

RECENT ADVANCES IN THE CHEMISTRY OF ELECTRONICALLY EXCITED ATOMS

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I. Introduction

The marked difference in the chemical behavior exhibited by the first singlet states of atomic oxygen and sulfur relative to their ground states has been the subject of a large number of investigations. However, data on the reactivity of the electronically excited states of other nonmetal atoms, particularly those atoms that may lead to bond formation following reaction, are relatively limited. Historically, the work on atomic oxygen and sulfur, principally in the 1D_2 state, followed extensive and detailed studies on photosensitization by metal atoms in which the atoms, excited electronically by resonance radiation, passed on their energy by collisions of the second kind, thus being deactivated to the ground state or a lower lying state. In general, the metal atom remained chemically unchanged and essentially provided the source of energy for the reaction. These classical investigations have undoubtedly

stimulated a great deal of the current interest in the reactions of electronically excited atoms in general, including those in which the atom is incorporated in a chemical product. Thus in recent years there has been a growth in the kinetic investigations of the electronically excited states of nonmetal atoms following the development of gas chromatographic methods which have allowed detailed analyses of products formed in both static and flow photochemical systems. This area has been extended by the development of techniques that have permitted the direct study of these excited atoms, and the general field has received considerable impetus by the expansion of aeronomic research.

The main considerations that have often been applied in describing the kinetic processes that electronically excited atoms undergo have been the conservation of spin and the energy brought to the reaction by the excited species. However, the foundation of a more detailed consideration of symmetry had been laid by Mulliken¹ and has been presented more recently in a convenient form by Shuler.² The basis of this treatment involves an examination of the adiabatic correlations of both reactants and products in terms of their symmetry, and has been applied earlier to a limited number of reactions.³⁻⁵ A detailed treatment with this framework is limited to cases where the transition state or collision complex will have the symmetry species appropriate to the point group C_s or a group of higher symmetry. This will cover the large and important class of the reactions between atoms and diatomic molecules, and also some small polyatomic molecules, and it is with these processes that this review is primarily concerned. The method requires a full knowledge of the term manifolds of both reactants and products, and is aided further by a knowledge of the electronic states of the collision complex. Such information has only recently become available for a consideration of a large number of these reactions, mainly as a result of spectroscopic studies. Clearly, without detailed calculations to construct complete potential energy surfaces for each individual reaction, activation energies and hence absolute rates cannot be predicted *ab initio*. However, where a surface leads directly and exothermically to products, very low or negligible activation energies are generally observed for the reactions of these metastable atoms. A limited number of calculations confirm that low activation energies are involved

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(2) K. E. Shuler, *J. Chem. Phys.*, **21**, 624 (1953).

(3) K. J. Laidler and K. E. Shuler, *Chem. Rev.*, **48**, 153 (1951).

(4) K. J. Laidler, "The Chemical Kinetics of Excited States," Oxford, 1955.

(5) E. K. Gill and K. J. Laidler, *Can. J. Chem.*, **36**, 79 (1958).

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in these cases.^{6,7} Thus the adiabatic correlations allow one to predict which reactions are likely to be rapid and also the electronic states of the product molecules. It is the purpose of this review to discuss the present data on the reactions of the low-lying metastable states of the excited nonmetal atoms

C	N	O	F
Si	P	S	Cl
Ge	As	Se	Br
		Te	I

within this framework. The limitation of the present considerations to optically metastable states in which emission to a lower state is electric dipole forbidden arises from the requirement that the excited atom be sufficiently long-lived to undergo collisions and hence reaction, rather than be removed mainly by radiation under normal experimental conditions.

All relevant rate data on the reactions of the electronically excited atoms will be presented in tabular form, together with a concise discussion of the data which the authors feel most reliable. Detailed discussion will be limited for the most part to reactions involving excited atoms as the chemistry of ground-state atoms has been reviewed elsewhere. The data are presented on a group by group basis.

II. Adiabatic Correlations and Nonadiabatic Processes

Before proceeding with a detailed discussion of individual reactions it is convenient to summarize the general considerations necessary for a qualitative description of potential surfaces and the manner in which these influence the course of reaction. For collisions involving two atoms, the adiabatic correlations are straightforward as curves of the same species will strongly repel (*i.e.*, avoid crossing) even in low-order approximation. However, for triatomic molecules, this will not necessarily be the case, as the greater number of degrees of freedom allow simultaneous occurrence of the conditions for crossing, namely $W_{nm} = W_{tt}$ and $W_{nt} = 0$ (W_{nm} , W_{tt} , and W_{nt} are the matrix elements of the perturbation function in the Schrödinger equation). Thus it may be seen that a pair of three-dimensional surfaces may intersect along a line.⁸ Nevertheless, although the "noncrossing rule" does not rigorously apply for polyatomic molecules, the larger number of degrees of freedom involved gives rise to the situation under which noncrossing of states with the same species does effectively hold. In constructing the correlation diagrams which follow, we have therefore used the "noncrossing rule," and correlate a given electronic configuration of the reactants with the lowest product configuration of the same symmetry.

We must also consider the possibility of nonadiabatic transitions (*i.e.*, a transition from one potential surface to another surface following perturbations which may be neglected in low-order approximation) at the point of crossing between two surfaces having different electronic species. Such nonadiabatic transitions between states of the same multiplicity may be brought about by vibration or rotation of the collision complex and is entirely analogous to predissociation in polyatomic molecules. As the latter process has been discussed at some length,⁸ we summarize only the features

relevant to our discussion here. In those cases where reaction is highly exothermic, we may expect the collision complex to dissociate yielding the products, within the period of relatively few vibrations, and thus nonadiabatic transitions will have an extremely low probability. However, if reaction is not thermodynamically favorable and the collision complex persists for 10^{-12} – 10^{-11} sec, the Lissajous motions of the complex which occur during this period will increase the probability of a nonadiabatic transition as there is a greater chance that the collision complex will have the required *vibronic* species. Similarly, rotation of the complex may bring about nonadiabatic transitions between certain states of the same multiplicity. The selection rules for both types of processes are given in ref 8. For our purposes, we may note that for triatomic molecules, mixing of A' and A'' states may only occur by coupling with rotation for singlet states and is expected to be relatively weak. For states of higher multiplicity, mixing will occur by the agency of spin-orbit coupling, which will increase in magnitude with increasing atomic number and should be stronger than mixing induced by rotation. Thus when direct reaction is not possible and for favorable crossing of potential surfaces, we may anticipate that nonadiabatic transitions of the type ${}^nA' \rightarrow {}^nA''$ may occur relatively frequently (the results indicate that only *ca.* 10 collisions are required in some cases).

Mixing between states of different multiplicity may only take place if spin-orbit interaction occurs. Although this will in general only be important when heavy atoms are involved, the spin-orbit coupling may still be sufficiently important to cause nonadiabatic transitions to be rate determining in relatively light molecules. Thus the transition probability for ${}^1A' \rightarrow {}^3A'$ in N_2O may be as high as 0.08.⁹

III. Group IV. Carbon, Silicon, and Germanium

Table I^{10–13} lists the low-lying metastable states of carbon and germanium together with their respective term values and calculated radiative transition probabilities (only the fastest radiative process is given). Silicon has not been included as, to the best of our knowledge, no kinetic data exist concerning electronically excited states of this atom.

Both $C(2^1S_0)$ and $C(2^1D_2)$ have been observed directly in absorption *via* their resonance transitions at 175.2 nm ($3d\ ^1P_1^0 \leftarrow 2p^2\ ^1S_0$) and 193.1 nm ($3s\ ^1P_1^0 \leftarrow 2p^2\ ^1D_2$), respectively¹⁴ (wavelengths are given for vacuum ultraviolet throughout this review). The atoms were produced by vacuum ultraviolet flash photolysis of carbon suboxide, which proved a convenient source for kinetic studies. However, the mechanism for the formation of $C(2^1S_0)$ was not determined, and thus in certain cases where reaction between the precursor of $C(2^1S_0)$ and the added reactant appeared to be important,¹⁴

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(8) G. Herzberg, "Molecular Spectra and Molecular Structure. III, Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1966.

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Table I

Energies and Transition Probabilities for the Strongest Forbidden Lines of Low-Lying, Metastable States of Group IV (C and Ge)

Atomic state	Energy (cm ⁻¹) ¹⁰	Transition ¹¹	Einstein A coefficient (sec ⁻¹) ^a
Carbon ¹²			
C(2 ¹ S ₀)	21,648	2 ¹ S ₀ → 2 ¹ D ₂	0.5 (A _q)
C(2 ¹ D ₂)	10,194	2 ¹ D ₂ → 2 ³ P ₂	2.3 × 10 ⁻⁴ (A _m)
C(2 ³ P ₂)	43	2 ³ P ₂ → 2 ³ P ₁	2.7 × 10 ⁻⁷ (A _m)
C(2 ³ P ₁)	16	2 ³ P ₁ → 2 ³ P ₀	7.8 × 10 ⁻⁸ (A _m)
C(2 ³ P ₀)	0		
Germanium ¹⁸			
Ge(4 ¹ S ₀)	16,367	4 ¹ S ₀ → 4 ¹ D ₂	7.7 (A _m)
Ge(4 ¹ D ₂)	7,125	4 ¹ D ₂ → 4 ³ P ₂	9.7 × 10 ⁻² (A _m)
Ge(4 ³ P ₂)	1,410	4 ³ P ₂ → 4 ³ P ₁	8.2 × 10 ⁻³ (A _m)
Ge(4 ³ P ₁)	557	4 ³ P ₁ → 4 ³ P ₀	3.1 × 10 ⁻³ (A _m)
Ge(4 ³ P ₀)	0		

^a m = magnetic dipole, q = electric quadrupole.

no data were given for this atomic state. C(2¹S₀) has also been observed following the pulsed radiolysis of gaseous CO, CH₄, and CO₂.¹⁵ The excited atom was observed by means of the weak resonance transition at 247.9 nm (3s ¹P₁⁰ ← 2p² ¹S₀), and the intensity of this transition was monitored as a function of pressure for a number of reactive gases. Wolfgang, *et al.*,¹⁶ infer that both ¹¹C(2¹S₀) and ¹¹C(2¹D₂) atoms are present together with translationally hot ground-state ¹¹C atoms when a 120-MeV ¹²C ion beam undergoes neutron stripping on passage through a Pt-Au foil. However, no direct observations or specific rate constants involving these states were reported.¹⁶ Ge(4¹D₂) together with a non-Boltzmann distribution in the spin-orbit multiplets of the ground state (³P_J) of this atom have been observed following the flash photodissociation of a number of germanium compounds.¹⁷ The atoms were observed by means of their resonance transitions in the far-ultraviolet, using kinetic absorption spectroscopy.¹⁷

The lack of experimental data on silicon may in part be due to difficulties with kinetic spectroscopic analysis of such systems. Thus the capillary discharge sources commonly employed in such studies are constructed of quartz and usually exhibit strong reversal lines for this element. The use of the flash fluorescence techniques¹⁸ may be expected to avoid this difficulty and should be useful for kinetic studies involving excited silicon atoms.

The kinetic data for C(2¹D₂) and C(2¹S₀) are summarized in Table II and individual reactions are discussed below.

A. CARBON ATOMS

1. C + Noble Gases

Quenching of C(2¹D₂) by argon has been observed; however, quantitative data were not given.¹⁴ Under the same conditions, quenching of C(2¹S₀) was not reported and is presumably inefficient.¹⁴ These data may be understood in terms of the analogous potential curves given later in detail for O(2¹D₂)

Table II

Rate Data for the Collisional Quenching of C(2¹D₂) and C(2¹S₀)

Quenching species	k (cm ³ molecule ⁻¹ sec ⁻¹)	No. of collisions Z = Z _{coll} /k	Ref
a. C(2 ¹ D ₂)			
H ₂	4.15 × 10 ⁻¹¹	8	14
NO	9.2 × 10 ⁻¹¹	3	14
O ₂	<5 × 10 ⁻¹²	>40	14
N ₂	≈2.5 × 10 ⁻¹²	100	14
CH ₄	3.2 × 10 ⁻¹¹	13	14
b. C(2 ¹ S ₀) ¹⁴			
H ₂	<5 × 10 ⁻¹²	>66	14

^a The data of Meaburn, *et al.*,¹⁵ indicate that the reactivity of C(2¹S₀) with various species follows the sequence C₃H₆ > O₂ > CH₄ > H₂ > CO > CO₂. The kinetic order of the reactions involving C(2¹S₀) were not determined by Meaburn, *et al.*;¹⁵ thus, although data are given for their experimental conditions, this cannot be used to deduce reliable rate data.

with the noble gases (spectroscopic data for the diatomic species O-noble gas are known, and the curves may be constructed with reasonable confidence; however, no such data have been given for the species C-noble gas). The mechanism involves crossing between curves correlating with C(2³P_J) and with C(2¹D₂). For the heavier noble gases, spin-orbit coupling will cause a mixing between the two states at the point of "crossing," and nonadiabatic transitions can occur. The efficiency for such nonadiabatic transitions should be greatest for the heavier noble gases, and we may thus anticipate that Kr and Xe will quench C(2¹D₂) even more efficiently than Ar. By contrast, no crossings between the curves arising from C(2¹S₀) and lower states of carbon are expected at low energies, and nonadiabatic transitions leading to relaxation should be very slow.

2. C + H₂

If first-order kinetics are assumed for the decay of C(2¹S₀) following the pulsed radiolysis of CO-H₂ mixtures, then the half-life and conditions quoted by Meaburn, and Penner¹⁵ may be used to obtain a rate coefficient for H₂ of 6.4 × 10⁻¹¹ cm³ molecule⁻¹ sec⁻¹, in satisfactory agreement with the results of Braun, *et al.*¹⁴ (Table II). The latter work further demonstrates that C(2¹S₀) is significantly less reactive than C(2¹D₂), despite the apparently greater exothermicity and "spin-allowed" nature of the reaction.¹⁴ This result, together with data on C(2³P_J),¹⁴ can be understood in terms of the appropriate correlation diagram (Figure 1).

It can be seen from Figure 1 that C(2³P_J) may "insert" into the H₂ bond by following the lowest surface of ³A'' symmetry. The experimental results show that this process is very efficient¹⁴ and thus must have a negligible activation energy (as indeed do a number of reactions involving carbon atoms, many of which still occur at 14°K¹⁹). Following "insertion" the vibrationally hot CH₂(X³Σ_g⁻) molecules will either redissociate after *ca.* 10-100 vibrations, or may be stabilized by collision with a third body. These considerations are in accord with the experimental findings.¹⁴ It may also be anticipated that "hot" carbon atoms with translational

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of $C(2^1S_0)$ to $C(2^1D_2)$ will thus be slow, in accord with estimates from Meaburn's data,¹⁵ while quenching of $C(2^1D_2)$ should require *ca.* 10^3 collisions. "Recombination" to form singlet C_2O may become important at high pressures, as apparently does the process $C(2^3P_J) + CO(1^2\Sigma^+) + M \rightarrow C_2O(3^2\Sigma)$.¹⁴

B. PREDICTED BEHAVIOR OF SILICON ATOMS

No kinetic data have been reported for the electronically excited states of silicon. The physical relaxation of both $Si(3^1D_2)$ and $Si(3^1S_0)$ by CO and N_2 should proceed at similar rates to those discussed for the analogous states of carbon as reaction is again thermodynamically unfavorable. Reaction with NO will, however, differ markedly as the formation of SiN is endothermic for both (3^1S_0) and (3^1D_2) atoms. We have seen previously for carbon that the alternative paths to yield the oxide apparently required an activation energy which reduced the efficiency of these reactions by at least one order of magnitude. Thus we may anticipate that $Si(3^1D_2)$ atoms will react with NO to form $SiO(X^1\Sigma^+) + N(2^3P_J)$ or $SiO(a^3\Pi) + N(2^4S_{1/2})$ (the $a^3\Pi$ state of SiO has not been observed spectroscopically but will lie approximately in the region accessible to this reaction) and that it will proceed with a rate constant of $\leq 10^{-12}$ cm^3 molecule⁻¹ sec⁻¹. Reaction with H_2 to form $SiH(X^2\Pi)$ is energetically unfavorable for thermal (300°K) atoms, and $Si(3^1D_2)$ together with $Si(3^3P_J)$ will most probably be removed by three-body recombination processes to form the singlet and triplet states of SiH_2 , respectively.

The correlation diagram further shows that the surface for $Si(3^1S_0) + H_2$ leads to states of SiH above the $A^2\Delta$ state, and such paths are energetically inaccessible to thermal atoms. Thus $Si(3^1S_0)$ will relax *via* a nonadiabatic transition ($^1A' \rightarrow ^1A''$) to yield $Si(3^1D_2)$; this process should be relatively inefficient by analogy with $C(2^1S_0) + H_2$.

For reaction between $Si(3^3P_J)$ and O_2 , the situation should be very similar to that observed for $C(2^3P_J)$, and fast reaction to produce SiO is expected. There are insufficient data on the upper electronic states of SiO to arrive at strong conclusions regarding $Si(3^1D_2)$; however, reaction may be expected to be slow as for $C(2^1D_2) + O_2$.

C. PREDICTED BEHAVIOR OF GERMANIUM ATOMS

Although $Ge(4^1D_2)$ has been detected spectroscopically,¹⁷ no quantitative rate data for this or other electronically excited states of this atom have been given. We find that the predicted behavior of Ge in all its states parallels that of Si ; thus the comments of the previous section may be used to cover Ge .

IV. Group V. Nitrogen, Phosphorus, and Arsenic

Table III,^{18,23,24} lists the energies and the calculated transition probabilities for the strongest lines of some low-lying metastable stages of nitrogen, phosphorus, and arsenic atoms.

