Particular mention may be made of the as yet limited data[159–161] on the possible formation of singlet oxygen on the surface of solids as a result of the adsorption of O_2. An early suggestion,[162] subsequently discussed repeatedly,[1,163] proposed that the surface compounds formed on the chemisorption of molecules could be regarded as electronically excited states of these molecules. This idea has been confirmed for the case of $^1O_2$. In a number of cases, marked perturbation of the adsorbed oxygen molecules takes place, and the singlet-excited state of O_2 is produced. Thus in the case of oxygen there is apparently an analogy between the properties of electronically excited and surface-coordinated molecules.

4. The Formation and Emission of Electronically Excited Metal Atoms and Nitrogen Molecules from Solid Surfaces

There are few published data on the emission of electronically excited nitrogen molecules from solid surfaces.

A number of papers by Mannella and co-workers,[100–102] published in the nineteen-sixties, described the luminescence of the surfaces of cobalt and nickel during the simultaneous recombination of nitrogen and oxygen atoms. The experiments were carried out in a flow system at a pressure of 1.3 hPa. The stream of nitrogen and oxygen atoms, obtained in a discharge, was passed over the surface of metallic nickel or cobalt inserts embedded in a glass tube. The luminescence of the gas was recorded at the outlet from the reaction zone. The luminescence spectra in the case of cobalt showed the first positive bands of nitrogen. The authors cited consider that electronically excited $N_2(B^3\Pi_g)$ molecules, with an excess of vibrational energy ($v = 6, 8$), are formed on the cobalt surface and are desorbed into the gas phase, where they emit light as a result of the transition:

$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu$$

In the case of nickel, the luminescence spectrum of the gas shows both the first positive bands of nitrogen and the β-bands of nitric oxide. The authors cited suggested that the species desorbed from the nickel surface are electronically excited $NO(B^2\Pi)$ molecules, which subsequently either lose energy:

$$NO(B^2\Pi) \rightarrow NO(X^2\Pi) + h\nu \ (\beta\text{-band of NO})$$

or react with nitrogen atoms:

$$NO(B^2\Pi) + N(^4S) \rightarrow N_2(B^3\Pi_g) + O(^3P)$$

$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu \ (\text{first positive band of nitrogen})$$

In Ref. 102, the luminescence of N_2^* molecules above a nickel surface was observed only in the presence of O atoms.

The emission of various electronically excited atoms and molecules from solid surfaces also takes place as a result of electron bombardment. The extensive literature on electronically stimulated desorption (ESD) includes recent papers on the ESD of excited species. The ESD of excited Na, K, and Li atoms from NaCl, KCl, and LiF surfaces has been studied.[103,104,164] The intensity (I) of the resonance emission of the excited atoms was measured, and the dependence of I on the energy (E) of the electron beam (20–1000 eV) determined. The $I = f(E)$ curves for NaCl showed characteristic features which correlate with the energies of the electron levels of Na and Cl ions in the halide lattice. For example, for Na the luminescence appearance threshold (32 eV) is close to the 2p level of Na (31 eV), and the increase in I at 65 eV is associated with the 2s level of Na (63 eV). The fine structure at 200 eV on the $I = f(E)$ curve corresponds to the 2p level of Cl (200 eV and 202 eV). A mechanism was proposed for the ESD of Na*, according to which Na^{2+} ions are formed in the first stage. Subsequently, an Auger process produces Na^+ ions, which pass through the matrix next to the Cl^- ions in the surface layer and are neutralised with the formation of a resonance excited Na* atom. The radiative deactivation of Na* takes place beyond the NaCl surface.

A characteristic feature is that the excitation of the Na, K, and Li atoms takes place on the surface of the crystals, and not in the gas volume. This conclusion is based on the following facts: 1) the vapour pressure of the metals, determined by the temperature of the surface in the electron emission zone, is too low, and 2) slight displacement of the crystal target from the direction of the electron beam leads to disappearance of the effect.

The authors cited also found that excited hydrogen atoms and hydroxyl radicals are emitted in addition to metal atoms.

An energy analysis of the ESD relationships for excited alkali metal atoms[165] established that the transfer of the energy of the electrons takes place as a result of the formation of holes in the inner levels of the atoms. In subsequent stages, various electronic processes produce excited metal atoms, which are ejected from the surface. A characteristic feature is that the atoms are desorbed in the first (lowest) excited state.

The ESD of excited atoms and ions from different surfaces was described in Refs. 166–168. When a glass surface was irradiated with an electron beam (300 eV) at low cadmium vapour pressures (10^{-3} hPa), emission of excited cadmium ions took place, detected by the luminescence at 441.6 nm and 537.8 nm.[166] The same authors[167] previously detected the emission of excited cadmium ions from the surface of silvered copper.

Mass spectrometry has been used[168] to study the ESD of hydrogen ions and atoms from an Ni (111) surface covered with a film of water. It was found that at an electron energy of 22–30 eV, H^+ ions are ejected into the volume, whereas at 35 eV, electronically excited metastable H atoms in the (2s) state are ejected. It is emphasised that the metastable hydrogen atoms are not formed from H^+ ions, since the energy of the ejected H atoms is 4–5 eV higher than the energy of the desorbed H^+ ions.

Finally, emission in an electronically excited state takes place during the ionic sputtering of materials. Charged and neutral species in different states are formed on the surface and ejected into the gas phase.

Data on the emission of the species produced when solid surfaces are bombarded by inert gas or hydrogen ions with energies from 1 to thousands of eV have been reviewed.[169] Spectroscopic methods have been used to detect the excited species formed in various processes: 1) the scattering of the excited state of the atoms of the primary beam; 2) the emission from the excited state of atoms, molecules, or complexes formed from the atoms of the target; and 3) the formation of excited states of adsorbed molecules. The materials studied were mainly metals, and some metal oxides.[170] The mechanism of the emission by excited atoms and ions has recently been studied using a new spectroscopic method, involving the measurement of the Doppler shift of the fluorescent atoms ejected from metal surfaces during ionic sputtering (the fluorescence is excited by a laser light beam). For example, the yields and velocity distribution of sputtered barium atoms in the ground and metastable states Ba(^1S) and Ba(^1D) have been measured, and the influence of oxygen on these characteristics studied.[171] In Ref. 172, a similar study was carried out using metastable Fe* atoms sputtered from an iron surface. Studies in this field are developing rapidly.

The reported observation[173] of the formation of excited Na atoms on an NaCl surface during the recombination of deuterium atoms is of interest. On thin films of NaCl, for which the coefficient of the heterogeneous recombination of D atoms is high, the spectrum of the luminescence observed corresponds to the D line of sodium atoms. It is not clear, however, whether emission of Na* atoms takes place in this case.

Overall, it appears that published data on the emission of excited metal atoms deal only with the cases of the "strong" perturbation of solid surfaces by electron or ion bombardment. There are practically no published data on the emission of these species under "mild" conditions (chemical and structural-chemical processes, ultraviolet irradiation, etc.).

III. THE DEACTIVATION OF ELECTRONICALLY EXCITED ATOMS AND MOLECULES ON A SOLID SURFACE

In the reaction of electronically excited atoms and molecules with a solid surface, their deactivation can take place by the following paths: 1) relaxation of the excited state as a result of the dissipation of the excitation energy in the adsorbed layer and in the surface layers of the solid, which may involve both phonons and the electronic sub-structure of the crystal; 2) chemical reaction with atoms of the surface or the adsorbed layer; and 3) luminescence of electronically excited molecules in the adsorbed layer.

From a comparison of the values of the coefficients of the heterogeneous deactivation γ of electronically excited atoms and molecules (the terms deactivation, relaxation, or accommodation coefficient are also used), it is difficult to decide which deactivation channel predominates, since the value of γ gives a representation of the overall activity of different materials with respect to their reaction with excited species.

As shown below, in a number of cases it is possible to reach a conclusion about the mechanism of deactivation from the dependence of the value of γ on the conditions of the experiment, which alter the properties of the solid which are "sensitive" to the transfer of the energy of the excited atoms and moelcules. There have been practically no studies of the microscopic mechanism of the heterogeneous deactivation of electronically excited molecules.

Data have been published on the reactions of various solid surfaces with singlet oxygen, metastable inert gas atoms and nitrogen molecules, and triplet molecules of organic substances.

1. Electronically Excited Oxygen Molecules

The heterogeneous deactivation of singlet oxygen has been studied in most detail. It is appropriate to examine three classes of surface differing in their activity with respect to the deactivation of $^1O_2$ ($^1\Delta_g$) molecules: dielectrics ($\gamma = 10^{-5}-10^{-3}$), metal oxides ($\gamma = 10^{-4}-1$), and metals ($\gamma = 10^{-5}-1$).

Most values of γ on glass and quartz surfaces have been obtained by studying the gas-phase reactions of singlet oxygen, since the reaction vessels are usually made of these materials. The studies are usually carried out in a flow apparatus, and the singlet oxygen is obtained by a discharge in oxygen. This procedure has a number of significant unsatisfactory features: firstly, in a flow apparatus it is difficult to achieve the necessary cleanliness of the surface, since lubricant vapour is present, contamination from the gas phase is possible, etc.; secondly, in the generation of singlet oxygen in a discharge there are active products (oxygen atoms, ozone, etc.), which modify the surface. Moreover, at a high concentration of singlet oxygen the surface may again be modified, and this should lead to a change in the heterogeneous deactivation coefficient. For example, in Refs.106–109, 118, and 158, the coefficient of the deactivation of singlet oxygen on Pyrex varied from 7.6×10^{-6} to 5×10^{-5}. These results show convincingly that the magnitude of the coefficient of the heterogeneous deactivation of singlet oxygen is influenced considerably by the conditions of the experiment. This conclusion is confirmed by studies[2,140] in which a change in γ in the course of the experiment was observed, indicating that the surface is modified during the measurements. In Ref.105, the value of γ on silicon increased slowly with time. In the works cited, no mechanism was proposed for the deactivation of singlet oxygen, and all the values were obtained only for room temperature.

Thus to investigate the mechanism of the deactivation of singlet oxygen on a solid surface, it is necessary to carry out studies under clean conditions (high vacuum, absence of surface contaminants, a selective source of singlet oxygen) and at low concentrations of singlet oxygen.