Table III
Energies and Transition Probabilities for the Strongest Forbidden Lines of Low-Lying, Metastable States of Group V (N, P, As)

Atomic state	Energy ¹⁰ (cm^{-1})	Transition ¹¹	Einstein A coefficient (sec^{-1})
Nitrogen ²³			
$N(2^2P_{3/2})$	28,840	$2^2P_{3/2} \rightarrow 2^2D_{5/2}$	5.4×10^{-2}
$N(2^2P_{1/2})$	28,840	$2^2P_{1/2} \rightarrow 2^2D_{3/2}$	4.8×10^{-2}
$N(2^2D_{3/2})$	19,231	$2^2D_{3/2} \rightarrow 2^4S_{3/2}$	1.6×10^{-5}
$N(2^2D_{5/2})$	19,223	$2^2D_{5/2} \rightarrow 2^4S_{3/2}$	7.0×10^{-6}
$N(2^4S_{3/2})$	0		
Phosphorus ²⁴			
$P(3^2P_{3/2})$	18,748	$3^2P_{3/2} \rightarrow 3^4S_{3/2}$	$1.08 \times 10^{-1} (A_m)$
$P(3^2P_{1/2})$	18,722	$3^2P_{1/2} \rightarrow 3^2D_{3/2}$	$8.01 \times 10^{-2} (A_q)$
$P(3^2D_{3/2})$	11,376	$3^2D_{3/2} \rightarrow 3^4S_{3/2}$	$1.85 \times 10^{-4} (A_q)$
$P(3^2D_{5/2})$	11,362	$3^2D_{5/2} \rightarrow 3^4S_{3/2}$	$1.77 \times 10^{-4} (A_m)$
$P(3^4S_{3/2})$	0		
Arsenic ¹³			
$As(4^2P_{3/2})$	18,647	$4^2P_{3/2} \rightarrow 4^4S_{3/2}$	$1.6 (A_m)$
$As(4^2P_{1/2})$	18,186	$4^2P_{1/2} \rightarrow 4^4S_{3/2}$	$0.69 (A_m)$
$As(4^2D_{3/2})$	10,915	$4^2D_{3/2} \rightarrow 4^4S_{3/2}$	$3.3 \times 10^{-3} (A_q)$
$As(4^2D_{5/2})$	10,592	$4^2D_{5/2} \rightarrow 4^4S_{3/2}$	$7.3 \times 10^{-3} (A_m)$
$As(4^4S_{3/2})$	0		

Quantitative kinetic data on the transfer of energy from electronically excited N^{25} and As^{26} atoms are now available. The recent measurements on $N(2^2D_J)$ are particularly interesting as they provide the only detailed data on this species which must be of importance in aeronomic studies. Further, the behavior of $N(2^2D_J)$ and $N(2^2P_J)$ are relevant to an understanding of "active" nitrogen.²⁷⁻²⁹ No quantitative data on the collisional deactivation of excited phosphorus atoms have yet been reported although these species have been detected by kinetic absorption spectroscopy.³⁰

Emission from the transition $N(2^2P_J) \rightarrow N(2^4S_{3/2})$ and $N(2^2P_J) \rightarrow N(2^2D_J)$ at 346.6 and 1040 nm, respectively, may be readily observed from the aurora, and that from $N(2^2D_J) \rightarrow N(2^4S_{3/2})$ at 520 nm is prominent in the day glow.³¹ The relatively weak $N(2^2P_J) \rightarrow N(2^4S_{3/2})$ emission has been reported in laboratory experiments employing a high-pressure nitrogen afterglow,³² but that for $N(2^2D_J)$ was not observed. This is not surprising as this state is characterized by an Einstein A coefficient of approximately 10^3 times less than for the 2P state (Table III). Tanaka, *et al.*,³³ have detected the 4S , 2D , and 2P states of atomic nitrogen by absorption spectroscopy in the vacuum ultraviolet on the afterglow of a discharge. Morse and Kaufman³⁴ have

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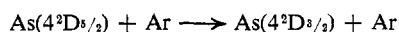
also observed vacuum ultraviolet transitions from these states from a flow discharge system, and this would indicate that the method could be used for energy-transfer studies if the sensitivity could be improved. $N(2^2P_J)$ and $N(2^2D_J)$ have been observed by a mass spectrometric investigation of the products of "active" nitrogen,³⁵ and $N(2^2D_{3/2,5/2})$ have been detected by electric spin resonance.³⁶ The principal method for determining rate data for the collisional quenching of $N(2^2D_J)$ has employed the β emission from $NO(B^2\Pi-X^2\Pi)$ following the reaction of $N(2^2D_J)$ with $N_2O(X^1\Sigma^+)$,²⁵ a process that has been proposed by Welge.³⁷ The rate constant for the quenching of $N(2^2P_J)$ by N_2 has been determined using a flow discharge system.³² The kinetic data for the metastable nitrogen atoms are given in Table IV.

Table IV

Rate Data for the Collisional Deactivation of $N(2^2D_J)$

Quenching species	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)	No. of collisions $Z = Z_{\text{coll}}/k$	Ref
He	$\leq 2 \times 10^{-16}$	$\geq 1.6 \times 10^6$	25
Ar	$\leq 2 \times 10^{-16}$	$\geq 1.2 \times 10^6$	25
N_2	$\leq 6 \times 10^{-15}$	$\geq 4.6 \times 10^4$	25
O_2	7×10^{-12}	36	25
	$5 \pm 1 \times 10^{-12}$	50	34
	10^{-12}	2.4×10^2	31
H_2	5×10^{-12}	99	25
CO	6×10^{-12}	45	25
NO	1.8×10^{-10}	1	25
CO_2	6×10^{-13}	4.6×10^2	25
N_2O	3×10^{-12}	90	25
NH_3	1.1×10^{-10}	3	25
CH_4	3×10^{-12}	1.1×10^2	25
C_2H_4	1.2×10^{-10}	3	25
$(N_2 + N(2^2P_J))$	$< 3 \times 10^{-19}$	$> 10^9$	32)

$As(4^2D_{3/2})$ and $As(4^2D_{5/2})$, as well as ground-state atoms, ($4^4S_{3/2}$), have been detected and monitored by kinetic absorption spectroscopy following the flash photodissociation of arsenic halides.²⁸ In this study, the $2^2D_{3/2}$ state is observed to decay significantly faster than the $2^2D_{5/2}$ state. If it is assumed that both $As(4^2D_{3/2})$ and $As(4^2D_{5/2})$ are quenched to the $4^4S_{3/2}$ ground state at equal rates, then the difference in the rates of removal of the two states may be ascribed to spin-orbit relaxation, which, for argon yields an upper



limit of $k = 4.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.²⁶ The results for the collisional deactivation of $2^2D_{3/2}$ atoms to the ground state with various gases are given in Table V; the population of $As(4^2D_{3/2})$ from $As(4^2D_{5/2})$ has been neglected.²⁶ The removal of the excited atoms by radiation is very much slower (Table III) than the overall decay rates observed by Callear and Oldman,²⁶ and thus its contribution to the decay may be ignored. Basco and Yee³⁰ have also reported the observation of $As(4^2P_{3/2,1/2})$ by kinetic spectroscopy in absorption following flash photolysis, but no rate data have been given. The same authors³⁰ also report the ob-

servation of $P(3^2D_{3/2,5/2}, 3^2P_{3/2,1/2})$ in absorption following the flash photodissociation of a number of phosphorus compounds but again report no quantitative rate measurements.

Table V

Rate Data for the Collisional Deactivation of $As(4^2D_J) \rightarrow As(4^4S_{3/2})$ ²⁶

Quenching gas	Temp ($^{\circ}K$)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)	No. of collisions ^a $Z = Z_{\text{coll}}/k$
Ar	296	$1.1 \pm 0.2 \times 10^{-16}$	1.7×10^5
Kr	296	$< 10^{-15}$	$> 1.6 \times 10^6$
Xe	296	$1.7 \pm 0.3 \times 10^{-12}$	98
Xe	403	$5.4 \pm 0.8 \times 10^{-12}$	36
SF_6	296	$< 10^{-15}$	$> 2.3 \times 10^6$
CO	296	$4.7 \pm 0.6 \times 10^{-11}$	5
N_2	296	$4.0 \pm 0.6 \times 10^{-12}$	58
N_2	403	$1.3 \pm 0.2 \times 10^{-11}$	21
H_2	296	$2.8 \pm 0.3 \times 10^{-11}$	22
D_2	296	$1.2 \pm 0.2 \times 10^{-11}$	36
CO_2	296	$7.8 \pm 1.2 \times 10^{-13}$	2.7×10^2
CH_4	296	$1.9 \pm 0.4 \times 10^{-12}$	1.6×10^3

^a Collision numbers have been calculated assuming that the Lennard-Jones σ value for As may be taken to be that for the nearest inert gas, Kr.

A. NITROGEN ATOMS

1. $N + Noble\ Gases$

Quenching of $N(2^2D_J)$ by He and Ar is clearly very inefficient (Table IV). Consideration of the data for $As(4^2D_J)$ with the noble gases indicates that quenching of $N(2^2D_J)$ by Xe should proceed with an efficiency of approximately one in 10^3 collisions, allowing for the weaker spin-orbit coupling that would be involved.

2. $N + N_2$

The relaxation of metastable nitrogen atoms by N_2 clearly requires nonadiabatic transitions. These considerations would be aided by a more detailed knowledge of the electronic states of N_3 , which has been detected by kinetic spectroscopy in absorption,³⁸ and the rough shape of the surfaces particularly where the states are attractive. The extremely low efficiency for the deactivation of $N(2^2P_J)$ and $N(2^2D_J)$ by N_2 (Table IV) indicates the absence of crossings between the surfaces leading to nonadiabatic transitions for thermal energies. The result for $N(2^2D_J)$ is somewhat surprising when compared with the data for $N(2^2D_J) + CO$ (Table IV) and $As(4^2D_J) + N_2$ (Table V) and can only be reconciled by a low binding energy for N_3 such that the potential surface is insufficiently attractive to bring doublet and quartet surfaces into close proximity. Discharge experiments have generally shown the walls of the system employed to be efficient in deactivating $N(2^2P_J)$ and $N(2^2D_J)$;^{33,35,39} the decay of $N(2^2D_J)$ is found to be inhibited by cooling the walls to

(35) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **37**, 1662 (1962).(36) K. M. Evenson and H. E. Radford, *Phys. Rev. Lett.*, **15**, 916 (1965).(37) K. H. Welge, *J. Chem. Phys.*, **45**, 166 (1966).(38) B. A. Thrush, *Proc. Roy. Soc., Ser. A*, **235**, 143 (1956); A. E. Douglas and W. J. Jones, *Can. J. Phys.*, **43**, 2216 (1965).(39) Y. Tanaka, A. S. Jursa, F. J. LeBlanc, and E. C. Y. Inn, *Planet. Space Sci.*, **1**, 7 (1959).

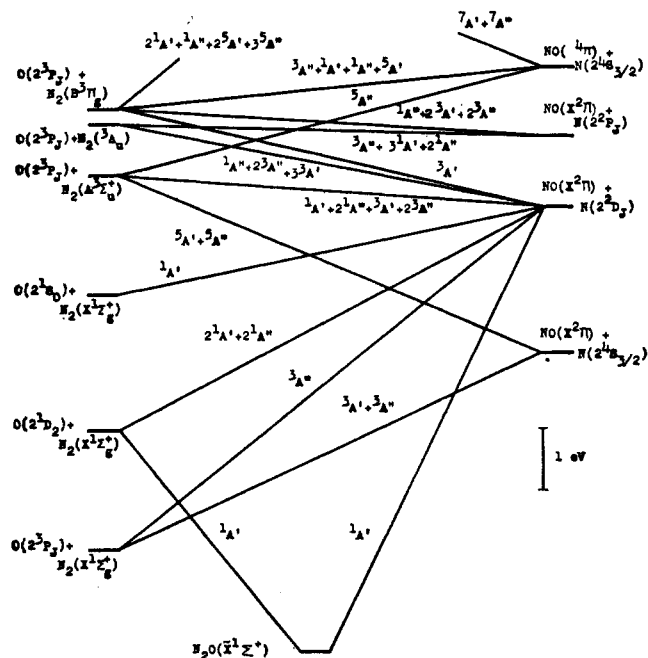


Figure 5. Correlation diagram connecting the states of $O + N_2$ and $NO + N$.^{8,10,20-22}

-195° where strong emission from the second positive system of nitrogen due to the recombination of $N(2^2D_j)$ and $N(2^4S_{1/2})$ may be observed.⁴⁰



Energy transfer involving metastable nitrogen atoms has been considered in discussions on "active" nitrogen.²⁷⁻²⁹ The suggestion²⁸ that the energy-transfer reaction

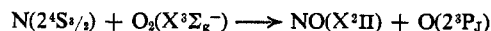


is the source of N^2P is not in accord with the findings of Noxon³² who showed that the majority of the $N(2^2P_j)$ atoms observed are those which survive the discharge and do not result from $N(2^4S_{1/2})$. If deactivation of the A state takes place by collision with ground-state atoms, the suggestion of Brocklehurst and Jennings²⁹ that the energy appears in vibration in $N_2(X^1\Sigma_g^+)$ seems reasonable. Relative translational energy could also be important.

3. $N + O_2$

$N(2^2D_j)$ and O_2 may react on at least six surfaces to yield $NO(X^2\Pi) + O(2^3P_j)$ ($2^2A' + 2^2A'' + ^4A' + ^4A''$) (Figure 11) and thus should be fast, as found (Table IV). In referring to Figure 11, it should be appreciated that this reaction may not necessarily proceed through the same NO_2 complex as for $O + NO$ as insertion would be required, but the overall correlations connecting both sides of the diagram are correct. Indeed, similar considerations to those given by Wolfgang for carbon atom reactions suggest that the linear collision complex NOO would be the most favorable.¹⁶ $N(2^2D_j)$ and O_2 may also react adiabatically to yield $NO(X^2\Pi) + O(2^1D_2)$ via a surface of symmetry $^2A'$ (Figure 11); the reaction is less exothermic, possibly requiring an activation

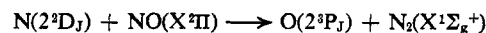
energy and thus should be relatively slow. The rate of the reaction of $N(2^2P_j)$ and O_2 has not been measured. Only excited oxygen atoms can result from adiabatic pathways, $^2A'' \rightarrow O(2^1D_2) + NO(X^2\Pi)$ and $^2A'' \rightarrow O(2^1S_0) + NO(X^2\Pi)$. The reaction with ground-state atoms



has been studied in detail,⁴¹⁻⁴⁵ and there is good agreement among the measurements which indicate that an activation energy between 0.26 and 0.33 eV is required.

4. $N + NO$

$N(2^2D_j)$ is removed on every collision with NO (Table IV). No data have yet been reported for $N(2^2P_j)$. Figure 5 indicates that rapid chemical reaction between $N(2^2D_j)$ and NO may be expected, and the unit efficiency for the removal of this excited nitrogen atom provides strong evidence for this mode of decay rather than physical relaxation. The reaction



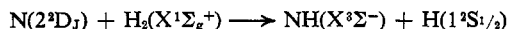
may proceed *via* one potential surface, $^3A''$, and should be of similar rate to that for ground-state atoms.



This process proceeds *via* two surfaces ($^3A' + ^3A''$) and has been characterized by Clyne and Thrush⁴⁸ ($k_{300^\circ K} = 3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$), Herron,⁴⁶ and Phillips and Schiff.⁴⁷ Potential surfaces are also available for the reaction of $N(2^2D_j)$ and NO to yield $O(2^1D_2) + N_2(2^1A' + 2^1A'')$ and $O(2^1S_0) + N_2(^1A')$ (Figure 5). Despite the larger number of surfaces, an activation energy may be expected. However, the direct adiabatic route to $O(2^1D_2) + N_2$ does correlate with ground-state N_2O , and hence the rate could be similar to or greater than that for $N(2^4S_{1/2}) + NO$. No chemical reaction by means of an adiabatic path between $N(2^2P_j) + NO$ is expected for thermal collisions (Figure 5). The most likely process would appear to be physical relaxation *via* a nonadiabatic transition of the type $A'-A''$ or $A''-A'$. Less likely would be chemical reaction to yield $O(2^3P_j) + N_2$ in an excited state which could still arise through a similar nonadiabatic transition.

5. $N + H_2$

The removal of $N(2^2D_j)$ by H_2 is a relatively efficient process (Table IV). Figure 6 indicates that this species should readily undergo chemical reaction



via a direct path ($^2A''$). $NH(a^1\Delta)$ may also possibly be produced from these reactants ($^2A' + ^2A''$), but the thermochemistry of this reaction is a little uncertain. No reaction is expected between $N(2^2P_j) + H_2$, but relaxation to $N(2^2D_j)$

(41) G. B. Kistiakowsky and G. G. Volpi, *ibid.*, **27**, 1141 (1957).

(42) F. Kaufman and L. J. Decker, 7th Symposium on Combustion, Butterworths, London, 1959, p 57.

(43) M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc., Ser. A*, **261**, 259 (1961).

(44) C. Mavroyannis and C. A. Winkler, "Chemical Reactions in the Lower and Upper Atmosphere," Interscience, New York, N. Y., 1961, p 287.

(45) I. M. Campbell and B. A. Thrush, *Annu. Rep. Chem. Soc.*, **LXII**, 17 (1965).

(46) J. T. Herron, *J. Chem. Phys.*, **35**, 1138 (1961).

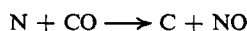
(47) L. F. Phillips and H. I. Schiff, *ibid.*, **36**, 1509 (1962).

(40) Y. Tanaka, F. J. LeBlanc, and A. S. Jursa, *J. Chem. Phys.*, **30**, 1624 (1959).

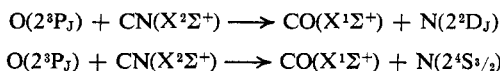
may occur *via* an $A'-A''$, $A''-A'$ nonadiabatic transition. Less likely would be the production of $\text{NH}(a^1\Delta)$ or $\text{X}^3\Sigma^-$ following a similar nonadiabatic transition. Hence for $\text{N}(2^2\text{P}_j)$ we may expect relaxation to $\text{N}(2^2\text{D}_j)$ followed by reaction as outlined above. Reaction of $\text{N}(2^4\text{S}_{1/2})$ with H_2 is highly endothermic.

6. $\text{N} + \text{CO}$

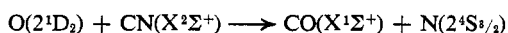
Thermochemical considerations indicated that $\text{N}(2^2\text{D}_j)$ undergoes physical relaxation on collision with CO . $\text{N}(2^2\text{D}_j) + \text{CO}(X^1\Sigma^+)$ correlates with $\text{NCO}(X^2\Pi_i)$, thus causing doublet and quartet surfaces to cross and hence facilitating relaxation, as observed (Table IV), by the agency of spin-orbit coupling. Direct recombination with a third body may also be expected for high inert gas pressures or in condensed phases. For $\text{N}(2^2\text{P}_j) + \text{CO}$, the process



is endothermic, and relaxation to $\text{N}(2^2\text{D}_j)$ *via* a transition $^2A' \rightarrow ^2A''$ may be expected. While reaction to yield $\text{CN} + \text{O}$ is exothermic ($\Delta H = -0.23$ eV), there is *no* potential surface available for a direct adiabatic route. Reaction would involve a nonadiabatic transition of the type $^2A' \rightarrow ^2A''$ or $^2A'' \rightarrow ^2A'$. An activation energy would also be expected for this close to thermoneutral reaction which should then be slow. Considering the reverse reactions, it is interesting to note that while there are potential surfaces available for the processes



there is no adiabatic route for exothermic chemical reaction between



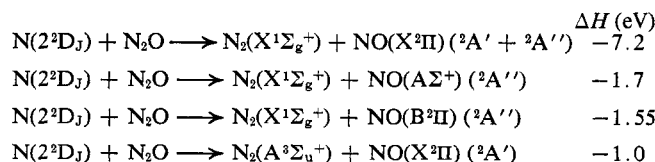
The direct route is endothermic and nonadiabatic transitions would be involved for an exothermic process. Also potential surfaces are available for the reactions



but there is no adiabatic route to $\text{N}(2^4\text{S}_{1/2})$.

7. $\text{N} + \text{N}_2\text{O}$

The removal of $\text{N}(2^2\text{D}_j)$ by N_2O , taking place once in 90 collisions (Table IV), appears to be relatively slow in view of the number of surfaces available for exothermic reaction. Writing the adiabatic surfaces in parentheses, the processes that may take place are



Indeed, Young, *et al.*,²⁵ have employed the β emission of $\text{NO}(B-X)$ to monitor $\text{N}(2^2\text{D}_j)$ produced in the photolysis of N_2O . γ emission from $\text{NO}(A-X)$ would also be expected. On the other hand, detection of the Vegard-Kaplan bands [$\text{N}_2(A^3\Sigma_u^+) - \text{N}_2(X^1\Sigma_g^+)$] would not be expected on account of their spin-forbidden nature. However, $\text{N}_2(A^3\Sigma_u^+)$ produced in this system would be expected to undergo energy

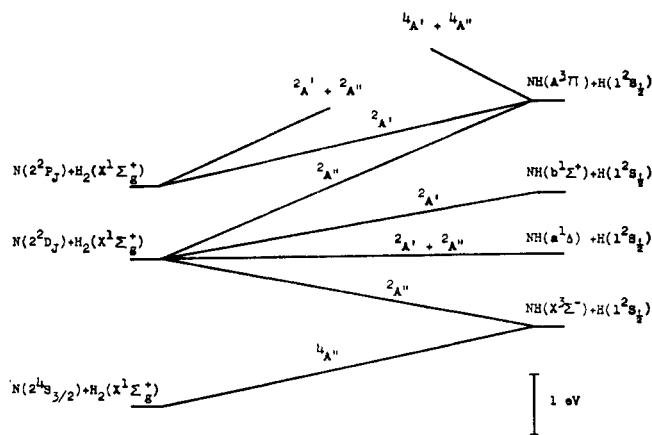
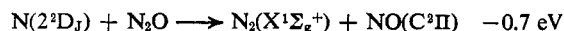


Figure 6. Correlation diagram connecting the states of $\text{N} + \text{H}_2$ and $\text{NH} + \text{H}$.^{8,10,20,21}

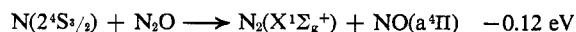
transfer on collision with NO , raising it to states (A and B) from which emission is electric dipole allowed. No surfaces are available for a direct route to $\text{NO}(C^2\Pi)$ *via* the reaction



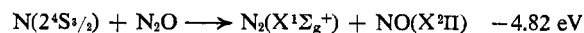
in spite of its being spin allowed and exothermic. Thus δ emission from $\text{NO}(C-X)$ could only arise following a nonadiabatic transition of the type $^2A', ^2A'' \rightarrow ^2A'', ^2A'$. It would therefore be instructive to compare the quantum yields for the γ , β , and δ systems in order to test whether those for the latter were significantly lower owing to the effect of a nonadiabatic transition.