Attempts have been made to satisfy these conditions.[112] The experiments were carried out under diffusion conditions, and the surface was treated by heating at 250–300 °C in a high vacuum (10^{-7} hPa), achieved using oil-free magnetic-discharge and zeolite pumps. Singlet oxygen was obtained by photosensitisation by an adsorbed dye (trypaflavine). The gas phase did not contain any other active species. The concentration of singlet oxygen in the gas phase (10^{10} cm^{-3}) was measured using semiconducting detectors. With increase in the temperature of the surface, the deactivation coefficient of singlet oxygen on glass decreases, and at 373 K is equal to 10^{-6} ($\gamma = 10^{-5}$ at 293 K). The activation energy of the change in γ is negative and equal to 6 kcal mole^{-1}. γ is independent of the oxygen pressure in the range $1-10^{-2}$ hPa. These data indicate that on a glass surface, singlet oxygen is deactivated as a result of physical adsorption with subsequent transfer of energy to the solid; this process is analogous to the relaxation of vibrationally excited nitrogen molecules on silver and Teflon at low temperatures.[111] The mechanism of the deactivation corresponds to the following scheme:

$$^1O_2 + Z \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^1O_2Z$$

$$^1O_2Z \xrightarrow{k_2} {}^3O_2Z$$

where Z is an adsorption centre.

If the rate of deactivation of $^1O_2$ is much lower than the rate of desorption ($k_2 \ll k_{-1}$), the adsorption of singlet oxygen on the surface can be regarded as a quasi-equilibrium process, and described by the Langmuir isotherm. Since the concentration of singlet oxygen is low, it can be assumed that the adsorption takes place in the Henry range. Thus

$$\gamma = \frac{4k_H k_2 kT}{\bar{v}} \frac{S}{V}$$

where k_H is the Henry constant, S the surface area, V the volume, k the Boltzmann constant, P the temperature, and $\bar{v}$ the average velocity of the particles.

The scheme describes the experimental results satisfactorily. The activation energy for the change in γ in this case is equal to the heat of adsorption of singlet oxygen on the glass surface.

The Henry constant can be estimated by the method of Zweitering and Krevelen:[141]

$$k_H = \frac{N_A}{(2\pi MRT)^{1/2}} \tau_0 \exp(Q/RT)$$

where N_A is Avogadro's number, M the molecular mass of the gas, R the gas constant, τ_0 the period of one vibration of the adsorbed molecule in a direction perpendicular to the surface, and Q the heat of adsorption.

The measured coefficient of the heterogeneous deactivation of the species (10^{-5} at room temperature) and the heat of adsorption (6 kcal mole^{-1}) can be used to estimate the relaxation time of the energy of singlet oxygen on the glass surface:

$$\tau_{rel} = k_3^{-1} = \frac{4k_H kT}{\gamma \bar{v}} = \gamma^{-1}\tau_0 \exp(Q/RT)$$

For $\tau_0 = 10^{-12}-10^{-13}$ s, $\tau_{rel} = 10^{-3}-10^{-4}$ s. This value is very much higher than the relaxation time of vibrationally excited nitrogen molecules on glass (10^{-8} s),[111] apparently because of the difficulty of the relaxation of the comparatively high energy (1 eV) on the surface.

In Ref.89, the relaxation time of singlet oxygen on a KBr surface was found to be greater than 10^{-2} s. In Refs.110 and 142, the factors influencing the heterogeneous deactivation of singlet oxygen were investigated by another method. The temperature dependence of the coefficient of the heterogeneous deactivation of singlet oxygen on quartz was determined by the standard method (flow system, $^1O_2$ produced by an ultrahigh-frequency discharge in oxygen) at temperatures of 350–900 K. In addition, the surface was modified by the adsorption of gases, as in Refs.143 and 150. The value of γ was measured by estimating the degree of deactivation of $^1O_2$ on a quartz rod introduced into the reaction vessel or directly on the walls of the cylindrical quartz reaction vessel. In the first case, in the temperature range 520–830 K at an O_2 pressure of 0.6 hPa, $\gamma = (7.4 \pm 0.5) \times 10^{-3}\exp(18.5 \pm 1.0/RT)$, where the activation energy is given in kJ mole^{-1}. In the second case, with increase in temperature from 350 K to 600 K, γ increases from 1.1×10^{-4} to 1.8×10^{-3} (the activation energy is 18.5 kJ mole^{-1}), but with further increase in temperature it remains unchanged up to 900 K. The values of γ differ by a factor of approximately 10, apparently due to a difference in the concentration of deactivation centres. Under the chosen conditions, the value of γ was independent of the oxygen pressure. When H_2O, NH_3, or oxygen atoms were added to the stream of oxygen, the concentration of $^1O_2$ increased, indicating a decrease in the deactivation of $^1O_2$. The addition of Ar, H_2, CO, or C_2H_4 had little influence on the deactivation. These data confirm the chemisorption mechanism of the deactivation of $^1O_2$ on the surface centres of quartz. When the quartz has been heated, the number of free centres increases (and γ

increases), and when active gases are introduced, the centres are blocked (γ decreases). The nature of these centres has not yet been determined. The authors cited[110,142] consider that these centres may be radical peroxide forms of oxygen.

After the adsorption of benzene on the glass surface, γ was found to be 4×10^{-5}.[143]

When all the material on the deactivation of $^1O_2$ on quartz and glass surfaces is reviewed, it is possible to make some generalisations. At temperatures close to room temperature, the deactivation coefficient is 10^{-5}, and the deactivation mechanism apparently involves the physical adsorption of $^1O_2$. At higher temperatures and concentrations of singlet oxygen, deactivation takes place by a chemisorption mechanism. The nature of the adsorption centres and the mechanism of the relaxation of the energy of $^1O_2$ on the glass surface is still not clear.

The deactivation of singlet oxygen on the surface of metal oxides has been studied for the case of zinc and oxide.[112] With increase in temperature, the value of γ increased from 10^{-4} to 10^{-2}, and the activation energy of the change in γ was 25 kcal mole^{-1}. γ decreased with increase in the oxygen pressure (in the range 5×10^{-2}–2 hPa). It was suggested that in this case the deactivation of singlet oxygen takes place as a result of its chemisorption on the zinc oxide surface:

$$^1O_2 + Z \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} {}^1O_2Z$$

$$^3O_2 + Z \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} {}^3O_2Z$$

$$^1O_2Z \xrightarrow{k_5} {}^3O_2Z$$

where Z is an adsorption centre.

According to this scheme, the loss of the energy of electronic excitation is due to the formation of a chemical bond, that is chemisorption. If the residence time of the singlet oxygen molecule in the adsorbed state is greater than the time for the loss of the excitation energy, that is $k_{-3} \ll k_5$, then in accordance with the method of stationary concentrations it is possible to write:

$$\gamma = \frac{s_1}{s_1[^1O_2]/[^3O_2] + s_2} \cdot \frac{4k_{-4}[Z]}{\bar{v}[^3O_2]} \qquad (5)$$

where s_1 and s_2 are the adhesion coefficients of $^1O_2$ and $^3O_2$, and $\bar{v}$ the average velocity of the particles. It follows from Eqn.(5) that γ should decrease with increase in pressure, in agreement with the experimental data. The temperature dependence of γ is determined by the rate constant of the desorption of O_2 from the zinc oxide surface (that is k_{-4}). Increase in temperature leads to an increase in the number of free centres for the chemisorption of $^1O_2$, and γ increases. The measured value of the activation energy of the change in γ (25 kcal mole^{-1}) agrees with published data for the activation energy of the desorption of oxygen from a ZnO surface (23 kcal mole^{-1}).[114] Under the conditions of the experiment, equilibrium chemisorption of oxygen on the zinc oxide surface is achieved, since γ changes little with time. The nature of the centres for the chemisorption of singlet oxygen is of considerable interest. Thus the electrical conductivity of a film of zinc oxide decreases under the influence of $^1O_2$.[17] The decrease in the concentration of conductivity electrons may take place as a result of the formation of a chemical bond between a singlet oxygen molecule and a superstoichiometric ionised surface zinc atom. In this case the coefficient of the heterogeneous deactivation of singlet oxygen on the zinc oxide surface should decrease with decrease in the concentration of zinc atoms, as observed experimentally.

In the reaction of electronically excited molecules, which are chemically inert with respect to zinc oxide (for example the triplet molecules of benzophenone or diacetyl and excited inert gas atoms), the excitation energy of the molecules is transferred to the layer of zinc oxide next to the surface, and the electrical conductivity of the film increases.[144,145] If the surface of the zinc oxide film is deactivated with respect to the chemical action of singlet oxygen, that is if the concentration of zinc atoms acting as chemisorption centres is decreased considerably, a similar effect should be observed. In fact, it has been found[113] that when a source of $^1O_2$ (an ultrahigh-frequency discharge, a photochemical source, or the reaction HgO + O) is included, the electrical conductivity σ of the film at the initial moment increases, passes through a maximum, and then decreases. The result can be understood if it is assumed that in the reaction of $^1O_2$ with the ZnO film, two processes take place simultaneously (but at different rates), one of which (the more rapid) is associated with the transfer of the energy of the $^1O_2$ molecule to zinc oxide and hence with an increase in σ, while the other (the slower) is associated with the chemisorption of $^1O_2$ on the zinc atom impurity centres responsible for the impurity conductivity of ZnO. The extremal character of the change in σ is attributed to the competition between these two processes. This system is characterised by chemical deactivation of $^1O_2$. These experiments lead to certain conclusions about the mechanism of the transfer of the excitation energy of singlet oxygen in ZnO. The existence of the donor signal of the change in the electrical conductivity σ on the adsorption of $^1O_2$,[113] which was also observed in the reaction of $^1O_2$ with a single crystal of ZnO in a solution of electrolytes,[146] indicates that the excitation energy is transferred to the surface layers of ZnO and brings about the ionisation of fine traps and the ejection of electrons into the conductivity band. The same results were obtained in experiments with zinc oxide photo-currents photosensitised by dyes.[85] Two mechanisms of the photosensitisation have been discussed. One assumes that the excitation energy is transferred to the semiconductor, and the other that the excited dye is ionised. When singlet oxygen is adsorbed on the surface of the semiconductor, the second mechanism is unlikely, since it is difficult to imagine the formation of positive oxygen ions.