No data are available on the removal of $\text{N}(2^2\text{P}_j)$ by N_2O . Direct routes to $\text{NO}(B^2\Pi)(^2A'')$, $\text{N}_2(A^3\Sigma_u^+)(^2A')$, and $\text{NO}(C^2\Pi)(^2A'')$ exist, and emission from the β and γ systems may be anticipated. Physical relaxation of both the ^2P and ^2D states of the nitrogen atom would involve nonadiabatic transitions. $\text{N}(2^2\text{P}_j) + \text{N}_2\text{O}(X^1\Sigma^+)$ do not correlate with ground-state products.

Ground-state nitrogen atoms would be expected to react slowly with N_2O despite the favorable thermochemistry. The only adiabatic surface ($^4A''$) connects reactants and products for the close to thermoneutral reaction



and hence a significant activation energy would be involved. Reaction to yield ground-state species



would involve a nonadiabatic transition $^4A'' \rightarrow ^2A''$. No particularly strong interaction between $\text{N} + \text{N}_2\text{O}$ may be envisaged to enhance the spin-orbit coupling that would facilitate this overall process. Indeed, Kistiakowsky and Volpi⁴¹ were unable to detect reaction at 553°K, and their results indicate that at least 10^8 collisions would be required.

B. ARSENIC ATOMS

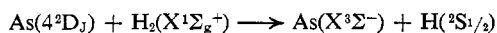
1. $\text{As} + \text{Noble Gases}$

The rapid quenching of $\text{As}(4^2\text{D}_j) \rightarrow \text{As}(4^4\text{S}_{3/2})$ by xenon (Table V) may be in principal compared with the efficient deactivation of $\text{O}(2^1\text{D}_2)$ by this noble gas. This latter process is discussed in detail in the appropriate section in group VI, principally on account of the existence of spectroscopic

data on XeO. The basis of the discussion involves the mixing of components for states of different multiplicity which will occur for crossings in regions where Hund's case (c) coupling holds. Callear and Oldman²⁶ have suggested the quenching of As(4²D_J) by Xe proceeds through a stabilized AsXe complex, and that transfer results from the crossing of potential curves. The spectrum of AsXe has not been reported. These authors suggest that the coupling should approximate to Hund's case (c) for the large internuclear separation in the complex. Thus, extending their discussion, and writing the case (c) components in parentheses, we may consider the states derived from As(4²D_u) + Xe(¹S₀) as ²Σ⁻(¹/₂), ²Π(¹/₂, ³/₂), and ²Δ(³/₂, ⁵/₂) which should be ordered according to Hund's rule; the state derived from As(⁴S_u) + Xe(¹S₀) is ⁴Σ⁻(¹/₂, ³/₂). Thus mixing and hence "avoided crossing" may arise in two cases both for the ³/₂ and for the ¹/₂ case (c) components in the upper and lower sets of states, allowing efficient transfer from one curve to another. The efficiency for argon is compatible with this mechanism, as the coupling will tend toward Hund's case (a) and show a reduced probability of transfer between curves. However, the result for krypton (Table V) is difficult to reconcile with this mechanism.

2. As + H₂, D₂

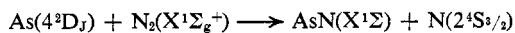
The main features of the correlation diagram for N + H₂ will apply to a discussion of the system As(4²D_J) + H₂(X¹Σ_g⁺) (Figure 6). The spectrum of AsH has recently been reported by Dixon, *et al.*,⁴⁸ and also by Basco and Yee.⁴⁹ The ground state of AsH is ³Σ⁻ similar to NH(X³Σ⁻); the upper states reported were ³Π_{0,1,2} lying approximately 30,000 cm⁻¹ above the ground state. No value for D₀(AsH) has, as yet, been published. Provided the value of D₀(AsH) is greater than 3.15 eV, the reaction



will be exothermic, and a potential surface (²A'') is available for a direct adiabatic route. A small activation energy may then be required for this process. Physical relaxation of As(4²D_J) → As(4⁴S_{3/2}) would require a nonadiabatic transition involving a doublet → quartet spin change. The highly efficient removal of As(4²D_J) by both H₂ and D₂ (Table V) suggests chemical reaction; however, AsH was not reported in the kinetic spectroscopic experiments.²⁶

3. As + N₂

The reaction



is strongly endothermic.^{22,50} Further there is no potential surface available for an adiabatic process, a spin change being required. Thus collisional quenching by means of a doublet → quartet transition must take place. The relatively high efficiency of N₂ therefore indicates that a favorable crossing occurs and that strong spin-orbit coupling expected for the heavy arsenic atom facilitates this process. A stable intermediate, AsN₂, analogous to N₃,³⁸ may be involved.

4. As + CO

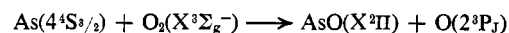
The extremely rapid deactivation of As(4²D_J) by CO (Table V) must occur by a similar process to that described above for N₂. An intermediate AsCO analogous to NCO(²Σ⁺), which will correlate with As(4²D_J) + CO(X¹Σ⁺), may be involved and may facilitate relaxation.

5. As + O₂

The removal of As(4²D_J) by molecular oxygen has not been investigated. A number of potential surfaces (2²A' + 2²A'' + ⁴A' + 2⁴A'') are available (Figure 7) for the exothermic (ΔH = -1.2 eV) chemical reaction



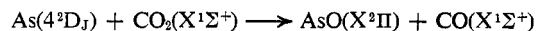
AsO has been observed by Callear and Oldman²⁶ in a system containing this atom and may result from this process. The reaction of ground-state atoms with ground-state O₂



may proceed *via* the surfaces ²A' + ⁴A', but this will only take place for translationally hot species on account of the small endothermicity (ΔH = +0.2 eV). Collisional quenching of As(4²D_J) to As(4⁴S_{3/2}) by O₂ may proceed *via* the non-adiabatic transitions ²A'' → ²A' and ⁴A'' → ⁴A'.

6. As + CO₂

The removal of As(4²D_J) by CO₂ requires 270 collisions (Table V). This could proceed by means of an exothermic (ΔH = -0.78 eV) chemical reaction



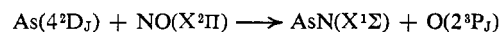
for which potential surfaces are available (2A' + 2A''). However, AsO was not reported in this system.²⁶ Relaxation to ground-state atoms requires a nonadiabatic transition of the type doublet → quartet.

7. As + CH₄

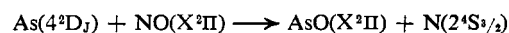
The observed removal of the excited arsenic atoms is relatively rapid (Table V). Hydrogen-atom abstraction from methane by As(4²D_J) would be an exothermic process provided D₀(AsH) > 3.07 eV. A value of this magnitude would be in accord with the discussion on As + H₂ and D₂. AsH was not reported in this system²⁵ although the spectrum of the species AsH(X³Σ⁻) has been established.^{48,49}

8. As + NO

The removal of As(4²D_J) by NO(X²Π) has not been investigated. The dissociation energy of AsN(X¹Σ)²² is not known with sufficient accuracy (5 ± 1 eV)²² to predict the sign of the thermochemistry of the reaction



The higher value indicates that the process is exothermic (ΔH = -0.82 eV) whereas the lower value indicates an endothermic reaction (ΔH = +0.18 eV). Potential surfaces would be expected to be available for an adiabatic route. The reaction



(48) R. N. Dixon, G. Duxbury, and H. M. Lambertson, *Chem. Commun.*, 460 (1966).

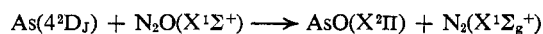
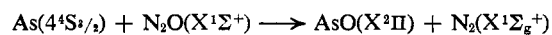
(49) N. Basco and K. K. Yee, *Spectrosc. Lett.*, 1, 13 (1968).

(50) J. W. T. Spinks, *Z. Phys.*, 88, 511 (1934).

is endothermic ($\Delta H = +1.3$ eV). Relaxation to $\text{As}(4^4\text{S}_{3/2})$ would involve a nonadiabatic transition involving a change of multiplicity.

9. $\text{As} + \text{N}_2\text{O}$

The removal of $\text{As}(4^3\text{D}_J)$ by N_2O has not been investigated. Atomic oxygen abstraction reactions of both $\text{As}(4^4\text{S}_{3/2})$ and $\text{As}(4^3\text{D}_J)$



are exothermic, being $\Delta H = -3.2$ and -4.5 eV, respectively. For symmetry C_s , adiabatic potential surfaces are only available for the second reaction, and the reaction should be fast.

C. PHOSPHORUS ATOMS

Unfortunately, there are no data as yet on the chemical reactions and physical relaxation of electronically excited phosphorus atoms although these species have been detected by kinetic absorption spectroscopy.³⁰ It will be interesting to compare the data, when available, with the other atoms of this group. The correlation diagrams that have been presented for the reactions of atomic nitrogen will form the framework for discussing the analogous processes for phosphorus atoms.

V. Group VI. Oxygen, Sulfur, Selenium, and Tellurium

Table VI^{12,13,51} lists the optically metastable states of group VI to be discussed in this section, together with their energies and the calculated Einstein A factors for the strongest forbidden transitions that the atoms in these states may undergo. The transition probabilities clearly indicate that radiative processes will generally be of little significance under laboratory conditions compared with collisional removal. The number of experimental investigations carried out on the electronically excited atoms of this group are in the order $\text{O} > \text{S} > \text{Se} > \text{Te}$, the relatively large body of data for $\text{O}(2^1\text{S}_0)$ and $\text{O}(2^1\text{D}_2)$ obviously being the result of present interests in the chemistry of the upper atmosphere. However, a considerable number of studies have been carried out on the reactions and relaxation of $\text{S}(3^1\text{S}_0)$ and $\text{S}(3^1\text{D}_2)$, and useful comparisons between oxygen and sulfur may be made.

A large number of investigations have been carried out on the kinetics of the (2^1D_2) and (2^1S_0) states of atomic oxygen but none, as yet, has been published on specified spin-orbit states of the $^3\text{P}_{2,1,0}$ ground-state configuration. In view of the small spin-orbit splittings, these have generally been assumed to be in Boltzmann equilibrium with each other and with the ambient surroundings. Experimental methods of studying $\text{O}(2^1\text{D}_2)$ may be essentially divided into those involving monitoring the very weak emission (Table VI) from this state to the ground state, $\text{O}(2^3\text{P}_2)$, at 630 nm, and those which depend on measuring the extent of a chemical reaction in which $\text{O}(2^1\text{D}_2)$ takes part. While the latter method yields relative rate data, it is capable of high accuracy and the data of many of the pioneering experiments remain the most precise. Laboratory-based studies of the emission $\text{O}(2^1\text{D}_2) \rightarrow \text{O}(2^3\text{P}_2)$ in the aurora are well

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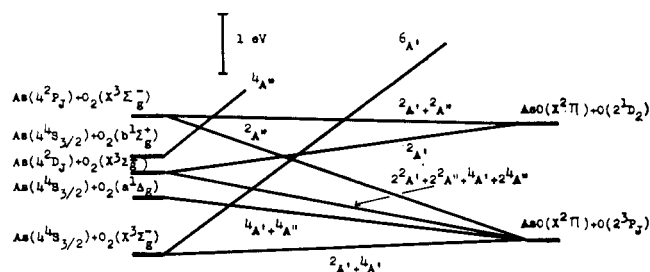


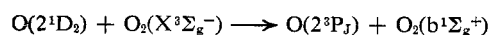
Figure 7. Correlation diagram connecting the states of $\text{As} + \text{O}_2$ and $\text{AsO} + \text{O}$.^{8,10,20,21}

Table VI

Energies and Transition Probabilities for the Strongest Forbidden Lines of Low-Lying, Metastable States of Group VI

Atomic state	Energy (cm^{-1}) ¹⁰	Transition ¹¹	Einstein A coefficient (sec^{-1})
Oxygen ¹²			
$\text{O}(2^1\text{S}_0)$	33,792	$2^1\text{S}_0 \rightarrow 2^1\text{D}_2$	1.28 (A_0)
$\text{O}(2^1\text{D}_2)$	15,868	$2^1\text{D}_2 \rightarrow 2^3\text{P}_2$	6.9×10^{-3} (A_m)
$\text{O}(2^3\text{P}_0)$	226	$2^3\text{P}_0 \rightarrow 2^3\text{P}_1$	1.7×10^{-5} (A_m)
$\text{O}(2^3\text{P}_1)$	158	$2^3\text{P}_1 \rightarrow 2^3\text{P}_2$	8.9×10^{-6} (A_m)
$\text{O}(2^3\text{P}_2)$	0		
Sulfur ⁵¹			
$\text{S}(3^1\text{S}_0)$	22,181	$3^1\text{S}_0 \rightarrow 3^1\text{D}_2$	1.78 (A_0)
$\text{S}(3^1\text{D}_2)$	9,239	$3^1\text{D}_2 \rightarrow 3^3\text{P}_2$	2.73×10^{-2} (A_m)
$\text{S}(3^3\text{P}_0)$	574	$3^3\text{P}_0 \rightarrow 3^3\text{P}_1$	2.95×10^{-4} (A_m)
$\text{S}(3^3\text{P}_1)$	397	$3^3\text{P}_1 \rightarrow 3^3\text{P}_2$	1.39×10^{-3} (A_m)
$\text{S}(3^3\text{P}_2)$	0		
Selenium ¹³			
$\text{Se}(4^1\text{S}_0)$	22,446	$4^1\text{S}_0 \rightarrow 4^3\text{P}_1$	7.7 (A_m)
$\text{Se}(4^1\text{D}_2)$	9,576	$4^1\text{D}_2 \rightarrow 4^3\text{P}_2$	0.62 (A_m)
$\text{Se}(4^3\text{P}_0)$	2,534	$4^3\text{P}_0 \rightarrow 4^3\text{P}_1$	8.5×10^{-3} (A_m)
$\text{Se}(4^3\text{P}_1)$	1,989	$4^3\text{P}_1 \rightarrow 4^3\text{P}_2$	0.17 (A_m)
$\text{Se}(4^3\text{P}_2)$	0		
Tellurium ¹³			
$\text{Te}(5^1\text{S}_0)$	23,199	$5^1\text{S}_0 \rightarrow 5^3\text{P}_1$	37 (A_m)
$\text{Te}(5^1\text{D}_2)$	10,559	$5^1\text{D}_2 \rightarrow 5^3\text{P}_2$	3.3 (A_m)
$\text{Te}(5^3\text{P}_1)$	4,751	$5^3\text{P}_1 \rightarrow 5^3\text{P}_2$	2.2 (A_m)
$\text{Te}(5^3\text{P}_0)$	4,707	$5^3\text{P}_0 \rightarrow 5^3\text{P}_2$	7.3×10^{-3} (A_0)
$\text{Te}(5^3\text{P}_2)$	0		

established, a recent example of which is given by Hunten and McElroy.⁵¹ This emission from the ^1D oxygen atom in a pumped discharge has also been employed to study the kinetics of this metastable state.⁵² Very recently, this emission at 630 nm, resulting from the production of $\text{O}(2^1\text{D}_2)$ following the photolysis of CO_2 in a static system, has been used to study the quenching of this atomic state in the presence of added gases.⁵³ The magnetic dipole-allowed emission from $\text{O}_2(\text{b}^1\Sigma_g^+)$ associated with the "oxygen atmospheric bands," $\text{O}_2(\text{b}^1\Sigma_g^+) \rightarrow \text{O}_2(\text{X}^3\Sigma_g^-)$, has been used to study the reactions of $\text{O}(2^1\text{D}_2)$ which gives rise to this excited molecular state on collision with a ground-state oxygen molecule.^{54,55} The spontaneous emission transition prob-



ability for the (0,0) band is sufficiently high for this emission to be readily observed in a flow system [$A(0,0) = 0.10$

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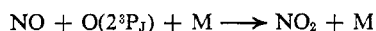
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sec^{-1} ^{56,57}. The magnetic dipole emission from the transition $\text{O}_2(a^1\Delta_g) \rightarrow \text{O}_2(X^3\Sigma_g^-)$ ("infrared atmospheric bands") is very much weaker than that for the oxygen atmospheric bands [$A(0,0) = 1.9 \times 10^{-4}$ ^{56,58}], and thus emission from $\text{O}_2(a^1\Delta_g)$ formed from the reaction



has not been employed to study the kinetics of $\text{O}(2^1D_2)$ in the photolysis of O_2 . Wayne has noted that the rate of this process could be up to a factor of 15 times greater than that leading to $\text{O}_2(b^1\Sigma_g^+)$ with the emission from $\text{O}_2(a^1\Delta_g)$ escaping detection.^{54,59} However, while the infrared atmospheric bands were not observed following the photolysis of O_2 ,⁵⁴ they have been observed in the photolysis of O_3 in a flow system⁵⁹ and have been attributed to the reaction of $\text{O}(2^1D_2)$ with O_2 .⁵⁹ A further spectroscopic method for the study of $\text{O}(2^1D_2)$ is the enhancement of the afterglow emission from NO_2 in a flow system from the reaction which



follows the relaxation of $\text{O}(2^1D_2)$ to the 3P ground state.⁶⁰

A number of methods which depend on the measurement of a stable reactant or product in a process involving a chemical reaction of $\text{O}(2^1D_2)$ have been developed and are too numerous to be listed. These methods include the determination of the fraction of ozone decomposed during the flash photolysis of this molecule, following the reaction of O^1D with O_3 ;⁶¹ similarly, the quantum yield of the decay of O_3 may be measured by classical photochemical investigation.⁶² Further, carbon monoxide, monitored by kinetic spectroscopy in the vacuum ultraviolet following the flash photolysis of CO_2 , has been employed by Clerc and Barat to determine the rate of the reaction between $\text{CO}(X^1\Sigma)$ and O^1D .^{63,64} The first detailed work on the quenching of O^1D by various gases was carried out by Cvetanović and his coworkers.⁶⁵ The source of O^1D in these experiments was the photolysis of N_2O in a static system, and the reaction of O^1D was monitored both from the N_2 formed from chemical reaction and by isotopic exchange with labeled CO_2 . The use of the isotopic exchange reaction between C^{18}O_2 and $^{18}\text{O}(2^1D_2)$ produced from the straight photolysis of NO_2 has also given rise to relative rate data for the reaction of this excited oxygen atom with various gases.⁶⁶ The isotopic exchange between $^{16}\text{O}(2^1D_2)$ and C^{18}O has also been explored.⁶⁷ Insertion of $\text{O}(2^1D_2)$ from the photolysis of N_2O into the $-\text{CH}-$ bond in hydrocarbons has also been used,⁶⁸ principally in propane.⁶⁸ This insertion method has further

been employed at low temperatures in liquid argon by DeMore and Raper.⁶⁹ Relative rate data for reactions of $\text{O}(2^1D_2)$ have been obtained from a number of low-temperature photochemical studies. These include the determination of the final yield of O_3 when this molecule is photolyzed in liquid argon in the presence of CO_2 .⁷⁰ The yield of CO_2 when ozone is photolyzed in liquid CO at 77°K permits the study of $\text{O}(2^1D_2)$ via the effect on the extend of the recombination reaction between $\text{O}(2^1D_2)$ and CO .⁷¹ Reaction of $\text{O}(2^1D_2)$ in a nitrogen matrix has also been studied.⁷²

By contrast with $\text{O}(2^1D_2)$, all the investigations of reactions of $\text{O}(2^1S_0)$ to date have employed the direct observation of the transition $\text{O}(2^1S_0) \rightarrow \text{O}(2^1D_2)$ at 555.7 nm which is facilitated by the larger Einstein spontaneous emission transition probability (Table VI). These have included ground based studies of the emission in the aurora and meteoric wakes.^{31,73-76} The $^1S-^1D$ emission from a pumped discharge containing O_2 has been investigated by Kvite and Vegard,⁶² and, more recently, this transition has been employed to monitor the excited atoms in flow discharge system.^{82,77-79} In static systems, the kinetics of $\text{O}(2^1S_0)$ have been followed by the steady-state emission accompanying the continuous photolysis of N_2O at low wavelength (147 nm),⁸⁰ and by time-resolved emission following the flash photolysis of CO_2 and of N_2O at low wavelengths.^{81,100} The rate data for

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Table VII
Rate Data for the Collisional Decay of O(2¹D₂)

Quenching species	10 ¹¹ k (cm ³ molecule ⁻¹ sec ⁻¹)	No. of collisions Z = Z _{coll} /k	Ref	Notes	Quenching species	10 ¹¹ k (cm ³ molecule ⁻¹ sec ⁻¹)	No. of collisions Z = Z _{coll} /k	Ref	Notes	
N ₂	2.2 ± 1	12	61		CO ₂	0.3 ± 0.1	88	53, 84		
	5	5	31			23	1	60		
	5	5	60, 83			0.02	1.3 × 10 ³	90	k	
	9 ± 4	3	53, 84			15.5	2	62		
	5-10	3-5	85			O ₃	33 ± 2	1	61	l
	3	9	13, 86			CH ₄	22	1	60	m
O ₂	12	2	54	a-d		0.88	35	61, 89	n	
	(~3 × 10 ⁻⁴)	(~8 × 10 ⁴)	87		C ₂ H ₆	1.5	21	61, 89	n	
	(~4 × 10 ⁻⁴)	(~6 × 10 ⁴)	31		C ₂ H ₄	2.0	15	61, 89	n	
	4	6	60, 83	e	C ₃ H ₈	40-108	1	60, 65, 66	o	
	6 ± 3	4	53, 84			1.2	30	61, 89	n	
	3	8	86, 88		C ₂ F ₄	1.2	23	61, 89	n	
NO	15	2	60, 83		He	2.3-6 × 10 ⁻¹	5-13 × 10 ¹	61, 66, 68, 91	p	
	9.5	3	62	j		0.67	47	53, 86	q	
N ₂ O	18	1	60, 83	g	Ar	1.3	18	5		
NO ₂	37.2	1	31, 66	h		0.092-0.23	96-240	61, 66, 68, 91	p	
H ₂	19	3	60, 83	i		2.3	10	53, 62	r	
	0.77	64	61, 89	n	Xe	6.4-16	1.6-4.0	61, 66, 68, 91	p	
CO	<5	>15	53, 84			9.5	3	53, 62	r	
	3	9	64		H ₂ O	3	10		t	
	1	26	63	j						
	5	5	60							

^a Deactivation is concluded to be the main process;⁹² <10⁻⁴ of the O₃ decomposed was converted to oxides of nitrogen. ^b The photolysis of O₂ + N₂ in the gas phase (λ 147 and 129.5 nm) was found to give rise to small yields of N₂O.⁹³ ^c Quantum yields for the photolysis of O₃ in liquid N₂:⁹⁴ φ_{N₂O} = 0.0035 at 334 nm, φ_{N₂O} = 0.016 at 248 nm. ^d In the photolysis of O₃ in solid N₂,⁷² up to 27% of the O atoms produced was observed finally as N₂O. The relaxation of O(2¹D₂) → O(2³P_J) was found to be ~75 times faster than the recombination with N₂ to yield N₂O. ^e The removal of O(2¹D₂) by O₂ is found to give rise predominantly to electronically excited O₂. In rate measurements for the reactions of O(2¹D₂) with O₂, O(2¹D₂) + O₂(X³Σ_g⁻) → O(2³P_J) + O₂(b¹Σ_g⁺) (a) and O(2¹D₂) + O₂(X³Σ_g⁻) → O(2³P_J) + O₂(a¹Δ_g) (b), that for process a has been determined by a number of investigators. k_a (cm³ molecule⁻¹ sec⁻¹) has been found to be (ref in parentheses) 1 × 10⁻¹¹ (95), 7 × 10⁻¹¹ (55, 60, 83), 6 × 10⁻¹¹ (53, 84), 6.7 × 10⁻¹⁴ (54), collision number (61, 96). According to Izod and Wayne,⁵⁴ k_b < 10⁻¹² cm³ molecule⁻¹ sec⁻¹. ^f The relative rate data from ref 62 has been converted into absolute rate constants by the authors using the absolute value for k(N₂) following ref 53. ^g Assuming O(2¹D₂) is removed totally by chemical reaction with N₂O, the data of ref 60 and 83 yield: O(2¹D₂) + N₂O → 2NO, k ~ 9 × 10⁻¹¹ cm³ molecule⁻¹ sec⁻¹; O(2¹D₂) + N₂O → N₂ + O₂, k ~ 9 × 10⁻¹¹ cm³ molecule⁻¹ sec⁻¹. The reactions of O + N₂O in the vacuum ultraviolet photolysis of N₂O (λ 147 and 184.8 nm) are considered by Zelikoff and Aschenbrand.⁸² ^h Total reaction is assumed. The value is based on the absolute value for k(O¹D + CO₂), ref 60. ⁱ The production of OH from reaction has been observed by kinetic spectroscopy.^{97, 98} ^j Reaction has been found to take place between O¹D and CO to yield CO₂.⁸⁴ A

similar mechanism to that in ref 64 is concluded from the study of the exchange of atoms in the ¹D state with C¹⁸O,⁹⁷ and for the reaction of O¹D with CO at 77°K.⁷¹ ^k While deactivation to O(2³P_J) is generally considered to be the major process, CO₂ has been observed by infrared spectroscopy at low temperatures.⁷⁰ The formation of CO₂ is generally used to account for the loss in an oxygen balance in such systems. ^l McGrath and McGarvey⁹⁹ favor O₂(A³Σ_u⁺), following its production via the reaction of O¹D with O₃, as the molecular chain carrier in the photochemical decomposition of ozone: firstly on account of the low probability of energy transfer of a large number of vibrational quanta on a single collision with O₃, secondly because of the more favorable energetics leading to this species compared with O₂(B³Σ_u⁻), and thirdly on account of the optical metastability of the O₂(A³Σ_u⁺) state. ^m DeMore and Raper⁶⁹ report that at low temperatures, 30% of the O(2¹D₂) atoms are physically deactivated, and 70% react chemically yielding a range of products. ⁿ The relative rate data of DeMore,⁸⁹ taking that for O₃ = 1.0, are converted into absolute units using k(O¹D + O₃) following Snelling and Bair.⁶¹ ^o The data of ref 65 and 66 are combined with the absolute value for k(O¹D + N₂) of ref 60. ^p The relative data from ref 66 and 68 are converted into absolute units using k(O¹D + N₂) following ref 61 and 91. ^q The relative data of ref 86 is combined with the absolute value of k(O¹D + N₂) of ref 53. ^r The relative data of ref 62 is combined with the absolute value of k(O¹D + N₂) of ref 53. ^s Collision numbers have been calculated assuming that O(2¹D₂) may be characterized by the same value of the Lennard-Jones σ for the nearest inert gas, namely neon. ^t Recent data by D. Biedenkapp, L. G. Hartshorn, and E. J. Bair, *Chem. Phys. Lett.*, 5, 379 (1970).

O(2¹D₂) and O(2¹S₀) are presented and summarized in Tables VII and VIII.

A. OXYGEN ATOMS

1. O + Noble Gases

O(2¹D₂) is quenched very efficiently by the heavier noble gases while O(2¹S₀) is seen to be highly metastable to collisions with all these gases. The quenching of O(2¹D₂) and O(2¹S₀) by the noble gases has been discussed in detail in a recent

publication by Donovan, Kirsch, and Husain.¹⁰² The discussion may be based on a semiquantitative potential energy diagram, employing Morse potentials, for XeO (Figure 8). These potential curves are derived from existing spectroscopic data^{103, 104} and empirical estimates of the appropriate interato-

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Table VIII
Rate Data for the Collisional Decay of O(2¹S₀)

Quenching species	k (cm ³ molecule ⁻¹ sec ⁻¹)	No. of collisions ^b $Z = Z_{\text{coll}}/k$	Ref ^c	Notes
O ₂	2.1 ± 0.4 × 10 ⁻¹³	1.1 × 10 ³	78	
	1 × 10 ⁻¹³	2.4 × 10 ³	77	
	3.2 × 10 ⁻¹³	7.5 × 10 ²	81	
	5 × 10 ⁻¹³	4.8 × 10 ²	91, 100	
	4 × 10 ⁻¹⁵	6.0 × 10 ⁴	31	
	1.4, 1.7 × 10 ⁻¹⁴	1.4, 1.7 × 10 ⁴	77, 80	a
N ₂	3.7 × 10 ⁻¹³	6.5 × 10 ²	d	
	<10 ⁻¹⁵	>2.7 × 10 ⁵	33	
	<10 ⁻¹⁷	>2.7 × 10 ⁷	77	
	<5 × 10 ⁻¹⁷	>5.2 × 10 ⁶	81	
	<3 × 10 ⁻¹⁵	>9 × 10 ⁴	100	
	<10 ⁻¹⁶	>2.7 × 10 ⁶	91	
CO ₂	<5.9 × 10 ⁻¹⁷	>4.5 × 10 ⁶	77, 80	a
	2.5 × 10 ⁻¹⁴	1.1 × 10 ⁴	77	
	3.18 ± 0.3 × 10 ⁻¹³	8.3 × 10 ²	101	
	4.6 × 10 ⁻¹³	5.8 × 10 ²	81	
CO	3 × 10 ⁻¹³	8.8 × 10 ²	100	
	2.5, 2.6 × 10 ⁻¹⁴	1.0, 1.1 × 10 ⁴	77, 80	a
	9.4 × 10 ⁻¹⁴	2.8 × 10 ³	81	
O	6.1 × 10 ⁻¹⁵	4.3 × 10 ⁴	77, 80	a
	1.8 × 10 ⁻¹³	1.2 × 10 ³	77	
N ₂ O	<4 × 10 ⁻¹³	>5.6 × 10 ³	31	
	1.5 × 10 ⁻¹¹	17	81	
	1.6 × 10 ⁻¹¹	16	91, 100	
H ₂ O	5.9 × 10 ⁻¹³	4.4 × 10 ²	77	
	~4 × 10 ⁻¹⁰	~1	81	
H ₂	1.1 × 10 ⁻¹⁵	4.5 × 10 ⁵	81	
	1 × 10 ⁻¹⁵	4.9 × 10 ⁵	91, 100	
	3.0 × 10 ⁻¹⁵	1.6 × 10 ⁵	77	
	2.5, 3.4 × 10 ⁻¹⁵	1.4, 2.0 × 10 ⁵	77, 80	a
NO	4 × 10 ⁻¹⁰	1	100	
	5.5 × 10 ⁻¹⁰	1	91	
	3.5 × 10 ⁻¹¹	7	77, 80	a
CH ₄	3.5 × 10 ⁻¹⁶	8.9 × 10 ⁵	77, 80	a
C ₂ H ₄	~8.9 × 10 ⁻¹¹	~3	77, 80	a
C ₂ H ₂	~5.9 × 10 ⁻¹¹	~5	77, 80	a
C ₂ N ₂	1.2 × 10 ⁻¹¹	24	77, 80	a
He	<5.9 × 10 ⁻¹⁷	>5.4 × 10 ⁶	77, 80	a
	<3 × 10 ⁻¹⁵	>1.1 × 10 ⁵	100	
Ar	<3 × 10 ⁻¹⁵	>8 × 10 ⁴	100	
	<10 ⁻¹⁷	>2 × 10 ⁷	77	
	<5.9 × 10 ⁻¹⁷	>3.9 × 10 ⁶	77, 80	a
Ne	<10 ⁻¹⁷	>2 × 10 ⁷	77	

^a For O₂, the data have been converted here into absolute units using $k(\text{O}^1\text{S} + \text{N}_2\text{O})$ of ref 77 by the same authors. (The data of ref 77 have been questioned by Zipf¹⁰¹ and the rates are now considered to be too low.) ^b Collision numbers have been calculated assuming that O(2¹S₀) may be characterized by the same value of the Lennard-Jones σ as that for the nearest inert gas, namely, neon. ^c Since the submission of the manuscript, Welge, *et al.* (S. V. Filseth, F. Stuhl, and K. H. Welge, *J. Chem. Phys.*, **52**, 239 (1970)), have revised data given in ref 81 and reported new data for other molecules (k (cm³ molecule⁻¹ sec⁻¹): CO₂, 3.6 × 10⁻¹³; CO, 4.9 × 10⁻¹⁵; SF₆, 4.9 × 10⁻¹⁴; O₂, 3.6 × 10⁻¹³; H₂O, 7 × 10⁻¹¹; NH₃, 5 × 10⁻¹⁰; CH₄, 4.7 × 10⁻¹⁴; C₂H₆, 1.0 × 10⁻¹²; C₂H₄, 9.6 × 10⁻¹⁰; N₂O, 1.1 × 10⁻¹¹; NO, 8.0 × 10⁻¹¹; NO₂, 5.0 × 10⁻¹⁰; H₂, 2.8 × 10⁻¹⁶; N₂, <2 × 10⁻¹⁶; He, 2 × 10⁻¹⁶; Ne, Ar, 3.9 × 10⁻¹⁶; Kr, 5.0 × 10⁻¹⁶; Xe, 6.7 × 10⁻¹⁶. ^d S. V. Filseth and K. H. Welge, *ibid.*, **51**, 839 (1969).

mic distances.¹⁰² The ³Σ⁻ state was assumed to be characterized by the same Morse parameters as the ¹Σ⁺ state correlating with O(2¹S₀). Further, the states correlating with O(2¹D₂) have been ordered on the basis of Hund's rule. For the justifi-

cation of the parameters employed, the reader is referred to ref 102. Approximate as the diagram is, it is useful for discussing the collision between ¹D and ¹S states of groups IV and VI with the noble gases.

The transfer of the large amounts of electronic energy from O(2¹D₂) and O(2¹S₀) to relative translational energy on collision with a noble gas will only occur if the potential curves describing the initial and final states "cross." For a nonadiabatic transition to take place, this requires a mixing of these states which must have some component of the same symmetry. These curves which may cross for Hund's coupling cases (a) and (b), may not do so for case (c). The case (c) components are written in parentheses on Figure 8. Thus, for example, we may consider mixing of the O⁺ (case (c)) components of the ¹Σ⁺ state correlating with O(2¹D₂) and the ³Σ⁻ state correlating with O(2³P_J), with a resulting "avoided crossing" shown in Figure 9. Thus the heaviest noble gas atom xenon, which will induce the strongest tendency toward case (c) coupling, should facilitate this avoided crossing. The quenching of O(2¹D₂) by the noble gases is in the order Xe > Ar > He^{104a} (Table VII), as expected. The probability of a transition from one curve to another must, however, be optimized rather than maximized for efficient electronic energy transfer. This probability will depend on the energy of mixing between the two states, the absolute difference in the slopes of the curves in the region of crossing, and the rate of change of internuclear separation at the point of crossing.¹⁰⁵⁻¹⁰⁷ If P = probability that the system starting at A will continue through to C, then the probability that a system starting at A will pass through to D (Figure 9) is given by $2P(1 - P)$. Thus the most favorable condition for quenching of O(2¹D₂) to O(2³P_J) occurs when $P = 1/2$. In addition to the example discussed above, it can be seen that four further possibilities exist for nonadiabatic transitions leading to relaxation of O(2¹D₂). Similar considerations apply to the crossing of the ³Σ⁻ and ³I curves correlating with O(2³P_J) and the ¹Σ⁺ state correlating with O(2¹S₀). However, crossing will only occur high on the repulsive limb and thus the quenching of O(2¹S₀) by xenon and the noble gases in general should be inefficient, as found (Table VIII).

2. O + N₂

Quenching of O(2¹D₂) by N₂ is efficient whereas O(2¹S₀) requires *ca.* 10⁵ collisions, thus showing a parallel pattern of behavior to that observed for the heavier noble gases. Metathetical atomic abstraction by O(2¹D₂) with molecular nitrogen to yield NO(X²I) + N(2⁴S_{3/2}) is an endothermic process, and the adiabatic correlation diagram (Figure 5) indicates that relaxation to O(2³P_J) is the most likely process. This involves a nonadiabatic transition from a singlet (¹A') to a triplet surface and is the reverse of the process involved in the spin-forbidden thermal decomposition of nitrous oxide.¹⁰⁸



(104a) G. Paraskevopoulos and R. J. Cvetanović (*J. Amer. Chem. Soc.*, **91**, 7572, (1969)) have recently shown that He is very inefficient.

(105) L. Landau, *Phys. Z. Sowjetunion*, **2**, 46 (1932).

(106) C. Zener, *Proc. Roy. Soc., Ser. A*, **137**, 696 (1932).

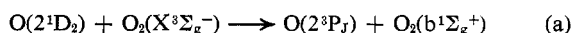
(107) C. Zener, *ibid.*, **140**, 660 (1933).

(108) H. S. Johnston, *J. Chem. Phys.*, **19**, 663 (1950).

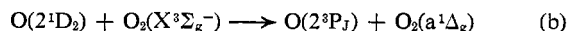
This value for the probability of a nonadiabatic transition for $O(2^1D_2) + N_2$ (Table VII) agrees with a value expectation from a consideration of the transmission coefficient for the unimolecular thermal decomposition of N_2O ($K = 0.018$).⁹ Some degree of stabilization of the highly vibrationally excited singlet N_2O molecule by a third body has been observed in the form of a small yield of this molecule in the gas phase⁹³ and higher yields in the liquid⁹⁴ and solid phases.⁷² On the other hand, while atomic abstraction by $O(2^1S_0)$ with N_2 to yield ground-state products is an exothermic process (Figure 5), there is no available potential surface and physical relaxation may be expected. Reaction would involve a singlet \rightarrow triplet or, more probably, a singlet \rightarrow quintet transition; relaxation of $O(2^1S_0) \rightarrow O(2^1D_2)$ would only entail a process of the type $^1A' \rightarrow ^1A''$, which would be of higher probability. The low probability observed (Table VII) indicates that such crossings can only occur at high energies. For $O(2^1S_0)$, there is only one surface from which nonadiabatic transitions can occur, but for $O(2^1D_2)$ there are five surfaces ($3^1A' + 2^1A''$) facilitating relaxation.

3. $O + O_2$

The quenching of electronically excited oxygen atoms by molecular oxygen clearly involves physical relaxation resulting from nonadiabatic processes. $O(2^1D_2)$ is deactivated more rapidly by O_2 by a factor of approximately 10^2 than $O(2^1S_0)$. Since the system $O(2^1D_2) + O_2(X^3\Sigma_g^-)$ lies close in energy to $O(2^3P_j) + O_2(b^1\Sigma_g^+)$, the observed efficient deactivation of the atom may be expected as the close proximity of the potential energy surfaces should enhance the probability of a nonadiabatic transition either of the type $A' \rightarrow A''$ or $A'' \rightarrow A'$ with no change of spin. Indeed, measurements of the rate constant for the process



(Table VII and footnote *e*) indicate that this sensibly accounts for the observed atomic deactivation rate. Izod and Wayne⁵⁴ state that the rate constant for the energy-transfer process



could be as high as $k_{(b)} = 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (Table VII, footnote *e*). However, this limit is principally controlled by the low transition probability of the infrared atmospheric bands [$O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)$].^{54,56,58} The appropriate correlation diagram indicates that process a should be the dominant one.^{108a} Thus $O_2(b^1\Sigma_g^+)$ was observed in emission following the photolysis of O_2 and has been ascribed to reaction a⁵⁴ while no emission from $O_2(a^1\Delta_g)$ could be detected in this system.⁵⁴ Although emission from $O_2(1^1\Delta_g)$ was detected in the photolysis of O_3 ⁵⁹ and ascribed to reaction b, the correlation diagram leads us to conclude that this state is produced by some other process.^{108b} For $O(2^1S_0) + O_2$, the $3^1A''$ surface arising from these states is considerably removed from the nearest lower triplet surface, which would appear to be the cause of the low probability of a nonadiabatic transition.