There are few published data on the reaction of $^1O_2$ with other metal oxides. The adsorption of $^1O_2$ on magnesium, nickel, and cobalt oxides has been studied.[147,148] On MgO there is weak adsorption of $^1O_2$, which decreases with increase in temperature from −78 °C to 20 °C (the adsorption of ordinary triplet oxygen on MgO increases with increase in temperature). The adsorption of $^1O_2$ on NiO takes place with a greater intensity than on MgO, and is independent of temperature. In the case of Co_3O_4, no differences in the adsorption of singlet and triplet oxygen could be observed. The authors cited did not examine the mechanism of the reaction of $^1O_2$ with the oxides. On the surface of cobalt oxides, the coefficient of the heterogeneous deactivation of $^1O_2$ is high (~1).[152] This property has been made the basis of a calorimetric method for measuring the concentration of $^1O_2$. The mechanism of the reaction of singlet oxygen with cobalt oxides is not clear. The strong heating of the Co_3O_4 film may be due not only to a thermal mechanism of deactivation but also possibly to a chemisorption mechanism, involving the heat of chemisorption.

The heterogeneous deactivation of singlet oxygen on a dye surface (trypaflavine) has been studied.[66] With increase in temperature from 293 K to 343 K, γ increases from 10^{-3} to 10^{-2}. The same dependence of γ on the O_2 pressure was observed for zinc oxide, so that the deactivation of singlet oxygen takes place by a chemisorption mechanism, and the

activation energy of the change in γ is the activation energy of the desorption of oxygen from the dye surface.

The heterogeneous deactivation of $^1O_2$ on metal surfaces has been the subject of a number of studies. The concentration of $^1O_2$ was measured from the singlet oxygen luminescence. The experiments were carried out at pressures of from tenths to several hPa, in a flow system. The following values of γ were obtained at room temperature:[105] Al (5.9×10^{-5}), Ti (6.5×10^{-5}), Mo (8.0×10^{-5}), Nb (1.2×10^{-4}), Pt (4.0×10^{-4}), Cu (8.5×10^{-4}), Ni (2.7×10^{-3}), Fe (4.4×10^{-3}), and Ag (1.1×10^{-2}). The results of the measurements for Ag, Pt, and Al agree with the data obtained by other authors, for example in Ref.115. On a stainless steel surface, γ varied from 7.6×10^{-6} to 1.3×10^{-5} at room temperature.[149] The coefficient of the heterogeneous deactivation of singlet oxygen on a gold surface with previously adsorbed HCl is $(1-3) \times 10^{-3}$.[150] On an annealed Au specimen, the value of γ changed from 5×10^{-2} to 2×10^{-1} in the temperature range 300–900 K. The adsorption of water at 300 K led to a decrease in γ by a factor of 20.[142,151] In the opinion of the authors cited, these results confirm that the deactivation of $^1O_2$ on an Au surface takes place by a chemisorption mechanism:

$$AuO + O_2(^1\Delta_g) \rightarrow AuO{-}O_2(^1\Delta_g) \rightarrow AuO + O_2(^3\Sigma_g^-)$$

It was suggested that the bond formed by the chemisorbed $^1O_2$ with gold oxide is strong, and that its energy is transferred to some degrees of freedom of the metal. Ordinary oxygen is not chemisorbed on these centres, and is readily liberated into the gas phase. By analogy with the gas-phase reactions of excited species, the proposed mechanism was described as an excimer mechanism. On a strongly hydroxylated gold surface, the chemisorption of $^1O_2$ is impossible, the value of γ is much lower, and the deactivation mechanism is different.

Other regular features were observed for platinum. On the surface of a Pt wire, γ increases from 10^{-3} to 10^{-1} with increase in temperature from 300 K to 450 K. The value of γ is almost independent of the O_2 pressure in the range 0.17–6.0 hPa. The effective activation energy decreases with increase in temperature, from 46.5 kJ mole^{-1} at 300 K to 0 at 450 K. The addition of water and hydrogen does not influence the rate of the deactivation of $^1O_2$, but the introduction of CO (7%) decreases γ at 400 K by a factor of ten. The authors cited consider that these results are consistent with a chemisorption mechanism. The increase in γ with temperature was related to an increase in the number of active centres on the surface, and the limiting stage is the adsorption of singlet oxygen on the free centres. These centres may be various forms of adsorbed oxygen. The action of CO involves either the blocking of these forms of oxygen or their removal from the surface as a result of a chemical reaction.