(108a) NOTE ADDED IN PROOF. The most recent data now confirm this (ref 84; M. Gauthier and D. R. Shelling, *Chem. Phys. Lett.*, **5**, 93 (1970); I. D. Clark, *ibid.*, **5**, 317 (1970)).

(108b) This has recently been shown to arise from the primary photochemical process (M. Gauthier and D. R. Shelling, *ibid.*, **5**, 93 (1970)).

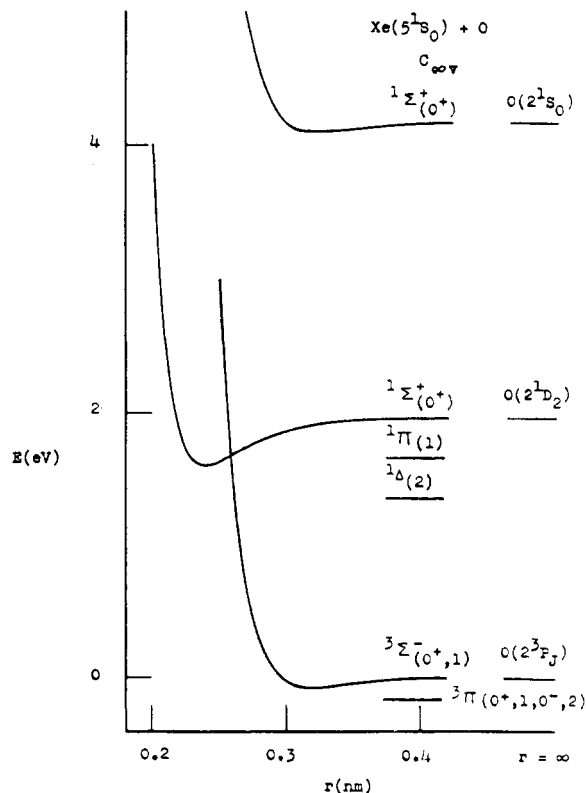


Figure 8. Part of the semiquantitative potential energy diagram (Morse potentials) for some low-lying states of XeO (positioning of $^3\pi$, $^1\Delta$, and $^1\pi$ states arbitrary).

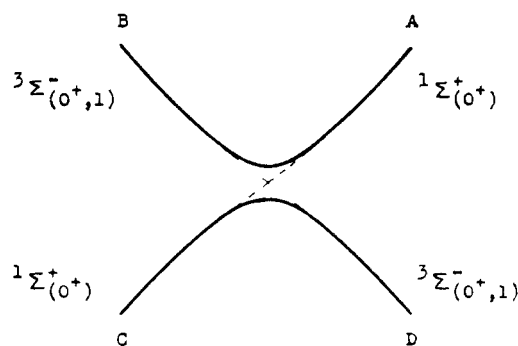


Figure 9. Adiabatic transitions in the collisional deactivation of $O(2^1D_2)$ by $Xe(5^1S_0)$.

4. $O + CO$

By monitoring carbon monoxide in the vacuum ultraviolet following the flash photolysis of CO_2 , Clerc and Barat⁶⁴ report a value for the recombination of $O(2^1D_2) + CO$ which is close to other values reported as quenching of $O(2^1D_2)$ (Table VII). This apparently highly efficient recombination would certainly require a third body; however, this mechanism has been rejected by Clerc and Barat.⁶⁴ Young, *et al.*,⁶⁰ also suggest reaction between $O(2^1D_2)$ and CO. Noxon's⁶³ brief communication does not differentiate between reaction and relaxation.^{108c} Physical deactivation would require a singlet-triplet transition analogous to that dis-

(108c) Recent work by Cvetanović and Paraskevopoulos^{104a} has shown that relaxation occurs.

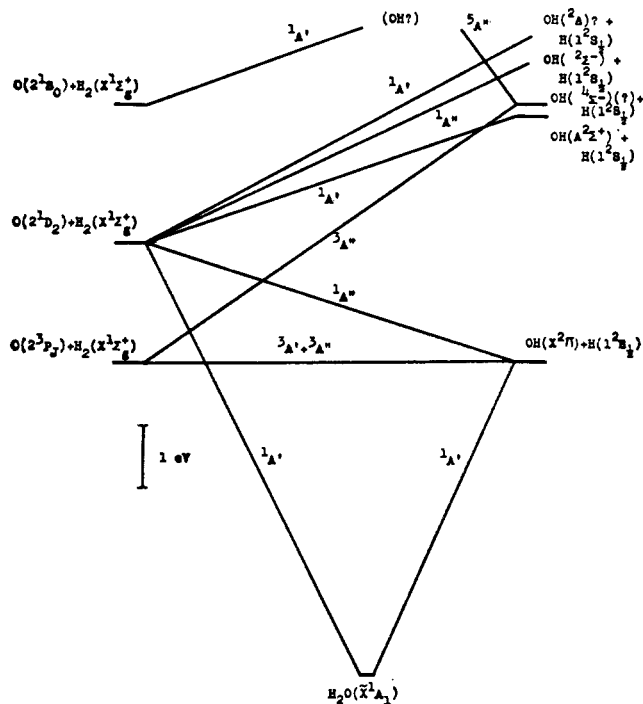


Figure 10. Correlation diagram connecting the states of $O + H_2$ and $OH + H$.^{8,10,20,21,109}

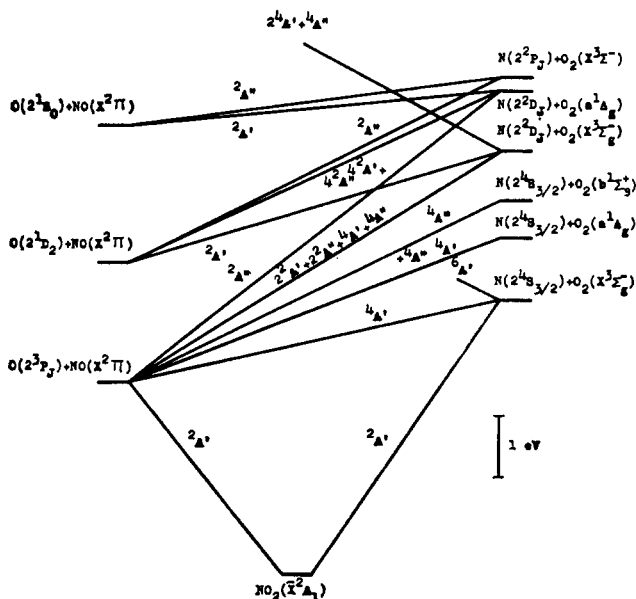


Figure 11. Correlation diagram connecting the states of $O + NO$ and $N + O_2$.^{8,10,20-22}

cussed for $O + N_2$, and the rates for these two processes are seen to be very similar (Table VII). The quenching of $O(2^1S_0)$ by CO is, by contrast, very much slower than for $O(2^1D_2)$ (Table VIII). Reaction to yield $O_2 + C$ is highly endothermic, and the $^1A'$ surface from these species correlates either with the highly lying $CO_2(C)$ state or a higher state of CO_2 . A comparison of the quenching of the two states of the oxygen atom by CO and N_2 shows a marked similarity as indeed would be expected as these molecules and the transition complexes involved are isoelectronic.

5. $O + H_2$

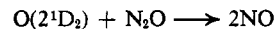
The reaction between $O(2^1D_2)$ and H_2 is very rapid, whereas the removal of $O(2^1S_0)$ by this molecule is slower by a factor of the order of 10^4 (Tables VII and VIII). Reaction of $O(2^1D_2)$ yielding $H(1^2S_{1/2}) + OH(X^2\Pi)$ may proceed by two paths: via a $^1A'$ surface (Figure 10) to give highly vibrational excited ground-state H_2O (A^1A_1) which fragments, or by a $^1A''$ surface, possibly correlating with a higher state of H_2O , which again yields $H + OH$. The construction of Figure 10 requires comment: three states of OH correlating with low-lying states of H and O atoms, $^2\Sigma^+$, $^2\Delta$, and $^2\Pi$, have not been observed spectroscopically. Provided two of these states lie 4.15 eV above the $^2\Pi$ ground state, the reaction of $O(2^1S_0)$ with H_2 will be endothermic. The positions of the quartet states have been calculated,¹⁰⁹ and their form has been shown to be repulsive, and thus should not be important in the processes considered here. Thus only relaxation by means of a nonadiabatic transition, yielding $O(2^1D_2)$ or possibly an excited state of OH , will take place.

6. $O + NO$

Both $O(2^1D_2)$ and $O(2^1S_0)$ are removed rapidly on collision with NO (Tables VII and VIII). Relaxation by means of nonadiabatic transitions of the $A'-A''$ type will be facilitated by the relatively large number of doublet surfaces correlating with the 3P , 1D , and 1S states of the oxygen atom^{109a} (Figure 11). Reaction yielding $N + O_2$ resulting from an adiabatic path will be endothermic. The primary products following the removal of $O(2^1D_2)$ and $O(2^1S_0)$ by NO have not been reported in any detail.

7. $O + N_2O$

$O(2^1D_2)$ is removed on every collision with N_2O (Table VII); $O(2^1S_0)$ requires $16-4.4 \times 10^2$ collisions (Table VIII). Assuming that $O(2^1D_2)$ is removed entirely by chemical reaction with N_2O ,⁸² the data of Young, *et al.*,^{60,83} yield the rate constants for the processes



$$k \sim 9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$



$$k \sim 9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

There are four potential surfaces for adiabatic pathways leading both to $N_2 + O_2$ (Figure 12) and to $2NO$ (Figure 13). The correlation diagrams used involving a tetratomic intermediate must assume the maintenance of C_s symmetry in the collision complex. For a symmetry reduced from C_s to C_1 , only spin conservation and energy considerations may be employed. For $O(2^1D_2)$, the adiabatic paths yielding $N_2 + O_2$ all give rise to electronically excited oxygen molecules, either $O_2(a^1\Delta_g)$ or $O_2(b^1\Sigma_g^+)$. For $O(2^1S_0)$, there is only one adiabatic path leading to $N_2 + O_2$.

8. $O + O_3$

$O(2^1D_2)$ undergoes reaction with O_3 at every collision (Table VII); the kinetics of $O(2^1S_0)$ in the presence of this molecule

(109) H. H. Michels and F. E. Harris, *Chem. Phys. Lett.*, **3**, 441 (1969).
 (109a) L. J. Kirsch (private communication) has suggested that ionic surfaces correlating with NO^+O^- may account for these efficient processes.

have not as yet been reported. McGrath and McGarvey⁹⁹ have discussed possible states of O₂ that could be produced following the reaction of O¹D with O₃, and have concluded that O₂(A³Σ_u⁺) is probably the chain carrier in the low-wavelength photolysis of ozone in view of its optical metastability (see footnote *l*). However, the correlation diagram constructed assuming the collision complex has the symmetry C_s indicates that the most highly excited state produced by this reaction will be O₂(a¹Δ_g). Reaction to yield O₂(A³Σ_u⁺) would require a nonadiabatic transition of the type ³A'' → ¹A'.

9. O + H₂O

Quantitative kinetic data for the decay of O(2¹D₂) on collision with H₂O have not been reported;^{109b} O(2¹S₀) is removed by H₂O on every collision (Table VIII). OH(X²Π, v'' = 2) is observed by kinetic spectroscopy when O¹D reacts with H₂O,^{97,98} and four potential surfaces (2¹A' + 2¹A'') are available for an adiabatic pathway (Figure 14) for this exothermic reaction. There are also three potential surfaces (2¹A' + ¹A'') available for the exothermic reaction of O(2¹D₂) leading to H₂ + O₂, in which the molecular oxygen would be electronically excited, O₂(b¹Σ_g⁺) and O₂(a¹Δ_g). This mode of reaction has not been reported. Finally, experiments in the liquid state have indicated that O¹D can insert into the water molecule to yield H₂O₂.^{110,111} The two adiabatic pathways for the reaction of O(2¹S₀) with H₂O either to yield OH + OH or H₂ + O₂ both involve electronically excited states and would be endothermic processes (Figure 14). The unit efficiency with which O(2¹S₀) is removed by H₂O leads us to conclude that either C_s symmetry is an inadequate description of the collision complex or that insertion to produce an excited state of H₂O₂ is followed by rapid nonadiabatic transitions. A nonadiabatic transition for C_s symmetry of the A'-A'' type would be of too low probability to account for the observations.

10. O + CO₂

Quenching of O(2¹S₀) by CO₂ is relatively inefficient (Table VIII). The efficiency with which CO₂ quenches O(2¹D₂) appears to be a matter of some controversy as indeed does the role played by the species CO₃ and CO₃*.¹¹² Incipient bond formation in this system was first suggested by Cvetanović.⁶⁵ An extended Hückel form of molecular orbital theory has been used to determine the molecular energy and shape of CO₃,¹¹³ and, in principle, the appropriate diagram required for a discussion of relaxation could be constructed. However, in practice, it would appear that rather more accurate data will be required before such a diagram can be used with confidence. Relaxation by CO₂ should be analogous to relaxation by CO if the singlet surface correlating with O(2¹D₂) + CO₂(X¹Σ_g⁺) is crossed by the triplet surface correlating with O(2³P₂) + CO₂(X¹Σ_g⁺). If favorable crossings occur, the rate of relaxation should be somewhat greater than that for CO, as the collision complex CO₃ should

(109b) Bair and Snelling⁶¹ (see footnote *e*, Table VII) have now reported data for this reaction.

(110) H. Taube, *Trans. Faraday Soc.*, **53**, 656 (1957).

(111) F. S. Dainton and P. Fowles, *Proc. Roy. Soc., Ser. A*, **287**, 295 (1965).

(112) G. Black, T. G. Slanger, and R. A. Young, *Can. J. Chem.*, **47**, 1873 (1969).

(113) B. G. Gimark and T. S. Chon, *J. Chem. Phys.*, **49**, 4043 (1968).

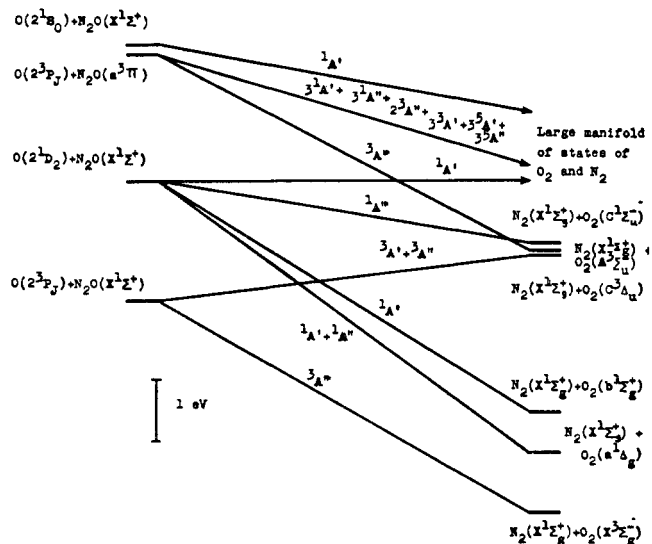


Figure 12. Correlation diagram connecting the states of O + N₂O and N₂ + O₂.

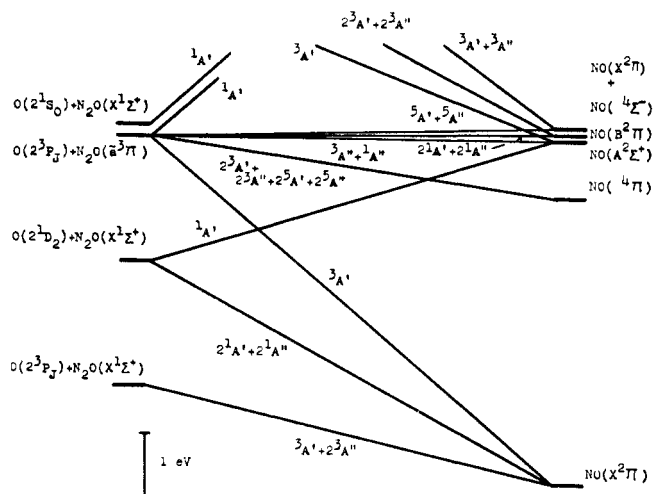


Figure 13. Correlation diagram connecting the states of O + N₂O and NO + NO.^{8,10,20-22}

persist longer before redissociation. On the basis of these considerations we feel that the higher values given in ref 60 and 62 are more likely to be correct.

11. O + SF₆

Quenching of O(2¹D₂) by SF₆ has been shown to be inefficient⁶⁶ as expected in the absence of any strong chemical interaction, and where the potential energy surfaces may be expected to run parallel.

B. SULFUR ATOMS

Although the probability for spontaneous emission from S(3¹D₂) and S(3¹S₀) is greater than that for the analogous states of the oxygen atom (Table VI), such radiation has not, in fact, been employed to monitor these excited sulfur atoms. However, the ¹S₀ state has been observed directly following the vacuum ultraviolet photolysis of OCS, by means of the first resonance transition at 178.2 nm (4s ¹P₁⁰ ←

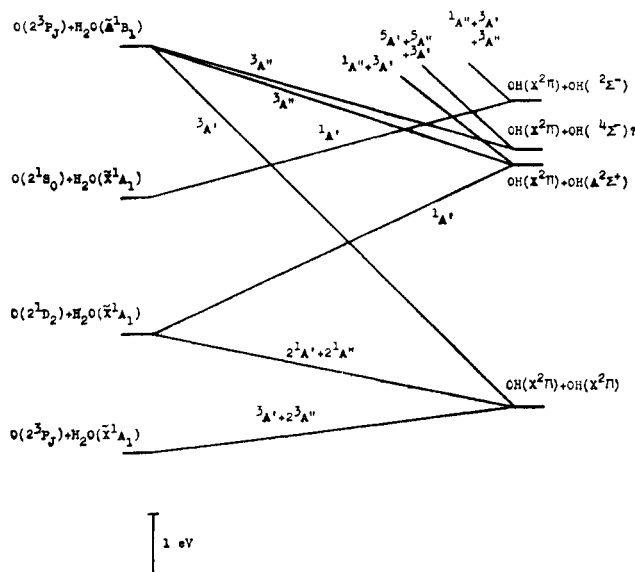
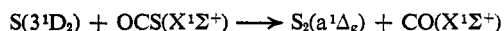


Figure 14. Correlation diagram connecting the states of $O + H_2O$ and $OH + OH$.^{8,10,20-22}

$3p^4 \ ^1S_0$) and the kinetics of its decay in a number of gases monitored¹¹⁴ (Table IX). Despite considerable effort, the 1D_2 state has not yet been observed directly, one reason for this being its extremely reactive nature and the consequent low concentrations that may be achieved under normal conditions. The rate of formation of $S_2(a^1\Delta_g)$ following the reaction



has been used to establish a lower limit for this rate constant as $k \geq 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.¹¹⁵ By observing the reduction in the yield of $S_2(a^1\Delta_g)$ when species removing $S(3^1D_2)$ are added to this system, a number of important relaxation and chemical processes have been investigated quantitatively,¹⁰⁹ and the data are included in Table X. For reactions of $S(3^1D_2)$ involving larger molecules, a considerable amount of relative rate data has been derived using classical techniques.¹¹⁶⁻¹¹⁸ As the present vehicle of discussion is unsuitable for a consideration of reactions involving large molecules, we have only included the simplest members of each series in Table X, and the reader is referred to existing reviews which consider the data in a more appropriate manner.^{116,117} The source of $S(3^1D_2)$ and $S(3^1S_0)$ in all these studies has been the ultraviolet photolysis of OCS.