The value of γ for nickel was found to be close to 1.[157]

Thus on metal surfaces the values of the coefficients of the heterogeneous deactivation of $^1O_2$ differ by several powers of ten, from 10^{-5} for Al to 1 for nickel. It should be noted that these values relate rather to the oxidised surface of the metals, since the measurements were made under fairly "severe" conditions (a high concentration of $^1O_2$ in a stream of oxygen). The results of the measurements depend on the conditions of the evacuation and the treatment of the specimens, particularly at high temperatures, and also on the composition of the adsorption layer. Thus in the discussion of a particular value of γ it is necessary to specify clearly the conditions of the experiments. There are few published data on the heterogeneous deactivation of the $^1O_2$ molecule in the state ($^1\Sigma_g^+$). The deactivation coefficient of this species was determined by measuring the intensity of the 7618 Å line in a stream of oxygen, passed through a discharge and mercury oxide, after reaction with a metal insert. According to Ref.115, for $^1O_2(^1\Sigma_g^+)$, γ has the values 0.3 (Fe), 0.25 (Al), 0.9 (Cu), 0.6 (Ag on Pt), and ~0 for pure Pt. Thus on all these metals (except Pt) the deactivation coefficient is very high. For a glass surface, the following values of γ were obtained: $10^{-3}-10^{-2}$,[116] 1.5×10^{-2},[117] 0.9×10^{-2},[118] 10^{-2},[119] and 2×10^{-2}.[107] The average value of the deactivation coefficient of $^1O_2(^1\Sigma_g^+)$ on glass is 10^{-2}, which is 10^3 times that for the state ($^1\Delta_g$). The lowest value of γ was obtained for a glass surface covered with a halocarbon lubricant, 1.1×10^{-3}.[154] The shrot lifetime and the high efficiency of the deactivation of $^1O_2(^1\Sigma_g^+)$ are the chief reasons for the considerable experimental difficulty of measuring γ, and this explains why few papers on this topic have been published. The published data indicate that the efficiency of the deactivation of singlet oxygen depends markedly on the excitation energy. The deactivation coefficient is higher (by a factor of 10^2-10^3) for the ($^1\Sigma_g^+$) state which has a higher energy than $O_2(^1\Delta_g)$, and this is related to the high efficiency of the conversion of the state ($^1\Sigma_g^+$) into ($^1\Delta_g$) on collision with the surface, and probably to the high chemical activity of the state ($^1\Sigma_g^+$). For oxygen in the $A\,^3\Sigma_u^+$ state with even higher energy, the deactivation coefficient on glass is ~1.[153]

In spite of the progress made in the study of the mechanisms of the deactivation of singlet oxygen on solid surfaces, all the studies discussed above have a significant unsatisfactory feature. In these studies the state of the surface was not examined by structure-sensitive methods, and this is necessary in the determination of the singlet oxygen adsorption centres.

2. Metastable Inert Gas and Mercury Atoms and Nitrogen Molecules

The heterogeneous deactivation of the metastable atoms of inert gases (MAIG) on metal surfaces is accompanied by secondary electron emission (SEE). There are two SEE mechanisms:[120,121] a two-stage mechanism based on the resonance ionisation (RI) of an incident excited atom, followed by Auger neutralisation (AN) of the ion formed, and a single-stage mechanism involving Auger deactivation (AD).

The mechanism predominating is determined by the position of the excitation level of the incident atom relative to the Fermi level of the metal, and by the ratio of the work function of the electron and the ionisation potential of the excited atom. For clean metal surfaces with a high work function, deactivation takes place by an RI + AN mechanism. If the ionisation potential is smaller than the work function, the process takes place by an AD mechanism. It should be noted that the presence of an adsorbed layer, which changes the work function and the conditions on the metal surface, may lead to a change in the deactivation mechanism, and in a number of cases to the existence of both mechanisms.[95] An important feature is that, irrespective of the deactivation mechanism, the SEE efficiency is high. This makes it possible to use the magnitude of the emission of secondary electrons to estimate the intensity of the heterogeneous deactivation on metal surfaces. No systematic quantitative determinations of the coefficients of heterogeneous deactivation γ for different metals have been carried out. Published data[95] indicate that on metals, the value of γ is close to 1.

The study of the scattering of atoms and the ejection of electrons has recently been described. Thus the reflection of a beam of He* atoms from different surfaces has been studied by measuring the concentration of He(^1S) atoms in

the gas phase.[121] The reflection coefficient of the He* atoms was 10^{-6} for Cu (110), 5×10^{-6} for Pd (110), 1.5×10^{-4} for polycrystalline W, 3×10^{-3} for Pd covered with CO, and 5×10^{-4} for oxidised Pd. Thus only a negligible fraction of the incident metastable He atoms are reflected from the surfaces of these metals, and the deactivation coefficient γ is close to 1. In the same work it was found that the reflection coefficients of He*, Ne*, and Ar* atoms from the surface of single crystals of LiF and NaCl are also extremely low and are respectively 2×10^{-4}, 4.6×10^{-2}, and 2×10^{-4} (LiF), and 1.2×10^{-4}, 2.8×10^{-3}, and 10^{-4} (NaCl), that is for the surfaces of these dielectrics, as in the case of metals, the deactivation coefficient is close to 1. The authors cited consider that these similar values of the reflection coefficients of the excited atoms for metals and dielectrics indicate that these quantities are independent of the nature of the surfaces. This conclusion, however, does not agree with the data obtained by other workers.

The reaction of beams of He atoms with the surface of the (110) face of a single crystal of tungsten was studied in Ref.122. It was established that the quantity of atoms reflected depends on the angle of incidence of the beam (θ is the angle between the direction of the beam and the normal to the surface). At low values of θ, a small fraction of the atoms (less than 10%) is reflected, and the coefficient $\gamma > 0.9$. At high values of θ (70–80°), 50–60% of the incident metastable atoms are reflected, and γ is 0.4–0.5. It was also found that for a clean surface, the yield of emitted electrons also depends markedly on the angle of incidence of the excited species, amounting to 5–8% at low angles of incidence and increasing markedly at high values of θ (60–80°). For an oxidised W surface, the yield reached 40%.