Little is known concerning the differences in chemical and physical behavior of the spin-orbit multiplets of $S(3^3P_J)$; however, the observation of a non-Boltzmann distribution in these states¹¹⁴ on the time scale of kinetic spectroscopic measurements implies that relaxation requires either 10^4 collisions by Ar, or *ca.* five collisions with OCS.

(114) R. J. Donovan, *Trans. Faraday Soc.*, **65**, 1419 (1969).

(115) R. J. Donovan, L. J. Kirsch, and D. Husain, *Nature*, **222**, 1164 (1969).

(116) O. P. Strausz and H. E. Gunning, *Advan. Photochem.*, **4**, 143, (1966); P. Fowles, M. de Sorigo, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 1352 (1967).

(117) O. P. Strausz, "Organosulphur Chemistry," M. J. Janssen, Ed., Interscience, 1967, and references therein.

(118) W. H. Breckenridge, Ph.D. Thesis, Stanford University, 1968; W. H. Breckenridge and H. Taube, submitted for publication.

Table IX

Rate Data for the Collisional Decay of $S(3^1S_0)$

Quenching species	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)	No. of collisions $Z = Z_{\text{coll}}/k$	Ref	Note
OCS	$1.0 \pm 0.2 \times 10^{-11}$	25	114	
H_2	$4.0 \pm 1 \times 10^{-16}$	1.5×10^8	114	
Xe	$<10^{-18}$	$>2.2 \times 10^8$	102	<i>a</i>
Ar	$<5 \times 10^{-16}$	$>4.4 \times 10^4$	102	<i>a</i>
He	$<1.3 \times 10^{-16}$	$>3 \times 10^8$	102	<i>a</i>

^a The decay of $S(3^1S_0)$ is dominated by collision with OCS, and only limits can be given for the noble gases.

Table X

Rate Data for the Collisional Decay of $S(3^1D_2)$

Quenching species	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$) (lower limits ^a unless otherwise stated)	No. of collisions $Z = Z_{\text{coll}}/k$ (upper limit ^a)	Ref	Notes
OCS	6.7×10^{-11} (reaction)	4	115	
	1.3×10^{-11} (quenching)	20	117	<i>b</i>
CO	2.2×10^{-11} (quenching)	20	118	
CO ₂	$\sim 10^{-11}$ (quenching)	~ 20	117	<i>c</i>
	2.6×10^{-11} (quenching)	10	118	
H_2	2.5×10^{-11} (reaction + quenching)	24	102	<i>d</i>
CH ₄	6.7×10^{-11} (reaction)	4	116	<i>e</i>
	1.9×10^{-13} (quenching)	1.7×10^8	116	
C ₂ H ₆	3.3×10^{-11} (reaction)	11	116	<i>f</i>
	1.0×10^{-11} (quenching)	31	116	
C ₂ H ₄	2.5×10^{-10} (reaction)	1	116	<i>g</i>
N ₂ O	4.0×10^{-11} (quenching + reaction)	6	118	<i>h</i>
SF ₆	5×10^{-13} (quenching)	6×10^2	118	
Xe	$1.1-0.7 \times 10^{-11}$ (quenching)	20	102	
	5.4×10^{-13}	40	117	
Ar	$2.7-1.0 \times 10^{-12}$ (quenching)	82	102	
He	$<4.4 \times 10^{-14}$ (quenching)	$>10^4$	102	

^a A lower limit for the reaction between $S(3^1D_2) + OCS$ yielding the state $S_2(a^1\Delta_g)$ has been given by following the rate of formation of this state;¹¹⁵ the high efficiency of this reaction allows useful lower limits to be placed on previously quoted relative rate data which are then presented in the table. ^b An approximate ratio for the rate of quenching to the rate of reaction has been given as *ca.* 0.2.¹¹⁷ ^c Reference 117 states that quenching by CO₂ is approximately as efficient as quenching by OCS. ^d The SH radical has been observed by means of kinetic absorption spectroscopy.¹¹⁶ ^e The main product is the mercaptan; however, some fragmentation and relaxation also occur, the proportions being pressure dependent.¹¹⁶ ^f For ethane and the higher homologs, the mercaptan is the dominant product of reaction. Relative rate data have also been given for C₂H₆, *i*-C₃H₈, cyclo-C₃H₆, and cyclo-C₅H₁₀, the rates being very similar.¹¹⁶ ^g Both addition to the double bond and insertion into C-H bonds is reported; more details are given in ref 117 where data are also given for CF₂CH₂, C₄H₆, C₂H₃F, C₂F₃H, and *cis*-C₄H₈ (all show efficiencies close to the collision number). ^h The product SO₂ is observed in classical experiments.¹¹⁸

1. S + Noble Gases

Relaxation of $S(3^1D_2)$ and $S(3^1S_0)$ by the noble gases shows a parallel pattern of behavior to that observed with the analogous states of the oxygen atom. Thus $S(3^1D_2)$ is relaxed most efficiently by the heavier noble gases requiring only *ca.* 20 collisions with Xe, while $S(3^1S_0)$ is found to be relatively metastable to collisions with all these gases ($>10^8$ collisions).¹⁰² Unfortunately, no spectroscopic data are available

for diatomic, sulfur-noble gas species, and it may only be surmised that the potential energy curves for these molecules are similar to those found for similar species involving oxygen atoms. Indeed, the kinetic evidence suggests that this is the case, and the increased efficiency for Ar and the decrease in efficiency for Xe may be understood in terms of the greater spin-orbit coupling (stronger tendency toward Hund's case (c) coupling) expected for sulfur; thus, the P factor (probability for "crossing") with Ar will be smaller than for oxygen, enhancing the probability of relaxation, while for Xe, P has fallen below the optimum value of 0.5. This optimum value for P appears to be achieved for $O(2^1D_2) + Xe$.¹⁰²

2. $S + SF_6$

No chemical interaction between SF_6 and the three lowest electronic states of sulfur, beyond weak van der Waals interaction, would be expected. Thus the relevant potential surfaces should run parallel and relaxation will be extremely inefficient.

3. $S + H_2$

The chemical behavior of both $S(3^1D_2)$ and $S(3^1S_0)$ is very similar to that observed for the same states of oxygen,^{102,114} this might have been anticipated from the correlation diagram as reaction *via* the lowest surface of symmetry $^1A'$ will be exothermic yielding $SH(X^2\Pi) + H(1^2S_{1/2})$ (Figure 10 may be used to illustrate this as the thermochemistry is sufficiently similar to give the same overall picture). Reaction for $S(3^1S_0)$ would have to proceed on a surface of the same symmetry ($^1A'$) but lying at higher energies and leading to highly excited states of SH. As for $C(2^1S_0)$ and $O(2^1S_0)$, this surface is expected to be well removed from the lower surfaces of symmetry $^1A''$, and nonadiabatic transitions will only be accessible to high-energy collisions, leading to slow removal, in agreement with experiment.

4. $S + CH_4, C_2H_6, \text{ and } C_2H_4$

The initially formed transition state following insertion of $S(3^1D_2)$ into the C-H bond may be considered in a manner similar to that for insertion into the H-H bond, and the same pattern of behavior is expected. This is confirmed by experiment which further shows that attack is indiscriminate of C-H bond order and exhibits no measurable kinetic isotopic effect.¹¹⁶ The increased rates observed for hydrocarbons beyond methane suggests that these surfaces have lower activation energies (~ 0.06 eV less) than those with CH_4 . The present considerations are unsuitable for a discussion of the reactions with C_2H_4 and other unsaturated species, and the reader is referred to existing treatments of such data.^{118,117}

5. $S + CO \text{ and } N_2$

Removal of $S(3^1D_2)$ by CO is found to be efficient;¹¹⁸ no data exist for the isoelectronic species N_2 . Chemical reaction is thermodynamically unfavorable, and physical relaxation may be expected to predominate in the gas phase. The potential surfaces should be similar to those for $O(2^1D_2)$; although the species N_2S has not been isolated it will probably have a transient existence and may even be stable under the

conditions of a low-temperature matrix. The probability of singlet to triplet nonadiabatic transitions should be enhanced relative to oxygen and relaxation should proceed somewhat more rapidly for $S(3^1D_2)$. The one experimental result for $S(3^1D_2) + CO$ is in agreement with these considerations.¹¹⁸ By analogy with $O(2^1S_0)$, it is expected that relaxation of $S(3^1S_0)$ by CO and N_2 will require *ca.* 10^4 collisions.

6. $S + OCS$

Reaction between both $S(3^1D_2)$ and $S(3^1S_0)$ with OCS is efficient,¹¹⁴ the former being faster by a factor of 6. A consideration of the potential surfaces available, assuming the transition state to have the symmetry C_s , shows that $S(3^1D_2)$ will yield $S_2(a^1\Delta_g)$ *via* two surfaces ($^1A' + ^1A''$) and $S_2(b^1\Sigma_g^+)$ by one surface ($^1A'$) (although the latter is expected to have a greater activation energy, and be relatively less important). The surface of symmetry ($^1A'$) correlating with $S(3^1S_0)$ should yield highly excited states of S_2 or CO, which will be inaccessible at thermal energies and nonadiabatic transitions ($^1A' \rightarrow ^1A''$) to the surfaces arising from $S(3^1D_2)$ may be expected.

7. $S + CO_2$

Carbon dioxide is efficient in relaxing $S(3^1D_2)$;^{117,118} however, no data have been given for $S(3^1S_0)$. The potential surfaces should be analogous to those discussed for $O + CO_2$, although the species CO_2S has not been observed. Provided the stability of singlet CO_2S is sufficient to cause singlet and triplet surfaces to cross, efficient relaxation is expected. The experimental results^{117,118} support those suggestions.

8. $S + N_2O$

Breckenridge and Taube¹¹⁸ have shown that $S(3^1D_2)$ reacts with N_2O ; however, details of this reaction are not yet completely understood. Reaction to produce N_2 occurs (*ca.* 10%) and a consideration of the correlation diagram suggests that $SO(a^1\Delta)$ and $SO(b^1\Sigma)$ should be produced. Reaction to form $NS(X^2\Pi)$ is also exothermic and may occur *via* four surfaces ($2^1A' + 2^1A''$); this may account for some of the difficulties encountered in the interpretation of classical experiments which rely on the determination of CO and N_2 yields.¹¹⁸

9. $S + O_2$

No quantitative experimental data involving $S(3^1D_2)$ or $S(3^1S_0)$ with O_2 have been given; however, the correlation diagram (Figure 15) can be used to predict certain features of these reactions which may be useful. Thus $S(3^1D_2)$ should yield $SO(b^1\Sigma^+)$ unless this surface possesses an appreciable activation energy when nonadiabatic transitions to the surface yielding $SO(a^1\Delta)$ may occur ($^3A' \rightarrow ^3A''$ or $^3A'' \rightarrow ^3A'$). The observation of emission from $SO(b^1\Sigma^+)$ ($b^1\Sigma^+ \rightarrow X^3\Sigma^-$)¹¹⁹ when mixtures of COS and O_2 are passed through a microwave discharge suggests that reaction is probably adiabatic. $S(3^1S_0)$ is expected to be fairly rapidly relaxed to yield $S(3^1D_2) + O_2(b^1\Sigma^+)$, following nonadiabatic transitions.

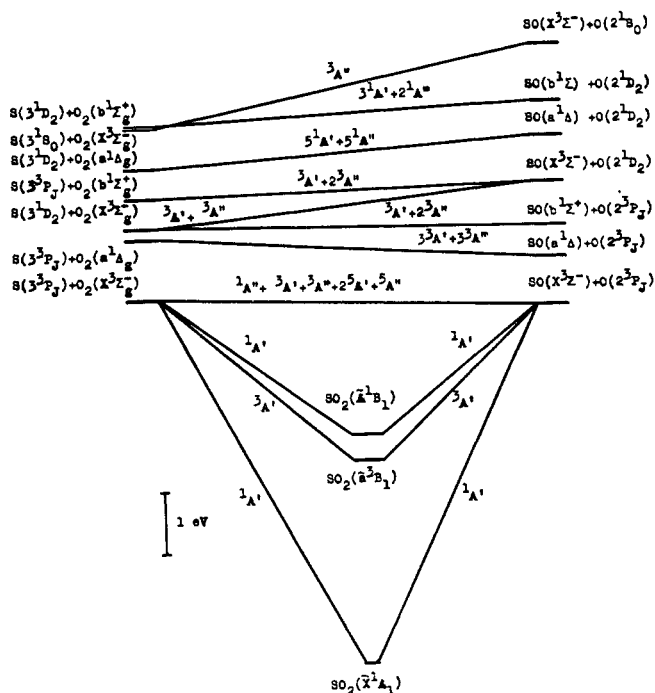
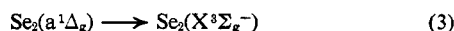
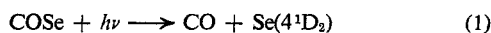


Figure 15. Correlation diagram connecting the states of S + O₂ and SO + O.^{8,10,20,21,109}

Reaction of S(3¹D₂) with a number of other molecules have been reported; these include C₂H₂,^{117,120} C₂N₂,¹²⁰ SiH₄,¹¹⁷ Si(CH₃)₃,¹¹⁷ Si(CH₃)₄,¹¹⁷ and B₂H₆.¹¹⁷ However, no quantitative data have been given.

C. SELENIUM ATOMS

Se(4¹S₀) has been observed directly *via* the first resonance transition at 199.5 nm, following flash photolysis of COSe.¹²¹ Unfortunately, the rapid decay of this state did not allow quantitative kinetic measurements to be made. The failure to observe Se(4¹D₂) under these conditions¹²¹ is compatible with this state being again more reactive than the ¹S₀ state. Indirect evidence that Se(4¹D₂) is produced in the photolysis of COSe has been obtained from two sources. First, time-resolved studies using flash photolysis coupled with mass spectrometric analysis¹²² shows that selenomercaptans are formed in the presence of propane, cyclobutane, ethane, and isobutane. Second, observations using kinetic absorption spectroscopy show that only a weak spectrum of Se(4³P_J)¹²³ is observed, while a strong spectrum of Se₂(X³Σ_g⁻) can be observed at short delays (20–200 μsec).^{121–123} These observations are compatible with the scheme previously proposed for S(3¹D₂) + OCS, namely



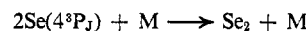
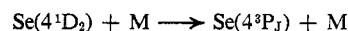
(120) W. D. McGrath, T. Morrow, and D. M. Dempster, *Chem. Commun.*, 516 (1967).

(121) F. C. James, D. C. Dobson, O. P. Strausz, and H. E. Gunning, submitted for publication.

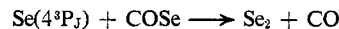
(122) W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **88**, 4277 (1966).

(123) W. J. R. Tyerman and A. B. Callear, *Trans. Faraday Soc.*, **61**, 2395 (1965).

The rapid appearance of Se₂(X³Σ_g⁻) and the failure to observe Se₂(a¹Δ_g) in absorption suggests that reaction 3 is very rapid (the nature of reaction 3 has not been established and both radiative and collisional processes may be involved). In the presence of CO₂, two maxima are observed in the graph of [Se₂(X³Σ_g⁻)] *vs.* time,¹²¹ which suggests the additional reactions



or



The second maximum in [Se₂(X³Σ_g⁻)] occurs at ~250 μsec¹²¹ and is consistent with efficient termolecular formation of Se₂. No quantitative data on Se(4¹D₂) have been given; however, the results do indicate qualitatively that SF₆ and He are inefficient in relaxing this state,⁷³ while CO₂ is very efficient.^{121,122}

The photolysis of COSe in the presence of O₂ leads to the formation of SeO₂; however, the spectrum of SeO was not observed in flash photolysis experiments.¹²³ The correlation diagram indicates that the surface correlating with Se(4¹D₂) + O₂(X³Σ_g⁻) and leading to SeO(b¹Σ_g⁺) + O(2³P_J) involves an endothermic process unless T₀ (SeO(b¹Σ_g⁺)) < 0.48 eV which is unlikely. Thus either nonadiabatic transitions to the surface yielding SeO(X³Σ_g⁻) or Se(4³P_J) occur (the surface yielding SeO(a¹Δ) will also probably be endothermic although the energies of the a and b states are not known with any certainty). Alternatively, three-body recombination into an excited singlet state followed by chemiluminescence may yield SeO₂.

Reaction of Se(4¹D₂) with H₂ to yield HSe(X²Π) may be thermodynamically favorable¹²⁴ (the limits given in ref 76 for D₀(HSe) are 3.2 ± 0.2 eV). However, if reaction proves to be endothermic, efficient three-body recombination to form H₂Se(X¹A₁), together with nonadiabatic transitions to yield Se(4³P_J), will occur. No data have been reported for this reaction.

A non-Boltzmann distribution in the spin-orbit multiplets of Se(4³P_J) has been reported following the flash photolysis of CSe₂.¹²⁵ The decay of Se(4³P₀) was monitored using kinetic absorption spectroscopy. The energy distribution in the quenching molecule was not observed; however, specific quenching processes have been proposed based on the assumption that "resonant" processes are dominant¹²⁶ (Table XI).

The rates of addition of Se(4³P_J) to a series of olefins have been reported, but no distinction was made between the relative rates for the various spin-orbit multiplets.¹²⁷

D. TELLURIUM ATOMS

The isothermal flash photodissociation of H₂Te yields Te(5³P_J) in a non-Boltzmann distribution together with Te(5¹D₂).¹²⁸ The latter was observed *via* the resonance transi-

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Table XI
Spin-Orbit Relaxation of Se(4³P₀)

Quenching species	Proposed quenching process ¹²⁶	Second-order quenching constant (cm ³ molecule ⁻¹ sec ⁻¹)
Ar	Se(4 ³ P ₀) + Ar → Se(4 ³ P ₁) + Ar	2.4 ± 0.3 × 10 ⁻¹⁴
N ₂ O	Se(4 ³ P ₀) + N ₂ O(<i>v</i> ₂ = 0) → Se(4 ³ P ₁) + N ₂ O(<i>v</i> ₂ = 1)	1.2 ± 0.15 × 10 ⁻¹⁰
CO ₂	Se(4 ³ P ₀) + CO ₂ (<i>v</i> ₂ = 0) → Se(4 ³ P ₁) + CO ₂ (<i>v</i> ₂ = 1)	1.4 ± 0.1 × 10 ⁻¹⁰
H ₂	Se(4 ³ P ₀) + H ₂ (<i>J</i>) → Se(4 ³ P ₁) + H ₂ (<i>J'</i>)	3.5 ± 0.7 × 10 ⁻¹⁰
CO	Se(4 ³ P ₀) + CO(<i>v''</i> = 0) → Se(4 ³ P ₂) + CO(<i>v''</i> = 1)	1.1 ± 0.3 × 10 ⁻¹²
N ₂	Se(4 ³ P ₀) + N ₂ (<i>v''</i> = 0) → Se(4 ³ P ₂) + N ₂ (<i>v''</i> = 1)	3.0 ± 0.3 × 10 ⁻¹²
O ₂	Se(4 ³ P ₀) + O ₂ (<i>v''</i> = 0) → Se(4 ³ P ₁) + O ₂ (<i>v''</i> = 0)	1.5 ± 0.3 × 10 ⁻¹²

tion at 277.1 nm (6s ³S₁ ← 5p⁴ ¹D₂). Unfortunately no kinetic data on these excited states have been reported.