Comparison of published data[120–122] shows that: 1) the deactivation coefficient on metals may be lower than 1; 2) the yield of secondary electrons depends on the magnitude of the angle of incidence of the atoms and the presence of an adsorbed layer on the metal surface, so that the determination of the value of γ from the emission of secondary electrons and the comparison of these values for different metals must be carried out with great care; and 3) the presence of an adsorbed layer on the metal surface leads to an increase in the yield of secondary electrons and the reflection coefficient of the metastable atoms.

It should be noted that in the works cited, the experiments were carried out with beams of atoms only on metal single crystals. It may be assumed that the coefficient γ will not always be equal to 1 in the case of polycrystalline metal surfaces under flow or diffusion conditions.

There are very few published data for non-metal surfaces. The deactivation coefficients of metastable atoms on semiconductors and dielectrics have not bee measured, and there is no method for studying heterogeneous deactivation for non-metals which is an informative as the SEE method for metals.

Optical methods for recording metastable atoms (MA) in the gas phase, for example laser-induced fluorescence spectroscopy,[123] have not yet been used to study the heterogeneous deactivation of MA, and the traditional absorption-spectroscopic method for measuring rhe concentrations of these species in a flow system has been found to be unsuitable.[124,125] For these reasons, there are few published papers on the heterogeneous deactivation of MA on non-metal surfaces. Apart from the work examined,[121] there are only a few published studies. In Ref.124, the radial concentration gradient of MA of helium in the flux leaving a glow discharge was measured from the intensity of the luminescence (in the visible range) of different forms of helium MA. It was found that the He* atoms are not completely deactivated on the walls, and the deactivation coefficients on glass are 0.35 for He 2^1S and 0.11 for He 2^3S. In Ref.125, an optical method was also used to determine the radial distribution of MA in a tube through which a stream of gas was passed after a discharge, and it was found that for Pyrex, $\gamma_{He^*} < 0.75$ and $0.12 < \gamma_{Ar^*} < 0.5$.

The reflection of a beam of inert gas MA from different surfaces has been studied.[126] The SEE was measured inside a metal cylinder when the MA struck the end face, which consisted of targets of different materials. The values of the reflection coefficients of the MA on glass and stainless steel were 0.01 for He*, 0.02 for Ne*, and 0.03 for Ar*, that is the values of γ were close to 1. In Ref.155, the deactivation of excited argon ($^3P_2$) atoms in the gas phase was studied, and the deactivation coefficient on the walls of the quartz reactor estimated ($\gamma > 0.4$).

A new method was recently proposed[127,128,135] for measuring the coefficients of the heterogeneous deactivation γ of metastable atoms, based on the use of semiconducting detectors of the active species.[129] A reversible change in the electrical conductivity of a film of ZnO activated by gold micro-crystals was detected on reaction with MAIG.[127] Comparison of the values of the initial rate of change in the electrical conductivity of the detector (ν) and the emission current of the magnesium plate I_m (the detector and the magnesium target were placed in the same vessel) under the conditions of the generation of MA of helium or krypton (a low-voltage discharge with an incandescent cathode, at 10^{-2} hPa and room temperature) showed that there is a linear relationship between ν and I_m. The emission current is proportional to the concentration of MAIG in the gas phase.[130] Thus a ZnO/Au film can be used as an MAIG proportional detector. In these experiments, the MAIG concentration was 10^7–10^8 cm^{-3}. The range of concentrations measured can be extended considerably both into the range of lower MAIG concentrations (by increasing the sensitivity of the measuring scheme) and into the range of higher concentrations (by strobing the flux of MAIG reaching the ZnO/Au film).

This detector was used to determine the values of γ on various surfaces.[127] The change in the concentration of MAIG was measured along a cylinder whose inner surface was covered with the substance being studied, with increase in the distance from the MAIG source. The coefficient γ was calculated from the equation

$$\frac{2\gamma}{2-\gamma} = \frac{4Da}{c} \frac{I_1(ar)}{I_0(ar)}$$

where D is the diffusion coefficient, c the thermal velocity of the atoms, r the radius of the vessel, I_1 and I_0 the Bessel functions of first and zeroth orders, a the slope of the straight line ($n/n_0 - h$), h the distance from the detector to the inlet into the cylinder, n the MAIG concentration at a distance h, and n_0 the MAIG concentration at the inlet into the cylinder. To confirm that the constant obtained does in fact characterise the heterogeneous and not the homogeneous deactivation of the MA, the values of γ in helium were determined at different pressures (10^{-2}–10^{-3} hPa). It was found that in this range, γ is independent of pressure, that is under the chosen conditions the homogeneous quenching of the excited atoms is not significant. The coefficients γ on glass are 2.0×10^{-3} (He*), 7.3×10^{-3} (Kr*), 3.5×10^{-3} (Xe*), and those on polycrystalline zinc oxide 3.4×10^{-3}, 4.1×10^{-3}, and 4.4×10^{-3} respectively.