VI. Group VII. Fluorine, Chlorine, Bromine, and Iodine

There has been a considerable growth in the direct study of electronically excited halogen atoms in the last few years. These refer to studies on the higher spin-orbit multiplet, *J* = 1/2 of the ground-state np⁵ electronic configuration. The energies of these metastable states are listed in Table XII.^{129, 130} The electronically excited iodine atom, as the most striking example, possesses nearly 1 eV of energy, and this endows I(5²P_{1/2}) with considerable chemical reactivity by comparison with the lower ground-state multiplet, I(5²P_{3/2}). The area of electronically excited halogen atoms has been reviewed recently in detail by the authors.¹³¹ Here we are concerned with presentation of quantitative kinetic data on the chemistry and physical relaxation of these excited atoms, combined with a brief consideration of the numerous, principally direct, methods that have been employed in the determination of rate constants characterizing these processes. While a number of methods have been reported for monitoring these excited atoms, the great majority of the quantitative data describing reaction and relaxation has been determined by the authors using kinetic absorption spectroscopy following flash photolytic production of the ²P_{1/2} atoms in the gas phase. Unfortunately, the symmetry considerations that have been employed in considering atoms of groups IV-VI do not appear to be applicable to these states which differ only in the spin-orbit states for a given electronic configuration. However, we feel that group VII now represents a sufficiently large area of our knowledge concerning quantitative data on metastable atoms and is relevant to many fields including flow discharges, shock tubes, laser studies, energy transfer from atoms in general, and the photochemistry of electronically excited atoms. The experimental context of the reactions of the ²P_{1/2} states of group VII clearly falls within our discussion; the theoretical framework in which these processes need to be considered remains to be developed. The data will be discussed by reference to existing general theories for energy transfer and the reactions of excited atoms as a whole.

Time-resolved absorption spectroscopy in the ultraviolet and vacuum ultraviolet following the flash photolysis of

Table XII

Spin-Orbit Energies of the ²P_{1/2} States of the Halogen Atoms and Mean Radiative Lifetimes for Magnetic Dipole Emission

Halogen atom	$\frac{E(^2P_{1/2}) - E(^2P_{3/2})^{10}}{cm^{-1}}$	A_m (sec ⁻¹) ¹³	τ_0 (sec)	A_m (sec ⁻¹) (exptl)
F 2p ⁵ ² P _{1/2}	404.0	0.0012	830	
Cl 3p ⁵ ² P _{1/2}	881	0.012	83	
Br 4p ⁵ ² P _{1/2}	3685	0.89	1.1	
I 5p ⁵ ² P _{1/2}	7603.15	7.8	0.13	22 ^{129, 130}

gaseous halides, leading to the production of electronically excited halogen atoms, np⁵ ²P_{1/2}, has been the main method employed by the authors¹³¹ for the study of the kinetics of these excited atoms. The strongly electric dipole-forbidden nature of the emission to the ²P_{3/2} ground state, dominated by the magnitude of the magnetic dipole transition probability (Table XII), coupled with the collisional metastability under a number of experimental conditions, brings the overall lifetime of the ²P_{1/2} atoms well within the time resolution of kinetic spectroscopy. A large number of absorption transitions from both the ²P_{1/2} and ²P_{3/2} states of the atoms Cl, Br, and I have been observed. The reader is referred to the review by the authors¹³¹ for those transitions that have been observed by kinetic spectroscopy. The longest wavelength transition that has been observed in absorption in such studies for a ²P_{1/2} halogen atom is the 206.2-nm line of iodine.¹³² The other transitions of I, Br, and Cl have been monitored in the vacuum ultraviolet. Thus a number of kinetic studies have been carried out on the ²P_{1/2} and ²P_{3/2} states of Cl,¹³³ Br,¹³⁴⁻¹³⁶ and I.^{132, 136-145} Braun and his coworkers¹⁴⁶ have developed a pulsed fluorescence tech-

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nique for studying transient atoms in the vacuum ultraviolet following their production by flash photolysis. This method increases the sensitivity of kinetic spectroscopy in this region and has been applied to the atoms of group VII. In general, the studies that have been carried out on the $^2P_{1/2}$ atoms of this group have involved separating the various contributions to the observed overall first-order decay coefficient which then yields quantitative data on spontaneous emission, diffusion, collisional relaxation, and chemical reaction.

The collisional metastability of $I(5^2P_{1/2})$ in the presence of noble gases and the large population of this excited atom that is produced on photolyzing a molecule such as CF_3I in the ultraviolet¹³⁸ offset the low Einstein A factor for spontaneous emission sufficiently to allow time-resolved atomic emission to be observed.^{129,130} The time profile of the emission in the infrared at 1.315μ (Table XII) follows the form $A_{nm}[I(5^2P_{1/2})]_{t=0} \exp(-kt)$, and thus the first-order decay coefficient (k) may be converted into collisional rate data. This method has only been applied to the iodine atom on account of the large concentration of $I(5^2P_{1/2})$ that is generated photochemically from CF_3I .

The flash photolysis of gaseous CF_3I and other iodides in the ultraviolet results in a population inversion between the $^2P_{1/2}$ and $^2P_{3/2}$ states, and with the use of a confocal cavity, can be made to generate stimulated emission $I(5^2P_{1/2}) \rightarrow I(5^2P_{3/2}) + h\nu$ (1.315μ).^{147,148} This inversion can also be demonstrated by kinetic absorption spectroscopy on the $^2P_{1/2}$ and $^2P_{3/2}$ states of the iodine atom in the vacuum ultraviolet.¹³⁸ Some kinetic data have been obtained from the time profiles of this emission, and Pollack¹⁴⁹ has employed a kinetic model to generate the output function. On the whole, these iodine atom laser studies have not been carried out for the purpose of measuring quantitative relaxation data but for studying energy distribution in primary photochemical products. Stimulated emission from $Br(4^2P_{1/2})$ has been observed following the flash photolysis of IBr ,¹⁵⁰ which was in accord with the kinetic spectroscopic observations in the vacuum ultraviolet following the flash photolysis of this molecule.¹³⁶ However, this laser emission has not been employed for the kinetic study of decay rates of the excited bromine atoms.

Spontaneous emission from $I(5^2P_{1/2})$ generated from the photolysis of HI and from the reaction of $H + HI$ in a flow system has been used by Polanyi, *et al.*,^{151,152} to monitor these excited atoms and has obtained quantitative data for the collisional quenching of $I(5^2P_{1/2})$. Spontaneous emission from $Br(4^2P_{1/2})$ in a flow system has also been observed by Polanyi and his coworkers,^{153,154} but this kinetic study has not been reported in a similar detail to that for HI . Emission from $Cl(3^2P_{1/2})$ was not reported under comparable conditions.¹⁵⁵ This would be expected to be extremely weak

on account of the low population of $Cl(3^2P_{1/2})$ ¹³³ and the low coefficient for spontaneous emission (Table XII). Electron spin resonance spectra of the $^2P_{3/2}$ states of F , Cl , Br , and I are established,¹⁵⁶ and more recently, Carrington, *et al.*,¹⁵⁷ have detected F and Cl in a non-Boltzmann distribution in the $^2P_{1/2}$ states in flow discharges. Detailed kinetic studies leading to quenching data were not given, the emphasis being on spectroscopic aspects. These observations are particularly relevant to the study of the collisional deactivation of $F(2^2P_{1/2})$ as the absorption transitions in the electronic spectrum of the fluorine atom lie beneath the low-wavelength cutoff of the transmission of lithium fluoride (the optical material employed in kinetic spectroscopy in the vacuum ultraviolet).

Time-resolved emission from $I_2(B^3\Pi_{0u^+})$ following the flash photolysis of CF_3I in a static system has been studied by Abrahamson, Husain, and Wiesenfeld.¹⁵⁸ This has involved the use of a rapid scan spectrometer. In this system, I_2 is formed in the $B^3\Pi_{0u^+}$ state by the three-body recombination of $M + I(5^2P_{1/2}) + I(5^2P_{3/2})$, as may be readily demonstrated by the wavelength dependence of the banded emission. The time dependence of the $B-X$ emission follows the kinetics of the atomic precursors $I(5^2P_{1/2,3/2})$. Thus the kinetics of the molecular emission gives rise to the overall decay coefficient for $I(5^2P_{1/2})$ which may then be split into the various contributions causing the removal of the excited atom, namely, spontaneous emission, diffusion, and collisional relaxation. The data may then be compared with those obtained by time-resolved atomic absorption¹³⁸ and emission^{129,130} for the excited atom.

Time-resolved mass spectrometry has been used to monitor the rapid formation of I_2 following the flash photolytic dissociation of CH_3I , and this has been attributed by Meyer¹⁵⁹ to I -atom abstraction from CH_3I by $I(5^2P_{1/2})$. A rate constant is reported for this process,¹⁵⁹ but the result is controversial. The experimental difficulties of this technique are discussed by Meyer.¹⁶⁰ The classical photolysis of I_2 in the $B-X$ continuum, giving rise to $I(5^2P_{1/2}) + I(5^2P_{3/2})$, in the presence of propane and other molecules has been reported.¹⁶¹⁻¹⁶³ Callear and Wilson have studied this system in some detail.^{161,162} Hydrogen atom abstraction from the paraffin is much more rapid for $I(5^2P_{1/2})$ than for $I(5^2P_{3/2})$ and competes with collisional quenching. Chemical analysis of the products permits the determination of the relative rates of reaction and relaxation by a number of gases. These results are in general agreement with those obtained by kinetic spectroscopic methods. Molecular emission from flow discharges and shock tubes from halogens and interhalogens in states correlating with ground and excited atoms have been studied

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in some detail. This has been reported for Br₂,^{164, 165} Cl₂,¹⁶⁶⁻¹⁶⁹ and BrCl¹⁷⁰ from flow discharges, and for Br₂^{171, 172} and Cl₂^{173, 174} in shock tubes. No emission from F₂¹⁷⁵ or I₂¹⁷⁶ has been reported from shock-tube studies. While these emission studies relate to states correlating with ²P_{1/2} atoms, the emphasis on such studies has been the relative importance in each case of inverse predissociation and direct recombination of ²P_{1/2} + ²P_{1/2} atoms. Quantitative kinetic data on reactions and relaxation of ²P_{1/2} atoms have not been obtained from these studies.

A. COLLISIONAL REMOVAL OF ELECTRONICALLY EXCITED HALOGEN ATOMS

The authors have previously discussed three cases for spin-orbit relaxation in terms of the potential surfaces,¹⁸¹ and it is useful to state those cases here: first, relaxation between potential surfaces which are essentially parallel in the region accessible to thermal velocities; second, potential surfaces which converge or cross due to a strong coupling between electronic and nuclear motion; and third, potential surfaces which cross due to a coincidental electronic degeneracy at a given point on the multidimensional energy surface. For weak spin-orbit coupling, and in the absence of strong chemical interaction on collision, the potential surfaces representing collision should be essentially parallel as the interaction with the two multiplets should be similar. Transitions must occur by tunneling and may be treated in terms of the "distorted wave approximation" first given by Zener.¹⁷⁷ The rate of tunneling will be determined by the magnitude of the "overlap" of the translational wave functions on the interaction potential, and will be greatest when the surfaces are close, that is, when the energy to be converted to translation is small and when the incoming particle waves are incident on a strongly repulsive interaction potential. Furthermore, tunneling should increase for light particles. A discussion of those factors governing spin-orbit relaxation in terms of the potential surfaces is given by Callear.¹⁷⁸ The coupling between the various degrees of freedom involved will also be important in affecting the rate of spin-orbit relaxation. For collisions between atoms, the coupling arises from an interaction between the small magnetic moment

generated by the rotation of the nuclei and that due to the electronic angular momentum, together with a contribution from the direct coupling between the angular momenta. For collisions with diatomic molecules, coupling may result from the interaction between the inplane motion of the nuclei and the electronic energy of the quasi-triatomic molecule (vibronic coupling). This may be extended to polyatomic molecules. Direct calculation of this coupling is difficult although it has been carried out for some cases where the potential surfaces are known to cross.¹⁷⁹ In cases where there is significant chemical interaction, the near convergence or crossing of potential surfaces induced by nuclear motion is important. A change in the Hund's coupling case for collision between atoms, for example, may occur as the internuclear separation changes or as the rotational energy changes for a given internuclear separation, which may thus lead to significant mixing between states, facilitating relaxation (see discussion of the quenching of electronically excited atoms of group VI, and also group IV, by noble gases). A theory permitting detailed discussion of the relative rates of chemical reaction and physical relaxation, even in cases where both are thermochemically favorable, remains to be developed for spin-orbit states.

B. SPIN-ORBIT RELAXATION ON COLLISION WITH ATOMS

1. Noble Gas Atoms

The data for collisional relaxation of the ²P_{1/2} states of I, Br, and Cl by noble gas atoms are presented in Table XIII. The majority of the data applied to I(⁵2P_{1/2}) for which there have been most investigations. The listed probabilities of transfer to the noble gases are upper limits in every case and result from attributing any small, remaining contribution to the overall decay to this mode of removal. The decay of I(⁵2P_{1/2}) is clearly found to decrease with increasing noble gas pressure and this permits a determination of the diffusion coefficient (*D*₁₂) of the excited atom to the walls of the vessel where efficient deactivation takes place. Thus *D*₁₂'s for I(⁵2P_{1/2}) + noble gas have been determined by kinetic absorption spectroscopy in the vacuum ultraviolet,¹⁸⁷⁻¹⁸⁹ time-resolved atom emission studies in the infrared following flash photolysis,^{129, 130} and also from flow discharge experiments.^{151, 152} The time-resolved atomic emission studies have permitted the experimental determination of the mean radiative lifetime for I(⁵2P_{1/2}) → I(⁵2P_{3/2}) + *hν* (1.315 μ) (Table XII).^{129, 130} Thus collisional removal of I(⁵2P_{1/2}) by noble gases, representing a contribution to the overall decay much smaller than that of diffusion, is very inefficient and indicates a weak interaction on collision. Callear¹⁸⁰ has proposed an empirical linear relationship between log (probability of transfer of electronic energy to translation) and Δ*E* (energy to be converted to translation) for weak interactions. On this basis, the transfer of 1000 cm⁻¹ of electronic energy to translation requires the order of 10⁵ collisions. The contribution of diffusion to the decay of Br(⁴2P_{1/2}) and Cl(³2P_{1/2}) in noble gases has not been observed and characterized, essentially on account of the domination of collisional quenching of the excited atom by the parent molecules present. Unfortunately, detailed studies on the collisional

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Table XIII

Rate Data^a for the Collisional Deactivation of Electronically Excited Iodine Atoms, I(5²P_{1/2})

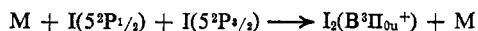
Quenching species	k (cm ³ molecule ⁻¹ sec ⁻¹)	No. of collisions $Z = Z_{\text{coll}}/k$	Ref	Notes
He	$<5 \times 10^{-18}$	$>10^8$	137	
Ar	$<2 \times 10^{-18}$	$>10^8$	129, 130, 138	
	$<2.9 \times 10^{-14}$	$>6.9 \times 10^5$	161, 162	
Xe	$<1.6 \times 10^{-18}$	$>10^8$	139	
I(5 ² P _{1/2})	$<1.6 \times 10^{-14}$	$>10^4$	131, 138	
N ₂	2.1×10^{-16}	1.3×10^6	138	
	1.5×10^{-16}	1.8×10^6	161, 162	<i>b</i>
	1.5×10^{-16}	1.8×10^6	130	
CO	1.2×10^{-15}	2.1×10^6	139	
	1.2×10^{-15}	2.1×10^6	130	
CO ₂	1.3×10^{-16}	1.8×10^6	139	
	1.7×10^{-16}	2.4×10^6	130	
	$<1.7 \times 10^{-16}$	$>2.4 \times 10^6$	161, 162	
SF ₆	3.1×10^{-16}	9.1×10^6	139	<i>c</i>
	2.4×10^{-17}	1.2×10^9	130	
CF ₄	4.5×10^{-16}	4.5×10^6	139	<i>c</i>
	4.6×10^{-16}	4.5×10^6	130	
N ₂ O	1.3×10^{-15}	2.1×10^6	142	
CF ₃ I	3.5×10^{-16}	6.3×10^6	130	<i>c</i>
	$\sim 3.7 \times 10^{-15}$	$\sim 5.9 \times 10^4$	137	<i>d</i>
CH ₃ I	1.7×10^2	97	140, 141	
C ₂ H ₅ I	1.9×10^{-13}	9.7×10^2	141	
	$\sim 3.2 \times 10^{-13}$	$\sim 6 \times 10^2$	132	
<i>n</i> -C ₃ H ₇ I	2.0×10^{-13}	1.1×10^3	141	
<i>i</i> -C ₃ H ₇ I	2.0×10^{-13}	1.1×10^3	141	
<i>n</i> -C ₄ H ₉ I	2.9×10^{-13}	7.2×10^2	141	
<i>t</i> -C ₄ H ₉ I	3.8×10^{-13}	5.9×10^2	141	
HI	1.3×10^{-13}	1.3×10^3	137	
	1.5×10^{-13}	1.1×10^3	151	
DI	1.2×10^{-13}	1.4×10^3	137	
D ₂	1.1×10^{-13}	1.1×10^3	137	
	2.2×10^{-15}	2.2×10^5	130	<i>c</i>
H ₂	8.8×10^{-14}	1.7×10^3	137	
	2.15×10^{-13}	7.0×10^2	152	
	3.13×10^{-14}	4.8×10^3	161, 162	<i>e</i>
CH ₄	5.9×10^{-14}	5.6×10^3	139	
	1.0×10^{-13}	3.3×10^3	130	
CF ₃ H	4.6×10^{-14}	5.0×10^3	139	
C ₂ H ₆	4.23×10^{-14}	7.0×10^3	161, 162	<i>b</i>
C ₃ H ₈	5.7×10^{-14}	5.3×10^3	138	
	5.7×10^{-14}	5.3×10^3	161, 162	<i>f</i>
	1.7×10^{-13}	1.8×10^3	130	
CH ₂ =CHCH ₂ Cl	1.3×10^{-13}	1.8×10^3	142	
CH ₂ =CHCH ₂ Br	2.4×10^{-13}	8.3×10^2	142	
CH ₂ =CHCH ₂ I	4.2×10^{-13}	4.5×10^2	142	
CH ₂ =CH ₂	7.0×10^{-14}	3.5×10^3	143	
CF ₂ =CFH	5.3×10^{-14}	3.7×10^3	143	
CF ₂ =CF ₂	3.7×10^{-15}	5.3×10^4	143	
CH ₃ CH=CH ₂	1.6×10^{-13}	1.6×10^3	143	
1-Butene	1.6×10^{-13}	2.0×10^3	143	
<i>trans</i> -Butene-2	2.1×10^{-13}	1.4×10^3	143	
<i>cis</i> -Butene-2	2.2×10^{-13}	1.5×10^3	143	
Isobutylene	3.0×10^{-13}	1.0×10^3	143	
Tetramethyl-ethylene	6.3×10^{-13}	4.8×10^2	143	
D ₂ O	6.2×10^{-14}	3.6×10^3	139	
H ₂ O	9.4×10^{-13}	2.3×10^2	139	
ICN	6.0×10^{-14}	4.2×10^3	142	
O ₂	9.3×10^{-12}	20	139	
NO	1.1×10^{-11}	19	139	

^a Rate data are presented for $\sim 300^\circ\text{K}$ unless otherwise stated. ^b 60° . ^c Preferred value. ^d Estimate. ^e 30° . ^f Callear and Wilson^{161,162} have chosen this value from ref 137 as a standard to convert their relative rate data into absolute numbers.

quenching by noble gases for atoms exhibiting weak spin-orbit coupling, *i.e.*, Cl($3^2P_{1/2}$) and F($2^2P_{1/2}$), have not been made. Only one estimate exists for Cl($3^2P_{1/2}$) in argon (Table XVI). In such cases, the effect of noble gases could be significant; the magnetic moment generated by rotation of the nuclei could be sufficient to break the magnetic coupling between the spin and orbital motions of the electrons.

2. Ground-State Halogen Atoms

An estimated limit for the collisional quenching of I($5^2P_{1/2}$) by I($5^2P_{3/2}$) is given in Table XIII. A mechanism involving predissociation by the I₂(C $^3\Sigma_u^+$) curve has been proposed. The low probability observed indicates that the speed with which the molecule moves through the region of crossing is too rapid for appreciable mixing to occur. Mixing would be increased by the presence of a magnetic field¹⁸¹ or by collisional perturbation¹⁸² involving a third body. Recent experiments employing electron spin resonance indicate the presence of predissociating states in addition to the C state which may also be of importance in this mechanism.¹⁸³ Time-resolved molecular emission studies¹⁸⁵ of I₂(B $^3\Pi_{0u}^+$) → I₂(X $^1\Sigma_g^+$) have shown that the B state may be populated directly by three-body recombination, namely



Unfortunately, the *absolute* intensity of the I₂(B-X) emission was not reported, and hence the efficiency of this process is not known. An upper limit of ten collisions has been given for the collisional relaxation of Cl($3^2P_{1/2}$) by Cl($3^2P_{3/2}$).¹⁸³ A similar but more effective mechanism to that described for the iodine atom may be involved. No estimate has been made for the quenching of Br($4^2P_{1/2}$) by Br($4^2P_{3/2}$). An estimate for the deactivation of Cl($3^2P_{1/2}$) by H($1^2S_{1/2}$) has been made (Table XVI), indicating unit efficiency. It has been suggested that crossing between the $^3\Pi_0^+$ and $^3\Pi_1$ or $^1\Pi$ states of HCl occurs in a region accessible to thermal collisions,¹⁸⁴ and thus relaxation proceeds by radiationless transitions.

C. COLLISIONAL DEACTIVATION BY DIATOMIC MOLECULES

Even for chemically inert species, collisional deactivation of halogen atoms in the $^2P_{1/2}$ state by diatomic molecules is at least two orders of magnitude more efficient than for the noble gas atoms (Table XIII). This indicates a relatively efficient coupling between the electronic and nuclear angular momenta in the quasi-triatomic molecular complex. The relatively low efficiencies for the quenching of both I($5^2P_{1/2}$) and Br($4^2P_{1/2}$) by CO and N₂, each characterized by weak interaction, is in accord with the expected low efficiencies for the transfer of electronic energy involving a multivibrational transition in the diatomic molecule.¹⁸⁵ The greater rates for Br($4^2P_{1/2}$) appears to result from an increased overlap of translational wave functions following the reduced separation of the potential surfaces for the bromine atom. For the relaxation of X($^2P_{1/2}$) by H₂, D₂, and HX, strongly at-

tractive potential surfaces may be expected to be involved. The deactivation rates for these processes are, on the whole, two orders of magnitude greater than for relaxation by chemically inert species (Table XIII). Discrepancies have arisen from measurements on the collisional quenching of I($5^2P_{1/2}$) by H₂ and D₂ employing different techniques (Table XIII). We feel that the isotopic effect observed when the collisional efficiencies for H₂ and D₂ are compared by time-resolved atomic emission¹⁸⁰ is the most reliable, suggesting the importance of near resonance with vibrational quantum states in the diatomic collision partner, or some more general reduced mass effect. Exceptionally high rates are observed for the deactivation of I($5^2P_{1/2}$) and Br($4^2P_{1/2}$) by both NO and O₂. It has been suggested that the inhomogeneous magnetic field present on collision increases the probability of energy transfer.^{134,139} This type of process has been considered earlier by Wigner,¹⁸⁶ *viz.* the ortho-para conversion of H₂, catalyzed by paramagnetic species in which the rate is found to depend on the square of the magnetic moment of the paramagnetic molecule. Similar behavior is observed for the deactivation of I($5^2P_{1/2}$) and Br($4^2P_{1/2}$) by NO and O₂ and a similar type of mechanism may operate, facilitated by the close proximity during collision induced by the strong chemical interaction. The extremely rapid deactivation of X($^2P_{1/2}$) by X₂ (Tables XIV and XV) observed for bromine and iodine could be either the result of "chemical reaction" or physical relaxation. While it has clearly been shown that X($^2P_{1/2}$) gives rise to rapid chemical reaction with a halogen or interhalogen molecule (see later, this section), experiments employing isotopic labeling with high-resolution mass spectrometry would be required. A strong coupling between electronic and nuclear motion could be expected in the transitory complex X₃. The deactivation of Cl($3^2P_{1/2}$) by Cl₂, highly relevant to the present discussion and to the question of direct recombination between Cl($3^2P_{1/2}$) + Cl($3^2P_{1/2}$) (+M) or inverse predissociation from two ground-state atoms in flow discharge experiments,¹⁶⁶⁻¹⁶⁹ remains to be measured. This is at present being carried out by the authors.

D. COLLISIONAL QUENCHING BY POLYATOMIC MOLECULES

The collisional quenching of excited iodine atoms by polyatomic molecules have been extensively studied (Table XIII). There is no simple correlation between any physical parameter and the deactivation rate constant for a given quenching molecule although some limited groups may be considered. Detailed discussion on each quenching molecule or group of molecules is not warranted in the present context, but a few pertinent examples will be considered. The relaxation of I($5^2P_{1/2}$) by the spherically symmetrical and inert molecules SF₆ and CF₄ is not significantly more efficient than for diatomic molecules. Clearly there is no strong interaction nor is there any pronounced effect of molecular complexity. Similarly, CO₂ is an inefficient deactivator. Further for polyatomic molecules which may be expected to show a marked chemical affinity, there is no trend in efficiency with molecular complexity. For example, H₂, CH₄, and C₃H₈ all show similar efficiencies in deactivating I($5^2P_{1/2}$). The clearly similar deactivation efficiencies observed for CH₄ and CF₃H, and

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Table XIV
Rate Data^a for the Chemical Reactions of Electronically Excited Iodine Atoms, I(5²P_{1/2})

Reactant species	k (cm ³ molecule ⁻¹ sec ⁻¹)	No. of collisions $Z = Z_{\text{coll}}/k$	Ref	Notes
Cl ₂	2.1×10^{-13}	930	144	
Br ₂	1.5×10^{-12}	107	144	
ICl	3.4×10^{-12}	51	144	
IBr	4.3×10^{-12}	39	144	
I ₂	5.0×10^{-12}	15	145	<i>b</i>
	2.46×10^{-11}	3	161, 162	
[Cf.				
I(5 ² P _{1/2}) + Cl ₂	6.1×10^{-21}	3.2×10^{10}	<i>d</i>	
I(5 ² P _{1/2}) + Br ₂	(2.7×10^{-14})	(5.9×10^3)	144	
I(5 ² P _{1/2}) + IBr	$\sim 10^{-17}$	$\sim 10^7$	144]	
NOCl	6.2×10^{-12}	30	142	
NOBr	9.6×10^{-12}	17	142	
C ₂ H ₆	8.9×10^{-18} (30°C)	3.4×10^7	161, 162	
C ₂ H ₄	6.5×10^{-19} (60°C)	2.2×10^9	161, 162	
CH ₃ I	$< 1.7 \times 10^{-15}$	$> 9.7 \times 10^4$	141	
	1.23×10^{-14}	1.3×10^3	159	
I(5 ² P _{1/2})	$\sim 1.6 \times 10^{-14}$ (relaxation)	$\sim 10^4$	131, 158	<i>c</i>

^a Rate data are presented for $\sim 300^\circ\text{K}$ unless otherwise stated. ^b Removal in the presence of I₂ could be either relaxation or reaction. An isotopic labeling experiment is required. ^c This refers to the relaxation of I(5²P_{1/2}) \rightarrow I(5²P_{3/2}) and not to the recombination process I(5²P_{1/2}) + I(5²P_{3/2}) \rightarrow I₂(B) \rightarrow I₂(X) + $h\nu$. ^d M. I. Christie, R. S. Roy, and B. A. Thrush, *Trans. Faraday Soc.*, **55**, 1149 (1959).

Table XV
Rate Data for the Collisional Removal of Electronically Excited Bromine Atoms, Br(4p⁵ 2P_{1/2})

Quenching species	k (cm ³ molecule ⁻¹ sec ⁻¹)	No. of collisions $Z = Z_{\text{coll}}/k$	Ref	Notes
Ar	$< 2 \times 10^{-16}$	$> 10^6$	134	
N ₂	2.5×10^{-15}	9.1×10^4	134	
CO	7.3×10^{-15}	3.1×10^4	134	
CF ₄	2.1×10^{-13}	1.1×10^3	134	
CF ₃ Br	5.0×10^{-14}	3.8×10^2	135	
HBr	1.1×10^{-12}	1.5×10^2	135	
D ₂	5.7×10^{-12}	56	134	
H ₂	4.7×10^{-12}	1.3×10^2	134	
CH ₄	4.2×10^{-12}	71	134	
D ₂ O	9.6×10^{-12}	20	134	
H ₂ O	3.2×10^{-11}	6	134	
Br ₂	1.9×10^{-11}	11	135	<i>a</i>
O ₂	$\sim 3.4 \times 10^{-11}$	~ 6	135	<i>a</i>
NO	4.7×10^{-11}	5	135	<i>a</i>
IBr	3×10^{-12}	40	136	<i>b</i>

^a Reaction? ^b Reaction. Br(4²P_{1/2}) + IBr \rightarrow Br₂ + I.

the alkyl iodides as a group on collision with I(5²P_{1/2}), suggests that where strongly attractive potentials are involved, the collision is effectively localized. The rate constants for the relaxation of I(5²P_{1/2}) by olefins (Table XIII) satisfies the same correlations to those observed for the addition of electrophilic reagents to these molecules.¹⁸⁷ Thus the rate constants increase with decreasing molecular excitation energy and ionization potential,¹⁴³ indicating that a charge-transfer interaction with the π -electron system results on collision. For the allyl halides, the deactivation rate constants for I(5²P_{1/2}), increases for the heavier halogen atom in the allyl halide molecules.¹⁴² A significant isotope effect is ob-

served for H₂O and D₂O (Table XIII). It has been suggested that this could be attributed to the importance of near-resonant transfer involving combination frequencies of vibration.¹³⁹ However, this may be fortuitous and a more general reduced mass effect may be operative in systems containing H and D atoms. In general, deactivation of Br(4²P_{1/2}), and also Cl(3²P_{1/2}), is more rapid than I(5²P_{1/2}) for a given polyatomic molecule. In any given case, all the effects discussed here must be considered, namely, the nature of the interaction potential, the coupling between the various degrees of freedom, and the quantity of energy to be transferred.

E. CHEMICAL REACTIONS OF ELECTRONICALLY EXCITED HALOGEN ATOMS

Differences in the chemical reactivity of halogen atoms in the two spin-orbit states of the np⁵ ground-state configuration may be expected both from the view points of the potential surfaces involving these states and the energetics. For the latter, this should be particularly marked for the iodine atom. For thermal velocities, the effect would be expected to be most marked where a change in the sign of the thermochemistry occurs for the analogous reactions of the two atomic states. From the experimental viewpoint, chemical reaction must be sufficiently rapid to compete with spin-orbit relaxation. In their study of the H atom abstraction from propane by I(5²P_{1/2}), a process which is close to thermoneutral ($\Delta H = 0.043$ eV),^{10, 188} Callar and Wilson^{161, 162} report that spin-orbit relaxation is 6.38×10^3 times faster than chemical reaction at 30°, and decreases to 3.05×10^3 at 90°. Thus the extent of reaction is small and requires the analysis of small product yields in this

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case. In other cases, reaction when exothermic may be found to dominate physical quenching. The nature of the potential surfaces describing this type of competition are not known at present in any detail. In the examples to be presented, the systems chosen will be those where chemical reaction is exothermic or close to thermoneutral for the excited atom, and so may compete significantly on energetic grounds with relaxation for thermal velocities. Tables XIV–XVI include the present data for the chemical reactions of the excited halogen atoms.

Table XVI

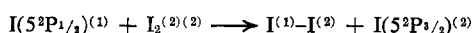
Rate Data for the Collisional Removal of Electronically Excited Chlorine Atoms, $\text{Cl}(3^2\text{P}_{1/2})$

Quenching species	k ($\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$)	No. of collisions $Z = Z_{\text{coll}}/k$	Ref	Notes
Ar	$< 2 \times 10^{-16}$	$> 10^6$	133	
H	$\sim 7 \times 10^{-10}$	1	133	
CF_3Cl	2.5×10^{-12}	1.3×10^5	133	
CCl_4	5×10^{-11}	7	133	
HCl	6×10^{-12}	33	133	
H_2	7×10^{-12}	1.3×10^2	133	
ICl	3×10^{-11}	10	136	<i>a</i>

^a Reaction. $\text{Cl}(^2\text{P}_{1/2}) + \text{ICl} \rightarrow \text{Cl}_2 + \text{I}$.

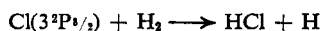
1. Halogens and Interhalogens

An extensive study has been made on the reactions of $\text{I}(5^2\text{P}_{1/2})$ with the halogens and interhalogens.¹⁴⁴ Chemical reaction of $\text{I}(5^2\text{P}_{1/2})$ with the molecules Cl_2 , Br_2 , ICl , and IBr is exothermic for all these systems, whereas for $\text{I}(5^2\text{P}_{3/2})$ reaction is endothermic and proceeds at a negligible rate at room temperature. Kinetic spectroscopy in the ultraviolet and vacuum ultraviolet has shown that chemical reaction dominates spin-orbit relaxation.¹⁴⁴ The rate constants for these processes are presented in Table XIV. The rate constants for the analogous endothermic processes for $\text{I}(5^2\text{P}_{3/2})$ are also presented in the Table XIV and are shown to be very much slower. A kinetic spectroscopic study in the vacuum ultraviolet of the flash photolysis of IBr^{136} demonstrates the rapid removal of $\text{Br}(4^2\text{P}_{1/2})$ by chemical reaction with the parent IBr molecule, the rate constant for which is presented in Table XIV. A similar study on ICl^{136} also indicated rapid chemical reaction of the excited chlorine atom with the parent ICl molecule (Table XVI). It may be concluded that the collision between an excited halogen atom (Cl , Br , $\text{I } ^2\text{P}_{1/2}$) with a halogen or interhalogen molecule leads to predominantly chemical reaction,¹⁴⁰ exhibiting rates close to the collision number. It may be noted that the removal of $\text{I}(5^2\text{P}_{1/2})$ and $\text{Br}(4^2\text{P}_{1/2})$ by I_2 and Br_2 , respectively, proceeds at rates of comparable magnitude to those for the chemical reactions described in this section (Tables XIV–XVI), and it is tempting to suggest that atomic reactions of the type



take place. However, this can only be resolved by an isotopic labeling experiment.

In considering the reactions of electronically excited halogen atoms with diatomic molecules, we note that if the activation energy of the reaction



obtained from a study of the reverse process by Clyne and Stedman,¹⁸⁹ were reduced by the electronic energy of the excited chlorine atom, a rate constant would result of magnitude comparable to that for the collisional removal of $\text{Cl}(3^2\text{P}_{1/2})$ by H_2 (Table XVI). Thus chemical reaction between $\text{Cl}(3^2\text{P}_{1/2})$ and H_2 may take place, and that the excited chlorine atom may play a significant role in the photochemical reaction between $\text{H}_2 + \text{Cl}_2$.

2. Nitrosyl Halides

Halogen-atom abstraction from NOCl and NOBr by iodine atoms is exothermic for both ground-state and electronically excited atoms.^{10,188} The quantitative separation of the overall decay rate into contributions by relaxation and reaction is experimentally difficult. The products of reaction, ICl and IBr , may be readily monitored in the far-ultraviolet,¹⁴² together with the decay of $\text{I}(5^2\text{P}_{1/2})$; reaction accounts for approximately 60% of the overall rapid decay (Table XIV) of the excited iodine atoms in both cases. While oxygen atom abstraction from N_2O by $\text{I}(5^2\text{P}_{1/2})$ is an exothermic process (-1.12 eV), $\text{IO}(A^2\Pi \leftarrow X^2\Pi)^{190}$ was not detected when $\text{I}(5^2\text{P}_{1/2})$ was generated in the presence of this molecule;¹⁴² indeed, the decay rate of the excited atom was found to be very slow (Table XIII).¹⁴² The relatively slow spin-orbit relaxation of $\text{I}(5^2\text{P}_{1/2})$ on collision with the molecules N_2O , CO_2 , and ICN (Tables XIII) has been attributed¹⁴² to the electronic stability resulting from the linear structures of these molecules¹⁹¹ with the outer 16 electrons in the lowest eight molecular orbitals.¹⁹¹ The rapid chemical reaction with the nitrosyl halides is accounted for¹⁴² in terms of the bent structures of these molecules,¹⁹¹ with the extra two electrons relative to N_2O , lying in a lone-pair orbital and being repelled by the electrons in the bonding orbital. This facilitates formation of the transitory complex with a small or zero activation energy.¹⁴²

3. H-Atom Abstraction from Paraffins by $\text{I}(5^2\text{P}_{1/2})$

The abstraction of a hydrogen atom by $\text{I}(5^2\text{P}_{1/2})$ from both propane and ethane is an endothermic process ($\Delta H = 0.043$ and 0.18 eV , respectively^{10,188}). Thus chemical reaction for these molecules is a factor of the order of 10^4 slower than spin-orbit relaxation (Table XIII and XIV) although this is not entirely due to the energetics. Indeed, the most striking aspect of these results are the low Arrhenius A factors for chemical reaction, corresponding to p factors of the order of 10^{-3} . Callear and Wilson^{161,162} have attributed this to a lack of equilibrium involving the transition state caused by relaxation to a lower surface.

4. Alkyl Iodides

Iodine atom abstraction from an alkyl iodide by $\text{I}(5^2\text{P}_{1/2})$ is an exothermic process^{10,188} and thus, on energetic grounds, would be expected to compete significantly with spin-orbit relaxation for thermal velocities. Abstraction by $\text{I}(5^2\text{P}_{1/2})$

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is strongly endothermic and the reactions are very slow.¹⁹² The decay of $I(5^2P_{1/2})$ on collision with alkyl iodides is rapid (Table XIII) and found to be dominated by physical quenching rather than chemical reaction.^{132, 140, 141} An upper limit for the relative contribution by reaction and relaxation in the case of $I(5^2P_{1/2}) + CH_3I$ may be made from the kinetic spectroscopic measurements^{140, 141} indicating $k_{\text{reaction}}/k_{\text{relaxation}} < 1/10$ at 300°K. Further, the data for the quenching of $I(5^2P_{1/2})$ by CH_3I ^{140, 141} and I_2 ¹⁴⁵ (Table XIII) coupled with the quantum yield measurements of Aditya and Willard¹⁹³ for the isotopic exchange of I_2 ,¹³¹ photolyzed in the B-X continuum in the presence of CH_3I , indicates that the rate constant for chemical reaction between $I(5^2P_{1/2}) + CH_3I$ is given by $k < 1.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 300°K (Table XIV). This is an order of magnitude slower than that reported by Meyer¹⁵⁹ whose result we feel must be questioned. However, the low p factor of the order of 10^{-4} from Meyer's data appears to compare reasonably with the p factors for the H-atom abstraction from paraffins by $I(5^2P_{1/2})$,

being the order of 10^{-3} .^{161, 162} $I(5^2P_{1/2})$ predominantly undergoes relaxation rather than chemical reaction in the presence of an alkyl iodide.

5. Olefins and Allyl Halides

While hydrogen atom abstraction from propylene, for example, is an exothermic process,^{10, 188} spin-orbit relaxation accounts completely for the decay of $I(5^2P_{1/2})$ in the presence of olefins as evidenced by an iodine atom balance on the concentrations in the $^2P_{1/2}$ and $^2P_{3/2}$ states.¹⁴³ Although metathetical abstraction of a halogen atom from allyl chloride, bromide, and iodide by $I(5^2P_{1/2})$ is a strongly exothermic process,^{10, 188} the decay of the excited atom is entirely by spin-orbit relaxation¹⁴² (Table XIII). The products of any chemical reaction were not detected spectroscopically.¹⁴² The quenching efficiencies increase in the order $CH_2=CHCH_2-H$, $-Cl$, $-Br$, $-I$ (Table XIII), reflecting increasing strength of the interaction on collision.

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