The authors cited[127] concluded that the method of detecting MA using semiconducting detectors is highly sensitive, produces little perturbation in the system being studied, and is most suitable for measuring γ under diffusion conditions at low MA concentrations. The deactivation of inert gas MA on glass and ZnO is described by an equation of first order with respect to the MA concentration in the gas phase.

The same method was used to measure the values of γ for discontinuous films of gold on glass and zinc oxide.[128] It was found that γ depends on the gold concentration (the covering coefficient f) on the surface of the support. Thus for the Au/glass system, the value of γ was 0.17 (f = 0.13) or 0.37 (f = 0.45), whereas for Au/ZnO the corresponding values of γ were 0.11 and 0.38. The heterogeneous deactivation of the metastable atoms of inert gases on discontinuous films of gold apparently takes place on the surface of the metal particles, since the values of γ and f coincide. In this case the deactivation of the excited atoms takes place with an efficiency close to 1, whereas it is lower by a factor of 100 on the surface of the support, irrespective of the electronic structure of the carrier (dielectric, semiconductor).

Thus the results of the measurement of the coefficients of the heterogeneous deactivation of the metastable atoms of inert gases on non-metals are few and contradictory. For example, for glass the following values of γ have been obtained: 0.35 and 0.11,[121] 0.75,[125] 1,[126] and 2×10^{-3}.[127] These marked differences are apparently related to the fact that in Refs.121, 125, and 126 the MA concentration was much higher than in Ref.127. In the deactivation of MA on non-metals, the excitation of the surface at sufficiently high concentrations of the excited species apparently facilitates the more effective loss of the energy of the excited atoms colliding with it.

Thus the deactivation of MA on non-metal surfaces takes place with a lower efficiency than on metal surfaces. In the last case the loss of the energy by the metastable atoms takes place chiefly in their reaction with the electronic system of the metal, leading to the emission of electrons. It is as yet difficult to say anything definite about the mechanism of the reaction of these species with non-metals.

The heterogeneous deactivation of electronically excited nitrogen molecules has been studied.[132,133] The longest-lived state was found to be $N_2(A^3\Sigma_u^+)$ with a radiative lifetime of 2 s. In Ref.133, the concentration of N_2^* was measured from the photo-ionisation in a mass spectrometer, and also using a platinum calorimeter with a stream of nitrogen passed through a discharge (p = 0.6–7 hPa). The coefficient of heterogeneous deactivation was found to be 3×10^{-5}, that is the efficiency of the deactivation of N_2^* on the glass walls is very low. The dependence of the value of γ on the concentration of excited nitrogen molecules was established;[132] the coefficient γ is low (7×10^{-4}) at low concentrations, and high (0.5) at high concentrations. Thus the concentration dependence of γ obtained for metastable nitrogen molecules was the same as that for metastable inert gases on a glass surface.

There are practically no published data on the deactivation of excited metal atoms on solid surfaces. Only a few papers have dealt with the reaction of excited mercury atoms with semiconducting films of zinc oxide.[136–138] The change in the electrical conductivity (σ) of ZnO films under the influence of mercury atoms (Hg*), obtained by photo-excitation in the gas phase (non-excited Hg atoms have no influence on σ), was studied. At room temperature the reaction with Hg* atoms produces a marked increase in σ for the ZnO films, and at "saturation" of the signal, σ increases by 80%. The authors cited attributed the effect of "saturation" of the change in σ to two processes taking place simultaneously on the ZnO surface: 1) the formation on the surface of zinc atoms, which bring about an increase in σ for ZnO:[114]

$$ZnO + Hg^* \rightarrow (HgO)_s + Zn_s \qquad (6)$$

(s = surface); and 2) the formation of surface zinc mercurides, which, like metal molecules (for example Ag_2),[114] apparently have no influence on the electrical conductivity of semiconducting films

$$Zn_s + Hg^* \rightarrow (HgZn)_s \qquad (7)$$

The simultaneous processes (6) and (7) are responsible for the establishment of the stationary value of σ for ZnO on bombardment of its surface.

The proposed scheme was verified by experiments in which zinc atoms were deposited on the ZnO surface, or oxygen was adsorbed on it. On the films activated by zinc atoms, the magnitude and the sign of the change in σ depend on the concentration of Zn atoms; at high zinc concentrations, the value of σ for ZnO decreases under the influence of Hg* atoms (process 7). On ZnO films treated with oxygen, the magnitude of the change in σ for ZnO increases (process 6).

In Refs.136–138 it was established that at a definite concentration of previously deposited zinc atoms, the value of σ for ZnO remains unchanged under the influence of Hg* atoms. From the change in the electrical conductivity of the adsorbate, the authors cited reached conclusions about the dissociation of the molecules adsorbed on ZnO in their reaction with excited mercury atoms. A marked increase in σ took place after the adsorption of hydrogen on bombardment with Hg* atoms, indicating that H_2 is dissociated to atoms, since it was previously shown[114] that H atoms are electron donors on a ZnO surface. The same effect was detected for adsorbed isopropyl alcohol.

Thus the action of excited mercury atoms (and possibly other metal atoms) leads to a change in the chemical composition of the clean surface of oxide semiconductors, and also of the adsorbed layer.

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